Synthesis, properties and applications of complex calcium aluminates and hydroaluminates

V. M. Sizyakov, *Doctor of Technical Sciences, Scientific Director of the Scientific Center "Issues of Processing Mineral and Technogenic Resources"[1], e-mail: Sizyakov_VM@pers.spmi.ru*
V. N. Brichkin, *Doctor of Technical Sciences, Head of the Science Project[2], e-mail: Brichkin_VN@pers.spmi.ru;*
R. V. Kurtenkov, *Candidate of Technical Sciences, Associate Professor[1], e-mail: Kurtenkov_RV@pers.spmi.ru;*
R. I. Maksimova, *Post-Graduate Student[1], e-mail: Maksimova_RI@pers.spmi.ru;*

[1] *Empress Catherine II Saint Petersburg Mining University, St. Petersburg, Russia.*
[2] *International Competence Centre for Mining Engineering Education under the auspices of UNESCO, St. Petersburg, Russia.*

Modern technologies for the processing of aluminium-containing raw materials invariably pose questions regarding the composition and properties of complex calcium aluminates, the practical significance of which not only remains within the existing technological processes for producing binding compositions, but also develops in connection with the complex processing of aluminosilicate raw materials and the potential for their individual synthesis for obtaining new types of by-products. In this connection the task of the performed research was to determine the composition and properties of calcium hydrocarboaluminate (CHCA) during its obtaining using alumina production solutions, depending on the nature of the alkali metal cation in the $Na_2O(K_2O)$ – CaO – Al_2O_3 – CO_2 – H_2O system. The performed works included the laboratory synthesis of calcium hydrocarboaluminates, in relation to the conditions of aluminosilicate raw materials processing by sintering. The obtained samples were subjected to a range of analytical methods, including differential thermal analysis, *X*-ray phase and *X*-ray fluorescence analysis, laser microanalysis and electron microscopy. Noticeable differences in the laboratory synthesis of CHCA based on sodium and potassium aluminate solutions in terms of the degree of conversion of calcium oxide into CHCA and its yield, the content of CHCA in the precipitate and its stoichiometry with CO_2 saturation from 0.79 to 0.62 mol, respectively, and for the industrial sample 0.45 mol, as a result of changes in the physicochemical and technological conditions of synthesis, have been established. The efficacy of utilising a complex physicochemical analysis of calcium aluminates, predicated on the determination and consideration of the phase composition of the precipitate and the characteristic chemical alterations of the system during the interaction of the lime component with the aluminate solution, is demonstrated. This approach, based on the findings of chemical, *X*-ray phase and combined thermal analysis, facilitates the determination of the material composition of multicomponent precipitates and the stoichiometry of CHCA.

Key words: calcium aluminates and hydroaluminates, aluminosilicate raw materials, complex processing, synthesis, aluminate solutions, indicators, properties, applications, phase composition, methods of analysis.
DOI: 10.17580/nfm.2025.01.02

Introduction

Modern technologies for complex processing of aluminium-containing raw materials invariably pose questions regarding the composition and properties of complex calcium aluminates, the practical significance of which was appreciated since antiquity and led to the appearance of such a characteristic of natural and artificial materials as pozzolanic activity (Italian: pozzolana, derived from the name of the city of Pozzuoli), i.e. their ability to interact with the formation of calcium silicates and aluminates [1-3]. In his treatise entitled "De architectura" (Ten Books on Architecture), Marcus Vitruvius Pollio (c. 80-70 BC – after c. 13 BC), an ancient Roman architect, mechanic, scholar and encyclopedist, provides a definition of natural pozzolana, i.e., a mixture of volcanic ash, pumice and tuff: *"...a kind of sand dust, a deposit near Mount Vesuvius. Three substances: lime, crushed stone and pozzolana sand, coming in a mixture with each other, immediately – as soon as they absorb water - interlock tightly and, under the influence of moisture, hardening quickly, form a mass - dense to such an extent that neither the surf of waves nor the pressure of water cannot break it." That dust "gives the property of indestructible fortress not only to all buildings but even to dams".*[1]

The actual chemistry and mechanism of manifestation of hydraulic (pozzolanic) activity of natural and artificial materials is of considerable complexity, which can be illustrated only in a first approximation by the scheme (taking into account the simplified chemical notation for cement) on the example of the interaction of metakaolin with lime milk, leading to the formation of hydrosilicates, stable and metastable calcium aluminates [3]:

[1] Yusupov E. S. Dictionary of Architectural Terms. St. Petersburg: Leningradskaya Galereya, 1994. 432 p.

$Al_2O_3 \cdot 2SiO_2 + Ca(OH)_2 + H_2O \rightarrow$
$CaO \cdot SiO_2 \cdot H_2O$ (CSH(I));
$4CaO \cdot Al_2O_3 \cdot 13H_2O$ (C_4AH_{13});
$3CaO \cdot Al_2O_3 \cdot 6H_2O$ (C_3AH_6);
$2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$ (C_2ASH_8).

The significance of the pozzolanic activity of various natural materials in the composition of water-resistant binders and products based on them, whether autoclaved or air-cured, has not diminished in the present time. This includes the utilisation of zeolite tuff and clay rocks, which led to the development of the theory and practice of producing appropriate building materials [4, 5]. It has been demonstrated that both primary and secondary interactions with the formation of calcium monocarboaluminate ($C_3A \cdot CaCO_3 \cdot 11H_2O$)[2] as well as the conversion of calcium-aluminate phases with the transformation of the initial crystalline structure into a new aluminate phase are essential in the solidification process [6].

