High-Void Non-Autoclaved Silicate Composites with Aluminosilicate Raw Materials

Volodchenko A.A.
Construction Engineering Institute
Belgorod State Technological University named after V.G. Shoukhov
Belgorod, Russia
alex-0904@mail.ru

Lesovik V.S.
Construction Engineering Institute
Belgorod State Technological University named after V.G. Shoukhov
Belgorod, Russia
naukavs@mail.ru
sk31.es@gmail.com

Glagolev E.S.
Construction Engineering Institute
Belgorod State Technological University named after V.G. Shoukhov
Belgorod, Russia

Erofeeva I.V.
NIISF RAACS
Moscow, Russia
ira.erofeeva.90@mail.ru

Cherepanova I.A.
Construction Engineering Institute
Belgorod State Technological University named after V.G. Shoukhov
Belgorod, Russia
inst703@intbel.ru

Lomov M.I.
Construction Engineering Institute
Belgorod State Technological University named after V.G. Shoukhov
Belgorod, Russia
mandragorushka@yandex.ru

Abstract **– Today, silicate wall materials are widespread among the applied wall materials in construction. Their traditional production technology involves the use of cementing component, obtained by the mixed grinding of unhydrated lime and silica materials. Nowadays, one of the main tasks is to reduce the production energy intensity of variously-functional wall composites through the use of unconventional, including man-mad, raw materials. From this perspective, non-traditional for the construction industry clay rocks of the unfinished minerogenesis stage, are of particular interest. To stabilize clay rocks, complex methods can be used, in which, as a rule, several additives are used, which effect on the rock can be different. It has been established that the use of aluminosilicate binder, including lime (Portland cement) for the production of non-autoclaved silicate wall materials based on non-traditional clay rocks, will contribute to achieving the necessary level of structure formation and maximum physical and mechanical properties of high-performance high-void wall products under non-autoclaved conditions.**

Keywords – aluminosilicon raw materials; clay rocks; heat and moisture treatment; non-autoclave silicate materials; geonics (geomimetics).

I. Introduction

Nowadays, one of the main tasks is to reduce the production energy intensity of variously-functional wall composites through the use of unconventional, including man-mad, raw materials [1-6]. The theoretical basis for solving this urgent problem is the transdisciplinary science of geonics (geomimetics).

One of the most common wall building materials is silicate brick and stones. In the traditional silicate materials technology, the main raw material is quartz sand. Tying themselves to this raw material type, enterprises lose the development chance in a rapidly developing competitive environment. Also, the process of synthesis of calcium hydrosilicates in composites based on quartz sand and lime proceeds at high temperatures and pressures.

The silicate brick manufacturing technology development is based on the achievements of many researchers who carry out their research activities on the development and evidence of the theory of silicate materials structure formation, as well as on the technology modernization and silica brick indicators improvement. This makes allows creating a theoretical base for further autoclaved materials technology. As a result of these works, new types of raw materials are used as a raw material used in silicate brick technology [7-8].

Based on the analysis of information [9-11] in the field of raw materials research, theoretical foundations were determined for autoclave materials, as well as their experimental confirmation of the possibility of synthesizing a durable skeleton from new formations when producing non-autoclaved silicate materials with a certain set of properties, due to the unconventional clay rocks use.

Such clay rocks are widespread and in large quantities simultaneously extracted during the mining of ore mineral resources. These rocks specificity is the presence of thermodynamically unstable compounds, such as the imperfect structure of hydromica, mixed-layer formations, finely dispersed poorly-rounded quartz, and also in a small amount of montmorillonite and kaolinite.

Clay rocks have a very diverse mineral composition and properties. In recent decades, using modern research methods (clay minerals structures and properties have been studied in detail), it was found that the elementary layers and the spaces between them in the clay system are nanoscale and have a highly developed active surface [12-16].

The use of specially selected aluminosilicate binder based on unconventional clay raw materials, as well as complex binder, including lime and portland cement for the production of non-autoclaved silicate wall materials based on unconventional clay rocks, will contribute to achieving the required level of structure formation and maximum physical and mechanical properties of products not only at high pressures and temperature, but also at temperatures up to 100 ° C. A particularly positive effect of the use of such systems is that the rheology of such systems allows formatting an effective high-void products.

II. Methods and materials

Clay rocks, including unconventional, of the Kursk Magnetic Anomaly Region, were used for the study. As binding components, unslaked ground calcium lime with an activity of 76.4% and Portland cement of class CEM I 42.5N GOST 31108-2003 were used.

In the samples preparation, there was used a mixture that included a previously prepared aluminosilicate binder by grinding clay and lime, and aeolian-eluvial-diluvial clay. To optimize the composition of synthesized cementing compounds, studies were carried out using a complex binder based on Portland cement and lime. Samples were obtained by the semi-dry molding method at a specific pressing pressure of 20 MPa. The new formations composition phase was studied by X-ray and thermographic analyzes. All samples were subjected to hydrothermal treatment at a temperature of 95 ºC according to the mode of 1.5 hours. + 9 hours. + 1.5 hours. Determination of the samples' physical and mechanical properties was carried out according to the requirements of the relevant regulatory documents.

To determine the particle size distribution of the materials, the MicroSizer 201 installation was used. To determine the material composition the clay rocks was used, as well as the forming composition of the new growths, X-ray phase analysis (ARL X'TRA model diffractometer) and differential thermal analysis (Derivatograph Q - 1500 D). For scanning electron microscopy (SEM), a scanning electron microscope of the model MIRA 3 LM was used.

III. Results

In the classical silicate materials production technology, a binder, obtained by the mixed grinding of lime and silica materials is used. However, the process of calcium hydrosilicates synthesis in such a system proceeds at high temperatures and pressures, which determines the high energy intensity of traditional production of silicate materials. To reduce production energy costs by using silica-containing raw materials with high activity, which is determined by the low temperature of silica dissolution. It is possible to choose such raw materials only cnsidering its genesis, structural and textural features and mineral composition.

The purpose of the study is to explore the aluminosilicate binder and complex binder effect on non-autoclave silicate composites using non-traditional raw materials properties.

The most important properties of the obtained wall non-autoclaved silicate products primarily depend on the composition, and morphological features of the new formations, which is formed during the heat and moisture treatment under atmospheric pressure.

The improvement of the silicate materials physicomechanical properties and the reduction of their energy intensity can be achieved by obtaining hydrogranates and other compounds of the system $CaO–Al_2O_3–SiO_2–H_2O$ as part of the cementing compound. Therefore, the synthesis of new formations optimal structure at the nano-, micro and macro levels is an important task.

For studies, eolian-eluvial-deluvial mixed-layer formations selected in the Kursk Magnetic Anomaly region were used. As a genesis specificity result, this raw material consists of mixed-layer clay minerals, which is a very multicomponent and complex system with a diverse set of properties.

It was found that particles belonging to the aleuritic fraction (42.95%), as well as the pelitic fraction (22.63%) predominate in the clay used. Based on the data of particle size analysis and the established plasticity number, the clay used in the studies can be attributed to clayey sand.

In the study of the clay rocks microstructure, it was established that the structure refers to "skeletal". A multitude of particles of micro-dimensional level are found in the form of aggregates, as well as clay particles. Also the nanoscale level rock particles are observed in the composition.

Based on their material composition, such clay rocks are unsuitable as a raw material for the production of portland cement clinker and ceramic products; however, the special mineral composition of these rocks allows considering them as the main component in the non-autoclaved silicate materials preparation.

The objective of the research was to design and optimize the compositions of aluminosilicate and complex binder and raw mixtures based on natural unconventional aluminosilicate raw materials to achieve the required structural level and maximum physical and mechanical properties of the material.

Available studies have established that the unhydrated lime optimum content for clay rocks of different material composition is 10–12 wt. %, which is very important for real production conditions, since fluctuations in the material composition are unavoidable, and this makes it possible to obtain materials with stable properties [7–8].

Non-autoclaved silicate materials samples, for research, were obtained by the method of semi-dry pressing. The obtained product samples were subjected to heat-moisture treatment. The test results of the samples are given in table 1.