The development of the theory and practical application of complex calcium aluminates was significantly advanced by the invention of Portland cement by Joseph Aspdin (1778–1855). This hydraulic binder is obtained by joint grinding of cement clinker, gypsum and additives, with calcium silicates (70-80%) predominating in its composition. The appellation of this trademark is derived from the island of Portland in England, where natural stone was mined. This stone was comparable to beton (French béton – artificial stone), a compound obtained on the basis of the cement composition patented by J. Aspdin in 1824. The advent of mass production and the exceptional importance of Portland cement as a building material provided a further basis for the formation of knowledge about complex calcium aluminates formed during clinker firing (from German "Klingel" - ringing, emitting a ringing sound on impact) and their hydration products. These developments provided the foundation for the advancement of thermodynamics, mechanism and kinetics of key technological processes in Portland cement production [7–9]. As evidenced by these and subsequent studies, complex calcium aluminates have been demonstrated to be of significance in the formation of cement stone, acting as regulators of curing, as well as densifiers of components and corrosion protectors [10–12]. Moreover, the utilisation of hydraulically active additives has been demonstrated to engender substantial energy savings, a consequence of the diminution of clinker content in cements of varying composition and application [13–15]. This effect includes the utilisation of aluminium-containing additives of technogenic origin [16–18].

The advancement of the theory and technology of complex calcium aluminates was facilitated by their function in the complex processing of aluminosilicates to produce alumina and by-products. This development also included the potential utilisation of slurries in the production of binders [3,4] [19–21]. The development of technology for synthesising calcium carboaluminate and its analogues in alumina production systems has initiated a paradigm shift in the production and utilisation of complex calcium aluminates [22–24]. These approaches have determined the direction of research for decades in relation to the efficiency of processing low-quality aluminosilicate raw materials. These approaches have also focused on improving the quality of alumina, soda products, Portland cement and other by-products, as well as expanding their range of products [25–26]. At the same time, the theory of synthesis of complex calcium hydrocarboaluminates in alumina production systems was developed, and the existence of a continuous series of solid solutions, in contrast to cement production systems with the formation of CHCA of discrete composition, was substantiated[5]. A significant addition to these theoretical provisions was the development of the theory and technology of deep silicon extraction from alkaline aluminate solutions using carboaluminate reagent and precipitation of calcium hydrogranates [22]. In general, the necessary prerequisites have been established for the incorporation of low-quality raw materials of various natures into alumina production [27–29] without any efficiency loss in their processing or in the quality of the resulting products[6] [30, 31]. Such an approach includes the prospects of rational use of the lime component and, on this basis, harmonisation of the ratio of metallurgical and by-products [24, 32].

Despite the implementation of a large-scale solution to the problem of synthesising CHCA and its application in domestic enterprises processing nepheline raw materials, there are still issues related to the introduction of such technology in the processing of alkali-free aluminosilicates, as well as ultra-potassium feldspar rocks. These are of notable interest to the domestic mineral and raw materials complex in the medium term [22, 24, 27]. In this connection, the task of the performed research was to ascertain the composition and properties of calcium hydrocarboaluminate (CHCA) when synthesised using alumina production solutions depending on the nature of alkali metal cation in the $Na_2O(K_2O) – CaO – Al_2O_3 – CO_2 – H_2O$ system, as well as the potential for future studies with strontium and barium analogues of CHCA. Simultaneously, one of the most challenging aspects

[2] Stanaitis V.-I. I. Research of Formation of Hydroaluminates and Calcium Carboaluminates at Hydrothermal Treatment of Silicate Products. Thesis of Dissertation ... Candidate of Technical Sciences. Kaunas, 1970. 25 p.

[3] Bozhenov P. I., Kavalerova V. I. Nepheline Sludge. Leningrad-Moscow: Stroyizdat, 1966. 243 p.

[4] Uryvaeva G. D. Cements from Sludge. Novosibirsk: Nauka, 1970. 154 p.

[5] Sizyakov V. M. Mechanism of Calcium Hydroxocarboaluminate Formation and Conversion to Tricalcium Aluminate. *Russian Journal of Applied Chemistry.* 1998. Vol. 71, Iss. 8. pp. 1473–1475.

[6] Sizyakov V. M. Chemical and Technological Mechanisms of a Alkaline Aluminum Silicates Sintering and a Hydrochemical Sinter Processing. *Journal of Mining Institute*. 2016. Vol. 217. pp. 102–112.

of the study is determining the composition of CHCA, due to the imperfection of its crystal structure and the high dispersion of individuals formed under conditions of significant supersaturation of the crystal-forming medium.

Experimental and analytical studies were carried out on the basis of the Scientific Centre "Issues of Processing Mineral and Technogenic Resources", as well as the Scientific and Educational Centre for collective use of Empress Catherine II Saint Petersburg Mining University. The performed works included the laboratory synthesis of calcium hydrocarboaluminates, with a focus on the processing of aluminosilicate raw materials by sintering. The obtained samples were subjected to a range of analytical methods, including derivatography, *X*-ray phase and *X*-ray fluorescence analysis, laser microanalysis and electron microscopy.

Materials and methods

Synthetic aluminate solutions were prepared according to a well-known method, using chemically pure preparations (NaOH, Na_2CO_3, KOH, K_2CO_3) and technical aluminium hydroxide of GD-8 grade, produced by Pikalevo Alumina Refinery LLC. The composition of the aluminate solutions was meticulously controlled to ensure the content of Al_2O_3, caustic (Na_2O_k), and total alkali (Na_2O_t), utilising well-known chemical analytical methods of complexometric and acid-base titration[7]. Thus, stable aluminate solutions with a calculated Na_2O_k concentration of approximately 300 g/l were obtained, satisfying the following ratio:

$$\nu(Na_2O + K_2O) / \nu(Al_2O_3) \approx 1{,}6\ ,$$

where $\nu(Na_2O + K_2O)$, $\nu(Al_2O_3)$ – number of alkali metal moles sum and moles of aluminium in terms of oxides, respectively.