TABLE I. PRODUCT PERFORMANCE INDICATORS

Indicator	Количество вяжущего (CaO) в исходной смеси, мас. %	
	10	12
Tensile strength under compression, R, MPa	20.6	16.8
Softening coefficient	0.81	0.9
Average density, kg / m^3	1840	1810
Water absorption,%	13.5	13.9

In order to intensify the tumors synthesis and create a highly organized composite structure, part of the clay rock was subjected to joint grinding with lime in order to obtain an aluminosilicate binder (Table 2).

TABLE II. ALYUMOSILICATE BINDER COMPOSITION

№	The content of lime in the raw mix, wt. %	Ratio lime: clay in a binder
1	10	1 : 1
2	10	1 : 1,5
3	10	1 : 2

The samples were tested after the heat-moisture treatment and holding the samples for 3 days, (Table 3.).

TABLE III. PHYSICAL-MECHANICAL PROPERTIES OF NON-AUTOCLAVE SILICATE MATERIALS BASED ON ALYUMOSILICATE BINDER

Physical-mechanical properties	№ of composition		
	1	2	3
Compression resistance, MPa	21.7	22.8	22
Softening coefficient	0.8	0.85	0.9
Average density, kg / m^3	1815	1825	1800
Water absorption,%	11.6	9.8	9

The increase in the aluminosilicate binder in the proportion of clay rock leads to an increase in the compressive strength of the raw material. Thus, green strength based on lime-sand (control) mixture was 0.43 MPa. Use as a silica component of the clay rock with a lime content of 10 wt. % allows getting green strength of 1.85 MPa, which is higher than the strength of control samples 4.3 times. The green strength on the basis of aluminosilicate binder (the ratio of CaO: clay - 1: 1) increases 5 times.

Strength of steamed samples, based on aluminosilicate binder, compared with samples, where lime was used as the only binder, increased insignificantly. It can be assumed that the active element content in the clay rock, including nano-sized minerals, is sufficient to form a solid microstructure of the cementing substance and an increase in the fine fraction due to the additional the rock part grinding leads to a slight change in the strength properties. Probably, fine-dispersed quartz content increases in the raw mix after grinding, due to which more slightly- crystalline calcium silicate is synthesized under steaming conditions, i.e. the gelled new formations proportion increases. In this case, the optimal ratio between the gelled and crystalline component is probably disturbed, which causes a slight change in the operational performance of the products. Thus, when choosing the aluminosilicate binder composition, it is necessary to proceed from the particle size distribution of the original rock and to obtain the required products indicators.

According to the differential thermal and X-ray phase analyzes data, new formations are predominantly represented by slightly crystalline calcium hydrosilicate compounds - CSH (B) and C_2SH_2.

To optimize the process of structure formation and create a more highly organized structure at the macro, micro and nanoscale levels, studies were carried out using an integrated binder based on Portland cement and lime.

At the first stage, only Portland cement was used as a binder. The amount of binder used in the experiment was 10 - 16 wt. %. The study of samples based on aeolian-eluvial-deluvial clay rock showed that with an increase in the proportion of Portland cement in the raw mix from 10 to 16%, the compressive strength of the samples increases from 14 MPa to 19 MPa.

However, samples possess water resistance only when the content of the binder is more than 16%, the softening coefficient is 0.7. Probably, the available lime contained in the used binder is not enough to bind the free clay minerals contained in the rock (Table 4).

TABLE IV. PHYSICAL-MECHANICAL PROPERTIES OF NON-AUTOCLAVE SILICATE MATERIALS BASED ON ALYUMOSILICATE BINDER

Performance indicators	The binder content by dry mix weight,%			
	10	12	14	16
Compression resistance	14,2	15,1	17,3	18,5
Average density, kg / m^3	1925	1930	1940	1960
Softening coefficient	0.5	0.5	0.5	0.7
Water absorption,%	9.5	9.6	9.7	9.1

In this regard, to improve the water resistance of the samples, a complex binder was used. A sample was made containing Portland cement 12 wt. % in the presence of lime 5 wt. %. Tests of the obtained samples showed an increase in the softening coefficient from 0.6 to 0.8. Consequently, to obtain water-resistant specimens, the presence of lime in the binder is necessary, or the use of more Portland cement, which is not economically feasible.