Subsequent dilution of the initial solution, along with correction of the Na_2CO_3 and K_2CO_3 content, provides close correspondence of its composition to the technological solution supplied for the preparation of a carboaluminate suspension during the processing of nepheline raw materials.

The preparation of reactive calcium oxide involved a double calcination process of $CaCO_3$ (grade "puriss." or "p.a.") in a Nabertherm LHT 08/17/P470 muffle furnace at a temperature of 950 °C for a duration of 4 hours. The results of the carbon determination process, as conducted using a TOC-L analyser (Shimadzu), in conjunction with the titrimetric analysis method as outlined in GOST 4530–76, indicate that the activity of CaO following the initial calcination process was in the range of 75–80%. Subsequent to the second calcination, this parameter increased to a level of 96-98%.

The present study utilised HEL's AutoMate multifunctional platform to synthesise CHCA, which was equipped with four 0.5-litre stainless steel reactors for parallel processes at atmospheric pressure in a controlled slurry agitation mode. The system was configured to enable condensate return and temperature control with an accuracy of ±0.1 degrees Celsius. Regardless of the ratio of sodium and potassium in the alkaline aluminate solution, the synthesis was conducted under identical conditions at a lime dosage of 1 mol CaO to 1 mol Al_2O_3 in solution, at a solution temperature of 60 °C and a process duration of 60 minutes. This satisfies the prevailing theory and practice of their production. [22–24]. Following the conclusion of the isothermal holding process, the pulp was subjected to filtration under vacuum conditions. Thereafter, the precipitate was thoroughly washed with distilled water and dried at a temperature of 60°C until constant weight was achieved. This stage was then subjected to further analysis and physicochemical studies. Concurrently, the filtrate was analysed to determine the content of Al_2O_3 and alkaline components. This study employed a variety of sample examination methods and equipment, including laser microanalysis, combined thermal analysis, *X*-ray diffractometry and scanning electron microscopy.

In this study, the authors proposed a novel method for the complex physicochemical analysis of calcium aluminates. This method is based on the determination and accounting of the phase composition of the precipitate, as well as the characteristic chemical changes of the system during the interaction of the lime component with the aluminate solution[8] [33]. This approach allows us to formalise the material balance of the four components (CaO, Al_2O_3, CO_2, H_2O), involved in the synthesis of CHCA ($4CaO \cdot Al_2O_3 \cdot nCO_2 \cdot (13-2n)\ H_2O$) and the possibility of the precipitation of four solids ($Ca(OH)_2$; $CaCO_3$; C_3AH_6 and CHCA), which makes it fundamentally possible to estimate the degree of hydration of CHCA, its saturation with carbonate ion and the amount of the phase as a whole:

$$m_{CaO} = m_{CaO}^{Ca(OH)_2} + m_{CaO}^{CaCO_3} + m_{CaO}^{CHCA} + m_{CaO}^{TCA}\ ; \quad (1)$$

$$m_{CO_2} = m_{CO_2}^{CHCA} + m_{CO_2}^{CaCO_3}; \quad (2)$$

$$m_{Al_2O_3} = m_{Al_2O_3}^{CHCA} + m_{Al_2O_3}^{TCA}\ ; \quad (3)$$

$$m_{H_2O} = m_{H_2O}^{Ca(OH)_2} + m_{H_2O}^{CHCA} + m_{H_2O}^{TCA}; \quad (4)$$

$$m_{pr} = m_{CaO} + m_{CO_2} + m_{Al_2O_3} + m_{H_2O}\ . \quad (5)$$

[7] Sizyakov V. M., Brichkin V. N. Metallurgy of Light Metals. Alumina Production: Laboratory Practice. St. Petersburg: St. Petersburg State Mining Institute (Technical University), 2004. 90 p.

[8] Brichkin V. N., Maksimova R. I., Fedorov A. T. Certificate of State Registration of Computer Program No. 2024682672. Program for Calculation of Chemical and Material Composition of Solid Solutions Based on Complex Alkali Earth Metal Aluminates. Published 26.09.2024. Bulletin No. 10.

In the equations (1)–(5), the following notations are introduced: in the left part of the equations, the mass of the corresponding component in the precipitate and the mass of the precipitate or its sample for analysis are indicated; in the upper indices, the phase (substance) is denoted, which includes the corresponding component; TCA is the abbreviation for tricalcium aluminate hexahydrate ($3CaO \cdot Al_2O_3 \cdot 6H_2O$ or C_3AH_6). The potential for TCA formation is associated with metastable stability of CHCA, and the precipitation of $Ca(OH)_2$ and $CaCO_3$ with incomplete synthesis of CHCA in an aluminate solution. The left-hand sides of the equations contain known values that are determined by the experimental conditions (m_{CaO} and m_{pr}), as well as the results of chemical and thermal analyses (m_{CaO}; $m_{Al_2O_3}$; m_{CO_2} and m_{H_2O}). The right parts of equations (1)–(5) contain 6 quantities, which makes it necessary to either exclude one of the unknowns or utilise additional information to determine it. In consideration of the impurity character of $CaCO_3$ in the lime composition, its exclusion does not have a significant effect on the results of quantitative calculations, and additional information on the $Ca(OH)_2$ content can be obtained from the results of derivatographic analysis with a well-identified endothermic effect at 530 °C and water removal in the temperature range from 425 to 560 °C [34, 35].

Results and discussion

The quantitative parameters of the laboratory synthesis of CHCA, as determined by three parallel experiments, are presented in **Table 1**. These experiments involved the composition of aluminate solutions with mole fractions of K_2O equal to 0.0 and 1.0. The mole fraction of the alkali metal in the solution is calculated using the following equation:

$$n_{K_2O} = \frac{\nu_{K_2O}}{\nu_{K_2O} + \nu_{Na_2O}} = \frac{[K_2O]/94}{[K_2O]/94 + [Na_2O]/62};$$

$$n_{Na_2O} = 1 - n_{K_2O},$$

where n_{Na_2O} and n_{K_2O} are mole fractions of Na_2O and K_2O in aluminate solution; $[Na_2O]$ and $[K_2O]$ are volume concentrations of alkaline components, g/l; 62 and 94 are molecular weights Na_2O and K_2O, respectively, g/mol.

The initial volume of the aluminate solution in experiments 1–6 was 300 ml, and taking into account the dilution error of the initial concentrated solution, the real composition of the technological solution was determined and the dosage of calcium oxide for each experiment was calculated. The filtration and cake washing regime of the precipitate included the addition of washing water, which excludes the equality of volumes of the obtained solutions and the possibility of correct comparison of their composition. In this connection, the compositions of the final solutions were reduced to the initial volume of 300 ml **(Table 1)**.

Subsequently, the mean values of the indicators and compositions presented in **Table 1** were utilised to determine the quantitative phase composition of the CHCA precipitate. This approach served to enhance the accuracy and reliability of the results obtained. The chemical composition of the precipitate was determined by *X*-ray fluorescence using an EDX-7000P analyser (Shimadzu). The results of this analysis were supplemented by the determination of carbon content on a TOC-L analyser (Shimadzu) and loss on ignition (LOI), associated with the removal of crystalline hydrate and chemically bound water. These were determined according to the results of simultaneous differential thermal analysis on the DTG-60 device (Shimadzu), performed under atmospheric conditions at a constant heating rate of 15 °C/min in the temperature range from 25 °C to 1000 °C. The results are presented in **Table 2**.

In order to establish the phase composition of the synthesised products, the samples were analysed using an XRD 6000 diffractometer (Shimadzu). This analysis, when compared to the available database, allowed for the identification of $Ca(OH)_2$ and CHCA as the main crystalline components of the precipitate, but without linking it to the saturation value by CO_2. In this connection, to clarify the phase composition of the synthesised samples, their simultaneous thermal analysis was performed on a DTG-60 (Shimadzu) instrument in the previously

Table 1

Initial materials and final products of CHCA synthesis in alumina production systems

No. of experience (sample)	n_{Na_2O}/n_{K_2O}	Initial composition of aluminate solution (g/l) and limestone dosage (m_{CaO}), g				Reduced composition of the final aluminate solution, g/l			Precipitate mass, g
		$R_2O_k^*$	$R_2O_{carb}^{**}$	Al_2O_3	m_{CaO}	$R_2O_k^*$	$R_2O_{carb}^{**}$	Al_2O_3	
1	1.0/0.0	80.77	25.08	81.32	13.92	91.28	14.64	63.24	33.44
2		80.51	24.96	82.35	13.80	89.56	15.98	65.31	32.13
3		81.28	24.74	81.88	13.87	90.55	15.69	62.95	32.01
4	0.0/1.0	123.86	38.08	83.30	13.82	137.15	24.85	67.08	32.00
5		122.98	37.92	82.82	13.79	137.59	23.81	66.19	31.24
6		122.98	37.92	82.82	13.98	136.94	23.93	66.59	31.14

*R_2O_k – accepted designation of the conditional alkali component by caustic alkali content in systems containing Na_2O and/or K_2O (given as a sum or in terms of one component);
**R_2O_{carb} – similar designation for carbonate alkali concentration in mixed sodium-potassium systems.

described mode. The characteristic DTA and TG curves for samples No. 2, 5 and 7 are shown in **Fig. 1, *a, b, c***, and the averaged analysis results with deciphering the mass loss of the sample for the corresponding phase transformation are given in **Table 3**. In addition to *X*-ray phase analysis, the findings of combined thermal analysis demonstrate that there are no effects on the DTA curves at 300-330°C, which are characteristic of the decomposition of cubic tricalcium aluminate hexahydrate (C_3AH_6). This indicates the absence of this compound in the analysed samples and suggests that the synthesised CHCA samples possess sufficient stability to undergo phase transition and form TCA.

The obtained results provide a significant addition to the extant theoretical concepts and the results of XRD analysis concerning the qualitative phase composition of synthesised precipitates, which allows us to use of calculation

Table 2
Chemical composition of precipitate (sample) during CHCA synthesis in alumina production systems

No. of experience (sample)	n_{Na_2O}/n_{K_2O}	Component content in terms of oxides, %								
		CaO	Al_2O_3	SiO_2	Fe_2O_3	MgO	R_2O	CO_2	LOI	other
1	1.0/0.0	41.34	16.21	0.15	0.11	0.12	0.07	6.41	34.73	0.85
2		42.66	15.92	0.38	0.09	0.23	0.07	5.88	33.76	1.02
3		43.03	17.74	0.18	0.08	0.25	0.14	5.86	31.59	1.14
4	0.0/1.0	42.89	15.21	0.18	0.08	0.17	0.21	5.80	35.03	0.43
5		43.84	15.97	0.32	0.12	0.24	0.26	5.95	33.03	0.27
6		44.59	15.67	0.28	0.17	0.21	0.16	5.80	32.88	0.24
7*	0.7/0.3	44.53	16.43	0.38	0.19	0.62	0.55	3.45	33.42	0.43

*No. 7 – the sample was obtained in industrial conditions of Pikalevo Alumina Refinery LLC during processing of nepheline concentrate from Apatit JSC.