To fully demonstrate the influence of the CaO and Portland cement presence in the complex binder on the products' performance properties, as well as to improve the processes of composite microstructure formation, studies were carried out using the methods of mathematical planning of the experiment. Conditions for planning two factor experiments are shown in Table 5.

TABLE V. PLANNING CONDITIONS FOR A TWO-FACTOR EXPERIMENT

Factors		Variation levels			Variation intervals
natural form	coded form	-1	0	+1	
CaO, %	x_1	4	8	12	4
cement content, %	x_2	4	10	16	6

After processing the results, the regression equations of compressive strength and softening coefficient of the obtained composites are:

$$R = 15{,}07485 + 2{,}100421 \cdot x_1 + 4{,}35087 \cdot x_2 + 1{,}770607 \cdot x_1^2 + 0{,}2206078 \cdot x_2^2$$

$$K = 0{,}71029 + 0{,}058345 \cdot x_2 - 1{,}536703 \cdot 10^{-2} \cdot x_1^2 + 4{,}463291 \cdot 10^{-2} \cdot x_2^2$$

Using the obtained regression equations, nomograms of changes in operating non-autoclaved silicate composites were constructed (Fig. 1). The increase in the content of Portland cement contributes to an increase in strength from 10.3 MPa to 18 MPa, an increase in the content of lime increases the compressive strength to 24 MPa. However, an increase in the proportion of lime does not contribute to a greater increase in strength comparing with an increase in the content of portland cement.

The softening coefficient of the samples (Fig. 2) varies from 0.7 to 0.8. it is important to note that with a quantitative content of lime in 5 wt. %, in order to obtain good indicators of products' water resistance, the amount of Portland cement should be at least 15 wt. %

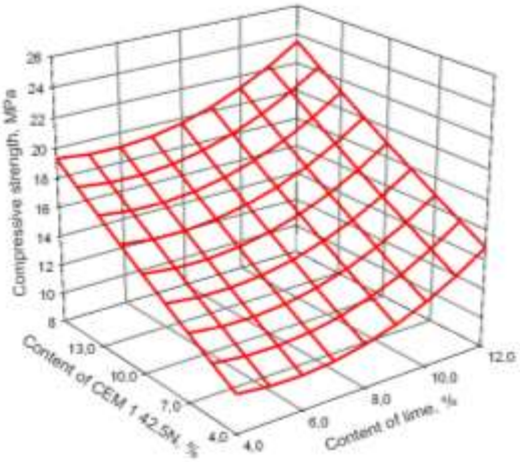

Fig. 1. Nomogram of the compressive strength dependence on the complex binder composition

The study of new formations in the synthesized samples was carried out by X-ray phase and thermographic analyzes methods. Based on these analyzes, the samples contain new formations in the form of low-basic calcium tobermorite-type calcium silicate. The identification of calcium hydrosilicates by radiographs (Fig. 3) is difficult due to the overlap of 3.04 Å on the same reflex of calcium carbonate. The reflections on radiographs in the range of 2.73–2.79 Å are likely to belong to the hydrogranates.

According to the results of thermographic analysis, the endothermic effect at 120 ° C and the exothermic effect at 870 ° C are recorded on the DTA curve, indicating the presence of tobermorite type low-basic calcium silicate. On the differential temperature curveat 180 ° C, the mass loss reflex is fixed, which is associated with the dehydration of new formation, most probably, well-crystallized calcium hydrosilicates. This reflex is absent in the sample based on lime only. It can be assumed that during the hydration of clinker minerals, hydrosilicates of a higher degree of crystallization are formed than during the interaction of lime and clay minerals.