Table 3
Sample mass losses and their correspondence to phase changes in the temperature range from 25 °C to 1000 °C according to combined thermal analysis data [22, 34, 35]

No. of experience (sample)	Quantitative change of sample mass at characteristic thermochemical transformations for the set temperature range, %			
	Removal of crystalline hydrate water, (110-400) ± 10 °C	Dissociation of $Ca(OH)_2$, (420-520) ± 20 °C	Removal of constitutional water, (540-620) ± 10 °C	Dissociation of $CaCO_3$, (650-830) ± 20 °C
1	31.81	1.64	1.28	6.41
2	30.82	2.41	0.53	5.88
3	29.69	1.07	0.83	5.86
Average value, 1-3	30.77	1.71	0.88	6.05
4	30.26	2.76	2.01	5.80
5	29.45	1.94	1.64	5.95
6	28.76	2.37	1.75	5.80
Average value, 4-6	29.49	2.36	1.80	5.85
7	30.81	2.61	0.00	3.45

Table 4
Quantitative phase composition of precipitate during CHCA synthesis in alkaline aluminate solutions of alumina production

No. of experience (sample)	Quantitative phase composition of synthesised CHCA samples, %				
	CHCA	$Ca(OH)_2$	$CaCO_3$	Other	Total sum
1	90.83	6.75	1.12	1.30	100.00
2	87.94	9.92	0.35	1.79	100.00
3	92.50	4.40	1.31	1.79	100.00
Average value, 1-3	90.43	7.02	0.93	1.62	100.00
4	85.98	11.36	1.59	1.07	100.00
5	85.96	7.98	4.85	1.21	100.00
6	84.19	9.76	4.99	1.06	100.00
Average value, 4-6	85.37	9.70	3.81	1.11	100.00
7	86.52	10.73	0.58	2.17	100.00

Table 5
Calculated stoichiometric composition of CHCA in the synthesised samples

No. of experience (sample)	Stoichiometric formula of CHCA per mole of Al_2O_3	Conversion rate of CaO to CHCA, %	Yield of CHCA per CaO unit, %
1	$4CaO \cdot Al_2O_3 \cdot 0.85CO_2 \cdot 11.56H_2O$	86.89	218.21
2	$4CaO \cdot Al_2O_3 \cdot 0.83CO_2 \cdot 11.16H_2O$	82.66	204.75
3	$4CaO \cdot Al_2O_3 \cdot 0.69CO_2 \cdot 9.75H_2O$	91.35	213.53
Average value, 1-3	$4CaO \cdot Al_2O_3 \cdot 0.79CO_2 \cdot 10.82H_2O$	86.97	212.16
4	$4CaO \cdot Al_2O_3 \cdot 0.78CO_2 \cdot 12.02H_2O$	74.19	199.08
5	$4CaO \cdot Al_2O_3 \cdot 0.55CO_2 \cdot 11.03H_2O$	81.60	194.73
6	$4CaO \cdot Al_2O_3 \cdot 0.53CO_2 \cdot 11.03H_2O$	78.62	187.53
Average value, 4-6	$4CaO \cdot Al_2O_3 \cdot 0.62CO_2 \cdot 11.36H_2O$	79.04	193.78
7	$4CaO \cdot Al_2O_3 \cdot 0.45CO_2 \cdot 10.62H_2O$	–	–

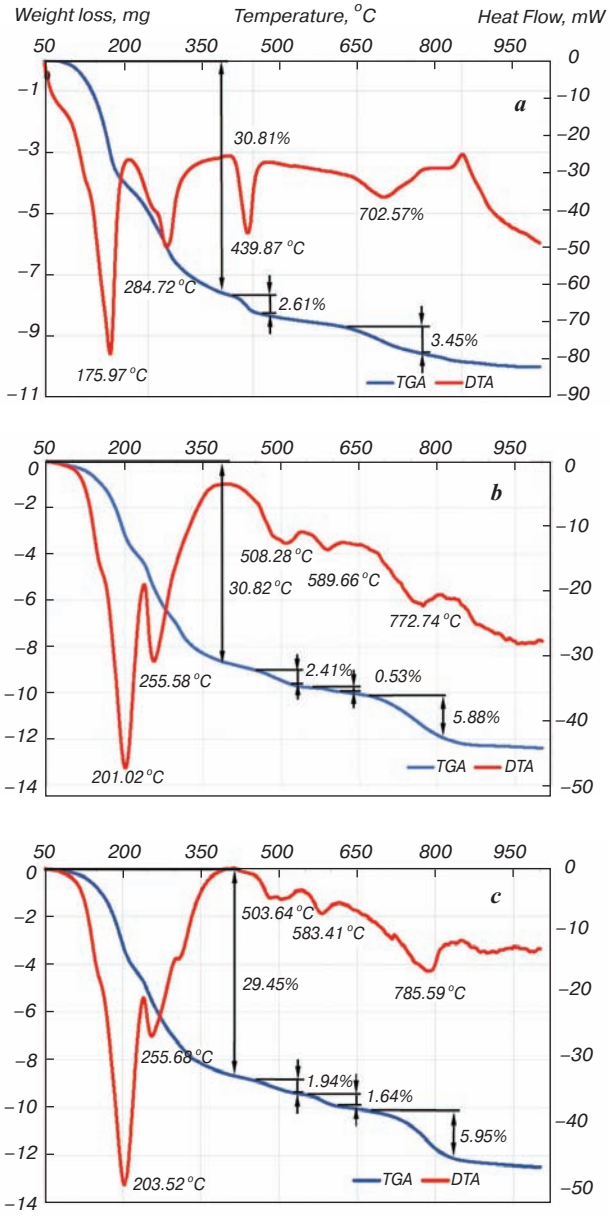

Fig. 1. Results of combined thermal analysis of CHCA precipitation for samples (experiments) with different mole fraction of alkali metals in solution:
a – No. 2, *b* – No. 7, *c* – No. 5

equations 1-5 to determine the amount of individual substances in the precipitate and the chemical composition of CHCA (**Tables 4, 5**). It is possible to note not only the proximity, but also noticeable differences in the compositions of synthesised CHCA depending on the nature of the alkali metal in the aluminate solution and peculiarities of the technological regime, which is typical for the production of carboaluminate suspension in industrial conditions.

The particle size distribution of the samples was analysed using a laser particle analyser, the Microsizer 201C. The results of this analysis are presented in **Fig. 2**. The analysis of the data allows for the conclusion to be drawn that there is a presence of fractions of materials of increased size in the industrial sample. This may be indicative of the peculiarities of production technology associated with the quenching of burnt lime and entrainment in the lime milk not fully reacted particles due to their reduced activity as a result of "overburning", i.e. increased temperature of burning limestone. The particle size distribution in the laboratory samples exhibits negligible disparities, thereby indicating the proximity of the mechanisms and growth processes involved in their formation. In general, the rather complex character of particle size distribution in CHCA samples, in our opinion, indicates the multistage nature of its formation, both during synthesis and during the preliminary preparation of starting materials.

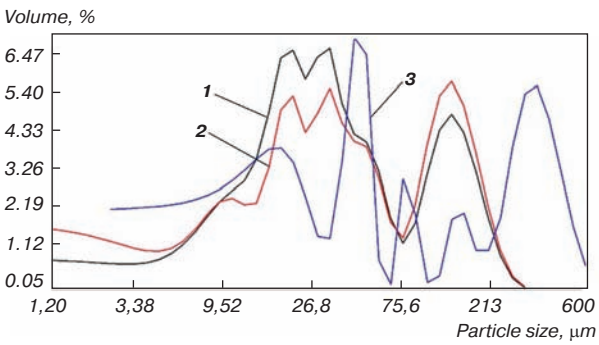

Fig. 2. Particle size distribution of CHCA samples obtained under laboratory and industrial conditions:
1 – average values for samples 1–3; *2* – average values for samples 4-6; *3* – industrial sample

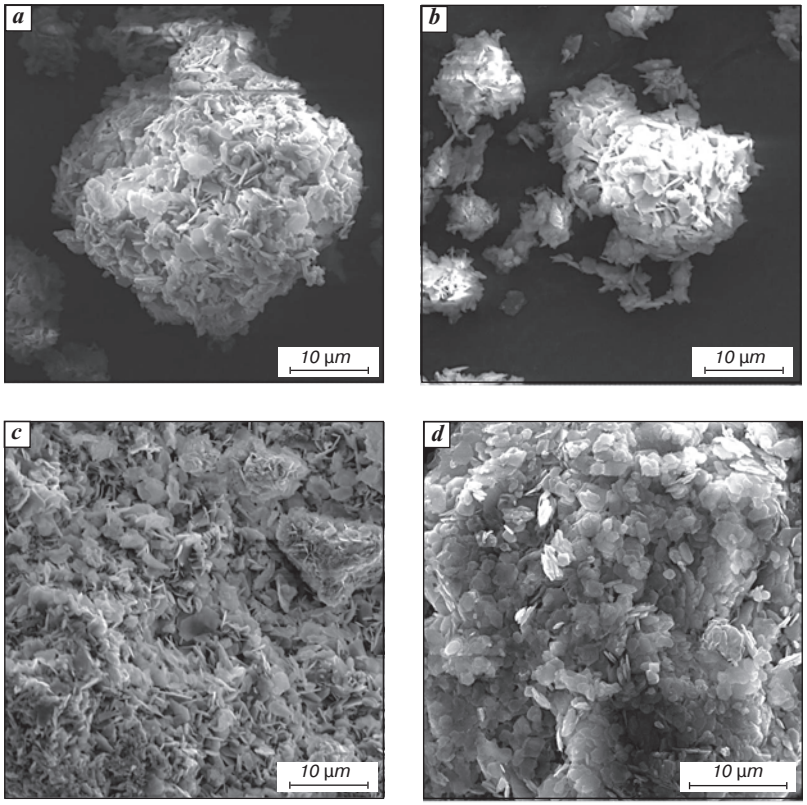

Fig. 3. Electron micrographs of CHCA samples:
a – synthesis in solution with $n$$Na_2O$ = 1.0; *b*, *c* – synthesis in solution with $n$$K_2O$ = 1.0; *d* – industrial synthesis in solution with $n$$Na_2O$ = 0.7