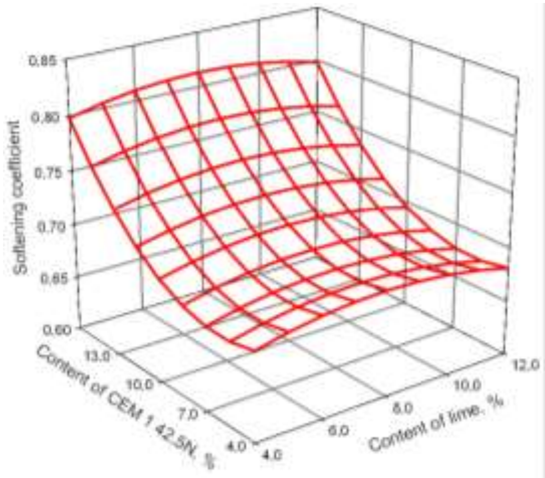

Fig. 2. Nomogram of the samples' softening coefficient dependence on the complex binder composition

It should be noted that calcium hydrosilicates are formed not only due to the interaction of lime and clay rock components, but also due to the hydration of Portland cement components. The formation of more highly basic calcium hydrosilicates predetermines the dense structure of cementing compounds. Due to this, higher performance is achieved on the complex binder basis.

IV. CONCLUSION

Thus, using aluminosilicate raw materials, represented by unconventional for the construction industry clay rocks, it is possible to produce high-void wall composites with improved performance characteristics. Use as a binder component of pure unhydrated lime or specially prepared binder, in order to produce composites with higher properties, depends on the specific rocks used and their composition.

The use of complex binder, including lime and Portland cement, for the production of non-autoclaved silicate wall materials based on unconventional clay rocks will provide an optimization for the composition of cementitious compounds and form a more suitable ratio between highly crystalline and gelled forms of new formations, which would allow obtaining non-autoclave wall silicate materials with higher strength. Lime in the complex binder speeds up the hardening process, increases the strength and stability of crystallization structures in non-autoclaved silicate composites containing cement.

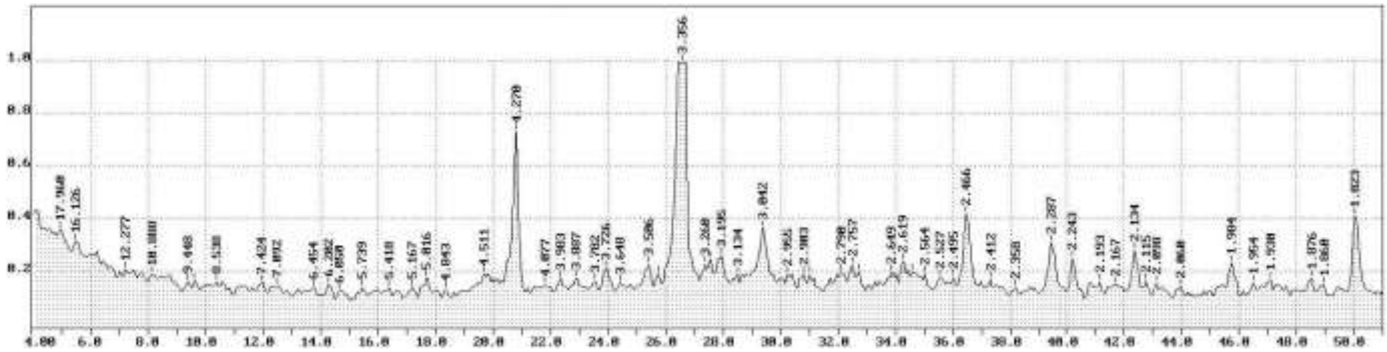

Fig. 3. The roentgenogram of a sample received by pressing

The operational characteristics of building materials based on clay rocks of the incomplete lithogenesis stage and heteroporosity at the nano-, micro- and macro-level contribute to the creation of a comfortable living environment residential compound, which can significantly increase the human life expectancy.

Based on this raw material type, an attractive investment technology has been developed for small and medium-sized businesses to produce energy-saving high-void non-autoclaved wall materials of the new generation with compressive strength up to 30 MPa, frost resistance F15-25, with an average density of 1100-1200 kg / m^3.

Acknowledgment

The reported study was funded by RFBR according to the research project № 18-29-24113.

References

[1] M.Yu. Elistratkin, M.I. Kozhukhova, "Analysis of the factors of increasing the strength of the non-autoclave aerated concrete", Construction Materials and Products, vol. 1, iss. 1, pp. 59–68, 2018.