In order to clarify the structural and textural features of the obtained samples, a comparative analysis was conducted using a TESCAN VEGA 3 scanning electron microscope and a Q150R E Plus vacuum sputtering unit manufactured by Quorum Technologies Ltd. **(Fig. 3)**. The data indicate that, under conditions of industrial synthesis, there is a higher degree of crystallinity of the CHCA precipitate, which corresponds to the lower supersaturation of the system by CaO, as a result of the lower rate of calcium oxide dissolution. This is due to the passivation of calcium oxide during industrial limestone burning. The increased temperature of the process by 10 degrees compared to laboratory conditions also causes a decrease in the equilibrium concentration of calcium oxide. This, in turn, decreases the limiting supersaturation in relation to the much less soluble CHCA precipitate [7]. It is evident that the laboratory samples demonstrate a sufficient degree of similarity in their crystal structure. However, in the system based on sodium aluminate solutions, there is a slightly better formation of crystalline individuals. This observed discrepancy in morphology may be attributable to the diminished metastable stability exhibited by potassium-containing aluminate solutions in comparison to sodium-based solutions. Moreover, this diminished stability can be attributed to a decline in the ionic radius of the cation, concomitant with an increase in the atomic mass of the alkali metal. The decline in ionic radius leads to a reduction in the viscosity of the solutions, thereby determining the intensity of the nucleation and growth processes.

Conclusions

1. It has been established that there are discernible discrepancies in the laboratory synthesis of CHCA, as evidenced by the varying degrees of conversion of calcium oxide into CHCA and its yield, the CHCA content in the precipitate, and its stoichiometry with CO_2 saturation, ranging from 0.79 to 0.62 mol, respectively. For the industrial sample, the result was 0.45 mol. These variations can be attributed to the alterations in the physicochemical and technological conditions of synthesis.

2. The potential for effective synthesis of CHCA in alumina production systems is demonstrated to be independent of the nature of aluminosilicate and, consequently, the composition of process solutions in terms of the ratio of sodium and potassium cations. These prerequisites are established as essential for the production of CHCA both in the processing of alkali-free raw materials using sodium aluminate solutions and alkaline aluminosilicates, including ultra-potassium raw materials with a dependent ratio of sodium and potassium in process solutions.

3. The morphological and particle size characteristics of the samples are quite similar, but there are also noticeable differences in the structure of crystalline aggregates, the degree of crystallinity and the size of crystalline individuals, which is reflected in such an aggregate indicator of the sediment as the particle size distribution, the complex nature of which may be related to the multistage formation of the fractional composition under the influence of a number of independent and significant factors.

Acknowledgements

The present work was carried out with the support of the International Competence Centre for Mining Engineering Education under the auspices of UNESCO under the project "Science", St. Petersburg, Russia.

References

1. Potapova E. N., Manushina A. S., Zyryanov S. M., Urbanov A. V. Methods for Determining Pozzolanic Activity of Mineral Additives. *Construction Materials, Equipment and Technologies of the XXI Century*. 2017. №7- 8. pp. 29–33.

2. Zyryanov M. S., Ahmetzhanov A. M., Manushina A. S., Potapova E. N. Determination of Puzzolanic Activity of Metakaolins. *Advances in Chemistry and Chemical Technology*. 2016. Vol. 30, Iss. 7. pp. 44–46.

3. Rakhimov R. Z., Rakhimova N. R., Stoyanov O. V. Clay Pozzolans. Part 1. Review. *Herald of Technological University*. Vol. 19, Iss. 1. pp. 5–13.

4. Smorodinova T. N., Kotvanova M. K. Pozzolane and Corrosion-Inhibiting Properties of the Natural Zeolite Tuff. *Bulletin of BSTU named after. V. G. Shukhov*. 2020. Iss. 8. pp. 78–86.

5. Amosova L. N. The Relationship of Genesis, Mineralogical and Chemical Compositions of Zeolite Tuffs with Their Pozzolanic Activity. *Polzunovskiy Vestnik*. 2014. №. 1. pp. 9–12.

6. Kozlova V. K., Wolf A. V., Karpova Yu. V. Conversion of Calcium Hydroaluminates and Its Influence on the Composition of Hydration Products of Cements at Elevated Temperature. *Polzunovskiy Vestnik*. 2016. No. 2. pp. 225–229.

7. Babushkin V. I. Matveev G. M., Mchedalov-Petrosyan O. P. Thermodynamics of Silicates. Moscow: Stroyizdat, 1972. 351 p.

8. Rumyantsev P. F. Khotimchenko V. S., Nikushchenko V. M. Hydration of Calcium Aluminates. Leningrad: Nauka, 1974. 80 p.

9. Taylor H. Cement Chemistry. Transl. from Eng. by A. I. Boykova, T. V. Kuznetsova. Moscow : Mir, 1996. 560 p.

10. Lebedev A. B., Bazhin V. Yu., Zhadovskiy I. T. Physico-Chemical Process Behind Self-Disintegration of Sinter Resulting in the Production of Aluminium Oxide and Calcium γ-Orthosilicate. *Tsvetnye Metally*. 2024. No. 2. pp. 80–86.

11. Siddique R., Klaus J. Influence of Metakaolin on the Properties of Mortar and Concrete. *Applied Clay Science*. 2009. Vol. 43, Iss. 3-4. pp. 392–400.

12. Golik V. I., Dmitrak Y. V., Komashchenko V. I., Kachurin N. M. Management of Hardening Mixtures Properties when Stowing Mining Sites of Ore Deposits. *Journal of Mining Institute*. 2020. Vol. 243. pp. 285–292.

13. Kolesnikova O. G., Vasilyeva N. V., Kolesnikov A. S., Zolkin A. L. Optimization of Raw Mix Using Technogenic Waste to Produce Cement Clinker. *Mining Informational and Analytical Bulletin*. 2022. Iss. 10. pp. 103–115.