[2] T.V. Dmitrieva, V.V. Strokova, A.A. Bezrodnykh, "Influence of the genetic features of soils on the properties of soil-concretes on their basis", Construction Materials and Products, vol. 1, iss. 1, pp. 69–77, 2018.

[3] S.-A.Y. Murtazaev, M. Salamanova, S. Zaurbekov, R. Bisultanov, M. Nakhaev, "Composite Binders with the Use of Fine Raw Materials of Volcanic Origin", International journal of environmental & science education, vol. 11, no. 18, pp. 12711–12716, 2016.

[4] S-A.Y. Murtazaev, Sh.Sh. A.Kh. Zaurbekov, M.S.Saydumov, T.S-A. Murtazaeva, M.R Khadzhiev, "Impact of technogenic raw materials on the properties of high-quality concrete composites", Advances in Engineering Research, vol. 177, pp. 275–279, 2018.

[5] Yu.V. Pukharenko, D.G. Letenko, V.A. Nikitin, V.I. Morozov, "Obtaining the nanomodifier for cement composites based on the "dealtom" carbon nanotubes", Materials Physics and Mechanics, no. 31, pp. 59–62, 2017.

[6] J. Pucharenko, V. Morozov, "Structural model and strength predicting of fiber-reinforced concrete", World applied sciences journal, no. 23, pp. 111–116, 2013,

[7] A.A. Volodchenko, V.S. Lesovik, A.N. Volodchenko, L.H. Zagorodnjuk, "Improving the efficiency of wall materials for «green» building through the use of aluminosilicate raw materials", International Journal of Applied Engineering Research, no. 10 (24), pp. 45142–45149, 2015.

[8] A.A. Volodchenko, V.S. Lesovik, A.N. Volodchenko, E.S. Glagolev, L.H. Zagorodnjuk, Y.V. Pukharenko, "Composite performance improvement based on non-conventional natural and technogenic raw materials", International Journal of Pharmacy and Technology, vol. 8 (3), pp. 18856–18867, 2016.

[9] D. Klimesch, A. Ray, "Evaluation of phases in a hydrothermally treated CaO-SiO2-H2O system", Journal of Thermal Analysis and Calorimetry, no. 70 (3), pp. 995–1003, 2002.

[10] S. Bernstein, T.K. Fehr, "The formation of 1.13 nm tobermorite under hydrothermal conditions: 1. The influence of quartz grain size within the system CaO–SiO2–D2O", Progress in Crystal Growth and Characterization of Materials, no. 58 (2–3), pp. 84–91, 2012.

[11] J. Brozovsky, "Rebound hammer tests of calcium silicate bricks – effects of internal compressive stress on measurement results", Applied Mechanics and Materials, vol. 595, pp. 155–158, 2014.

[12] A. Olad, "Polymer / Clay Nanocomposites", Advances in Diverse Industrial Applications of Nanocomposites, InTech, pp. 113–138, 2011.

[13] P. Kiliaris, C.D. Papaspyrides, "Polymer layered silicate (clay) nanocomposites: An overview of flame retardancy", Progress in Polymer Science, no. 35, pp. 902–958, 2010.

[14] A. Elamri, K. Abid, S. Dhouib, F. Sakli, "Morphological and Mechanical Properties of Nanoclay Coated Fabric", American Journal of Nano Research and Application. Special Issue: Nanocomposites Coating and Manufacturing, no. 3 (4-1), pp. 17–24, 2015.

[15] S.J. Emery, S. Masterson, M.W. Caplehorn, "Sand-clay pindan material in pavements as a structural layer", In the Proceedings of the 21st ARRB and 11th REAAA Conference. Transport. Our Highway to a Sustainable Future, p. 15, 2003.

[16] A. Elamri, K. Abid, S. Dhouib, F. Sakli, "Morphological and Mechanical Properties of Nanoclay Coated Fabric", American Journal of Nano Research and Application. Special Issue: Nanocomposites Coating and Manufacturing, no. 3 (4-1), pp. 17–24, 2015.