14. Miachai A. A., Baranovskaya Ye. I., Popova M. V. Composite Portland Cement Using Mineral Additives Based on Natural Raw Materials. *Proceedings of BSTU, Series 2: Chemical Engineering, Biotechnologies, Geoecology*. 2022. Vol. 259, Iss. 2. pp. 100–106.

15. Gu X., Tan H., He X., Smirnova O., Zhang J., Luo Z. Utilization of Carbide Slag by Wet Grinding as an Accelerator in Calcium Sulfoaluminate Cement. *Materials*. 2020. Vol. 13, Iss. 20. 4526.

16. Gerasimov A. M., Ustinov I. D., Zyryanova O. V. Use of Clay-Containing Waste as Pozzolanic Additives. *Journal of Mining Institute*. 2023. Vol. 260. pp. 313–320.

17. Aizenshtadt A. M., Morozova M. V., Frolova M. A., Tyurin A. M. Study of the Potential Use of Tailings from Severalmaz JSC for the Production of Mineral Additives to Cement Binders. *Obogashchenie Rud*. 2024. No. 3. pp. 42–48.

18. Pyagay I. N., Lebedev A. B. Effects of Alumina on the Stability of Ferrite–Calcium Sinter with Dicalcium Silicate. *CIS Iron and Steel Review*. 2023. Vol. 25. pp. 10–16.

19. Kitler I. N., Liner Yu. A. Nephelines – Complex Raw Materials of Aluminum Industry. Moscow: Metallurgizdat, 1962. 237 p.

20. Bazhin V. Y., Ustinova Y. V., Fedorov S. N., Shalabi M. E. K. Improvement of Energy Efficiency of Ore-Thermal Furnaces in Smelting of Alumosilicic Raw Materials. *Journal of Mining Institute*. 2023. Vol. 261. pp. 384–391.

21. Kutepova N. A., Kutepov Yu. I., Kudashov E. S., Daniliev S. M. Strength of Phosphogypsum Mixed with Nepheline Slime in Construction of Embankments of Gypsum Ponds. *Mining Informational and Analytical Bulletin*. 2020. Iss. 10. pp. 67–78.

22. Sizyakov V. M., Korneev V. I., Andreev V. V. Improving the Quality of Alumina and by-Products in the Complex Processing of Nephelines. Moscow: Metallurgiya, 1986. 118 p.

23. Alekseev A. I. Calcium Hydroaluminates and Hydrogranates (Synthesis, Properties, Application). Leningrad: Izdatelstvo LGU, 1985. 182 p.

24. Abramov V. Ya., Alekseev A. I., Badalyants H. A. Complex Processing of Nepheline-Apatite Raw Materials. Moscow: Metallurgy, 1990. 392 p.

25. Siziakova E. V., Ivanov P. V. Multifunctional Coagulants Based on Hidrocarboaluminates Calcium. *Journal of Ecological Engineering*. 2017. Vol. 18, Iss. 2. pp. 16–20.

26. Sizyakova E. V., Ivanov P. V. On the role of Hydrated Calcium Carboaluminate in the Improvement of the Production Technology of Alumina from Nephelines. *Journal of Physics: Conference Series*. 2020. Vol. 1515, Iss. 2. 022048..

27. Antropova I. G., Khomoksonova D. P. Existing and Promising Deep Processing Technologies for Refractory Potassium-Containing Aluminosilicate Raw Materials. *Obogashchenie Rud*. 2021. No. 6. pp. 3–8.

28. Al-Ajeel A. A., Abdullah S. Z., Muslim W. A., Abdulkhader M. Q., Al-Halbosy M. K., Al-Jumely F. A. Extraction of Alumina from Iraqi Colored Kaolin by Lime-Sinter Process. *Iraqi Bulletin of Geology and Minin*g. 2014. Vol. 10, Iss. 3. pp. 109–117.

29. Tian Y., Pan X., Yu H., Han Y., Tu G., Bi S. An Improved Lime Sinter Process to Produce Al_2O_3 from Low-Grade Al-Containing Resources. *Light Metals*. 2016. pp. 5–9.

30. Litvinenko V. S., Petrov E. I., Vasilevskaya D. V., Yakovenko A. V., Naumov I. A., Ratnikov M. A. Assessment of the Role of the State in the Management of Mineral Resources. *Journal of Mining Institute*. 2023. Vol. 259. pp. 95–111.

31. Panov A., Vinogradov S., Engalychev S. Evolutional Development of Alkaline Aluminosilicates Processing Technology. In: *Light Metals 2017*. Springer, 2017. pp. 9–16.

32. Brichkin V. N., Kurtenkov R. V., Maksimova R. I., Bormotov I. S. Regeneration and Recycling of Lime Component in Complex Processing of Kaolin Raw Materials. *Obogashchenie Rud*. 2024. No. 4. pp. 32–38.

33. Abramov V. Ya., Stelmakova G. D., Nikolaev I. V. Physico-Chemical Bases of Complex Processing of Aluminum Raw Materials. Moscow: Metallurgy, 1985. 287 p.

34. Shaaykhmetov A.U., Mustafin A.G., Massalimov I. A. Peculiarities of Thermal Expansion of Oxide, Peroxide, Hydroxide and Carbonate of Calcium. *Vestnik Bashkirskogo universiteta*. 2011. Vol. 16. Iss. 1. pp. 26–32.

35. Spetsov E. A., Artyushevskiy D. I., Konoplin R. R., Sizyakov V. M. Phase Composition of Aluminium Hydroxides and Its Calculation Based on Thermal Analysis Data. *Tsvetnye Metally*. 2023. No. 5. pp. 37–44.