Unconventional raw materials in silicate materials designing based on technogenic metasomatism knowledge

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Abstract. A large number of scientific schools is working over improving existing building materials and designing some new composites for various functional purposes, where the composites properties play a very important role. However, priority is given to the initial properties of building composites but one of the main indicators by which these properties could be evaluated after prolonged use and under the influence of natural and man-made processes is durability. The study on building materials under changing operating conditions, based on unconventional natural and man-made materials is becoming very interesting and relevant for today. The theoretical basis for increasing the durability of building materials may be the theoretical knowledge of technogenic metasomatism in building materials science. It has been established that the use of unconventional natural and technogenic raw materials, in particular unconventional clay rocks for production of hydrothermal hardening silicate materials will help to achieve the necessary structurization level and maximum physic-mechanical properties of highly efficient wall products under various operating conditions.

1. Introduction

Currently, one of the main tasks of building materials science is to reduce the energy intensity of building composites production through the use of non-traditional, inter alia, technogenic raw materials [1–7]. The theoretical basis for solving this urgent problem is the transdisciplinary science of geonics (geomimetics).

Many scientific schools of all world countries are working on creating new building composites, developing technologies for their production and studying composites’ properties, etc. However, priority is given to the initial properties of building composites but one of the main indicators by which these properties could be evaluated after prolonged use and under the influence of natural and man-made processes is durability. So, during operation, the same building composites fall into specific conditions, various processes are proceeding in them. Some buildings and structures during exploitation do not withstand external influences and for these reasons they are destroyed. Therefore a set of measures is needed aimed at more detailed studying the building materials under certain exploitation conditions, taking into account the environmental changes with increasing ecological stresses. The theoretical basis for increasing the building material durability can be the theoretical knowledge of technogenic metasomatism in building materials science. This is a stage in the evolution of building materials, characterized by the adaptation of the composite to some changing conditions during the exploitation of buildings and constructions.
The building industry evolves not only in the direction of production but also focuses on chemical and physicochemical processes. For example, the use of binders is being improved in the course of studying the processes which occur during the hardening and subsequent operation of materials produced on their base [9–11]. Using knowledge about chemical processes in developing building materials will dramatically improve the properties of composites and produce new-generation materials. Understanding these processes is extremely important when solving the problem of increasing the efficiency of any production technology and the quality of building materials.

The trend relating to deterioration of the quality and properties of materials is caused due to undesirable processes, not only external ones – exposure to CO$_2$, aggressive environment, but also internal ones – corrosion, recrystallization, aging, etc. For example, over the past 200 years, the carbon dioxide content in the Earth’s atmosphere has been steadily increasing. In the pre-industrial era, it did not exceed 280 volume parts per million (ppm), and today it reaches 365 ppm and has a tendency to increase. Based on some statistics, in 2012, world emissions of CO$_2$ amounted to 34 billion tons and exceeded the 1990 figures by 50%. According to the data announced at the International Economic Forum (IWR) in the city of Münster, if the current trend continues, the volume of global carbon dioxide emissions will increase by 20 % by 2020 and amount to more than 40 billion tons. For comparison: in 1990, global carbon dioxide emissions barely reached 22.7 billion tons. The concentration of carbon dioxide in the atmosphere has reached a high level over the past 420 thousand years. All this must be taken into account when designing and using building composites.

The whole set of complex physical and chemical transformations, that is, technogenic metasomatism, when designing the material, will allow the composite, in response to external influences, to self-heal the defects that form during operation, restore their original characteristics and lead to hardening of the material with an increase in load under technogenic stress conditions.

One of the most economical and common among wall materials are silicate materials and products from them. The raw materials for their producing are environmentally friendly materials: mineral binder, siliceous component and water. Portland cement and ground lime are used as a binder. It is possible to replace lime and Portland cement with ground slag (metallurgical, fuel, etc.). Being dependent on this type of raw material, enterprises lose the opportunity to develop in a rapidly developing competitive industrial world. Also, the process of synthesis of calcium hydro-silicates in composites based on quartz sand and lime proceeds at high temperatures and pressures [12-13]. In the process of hydrothermal processing of silicate materials, organic impurities that accidentally fall into the raw material blend can burn out and volatilize. Therefore, such products do not emit harmful components during exploitation under various internal and external impacts.

The development of technology aimed at silicate brick manufacturing is based on the achievements of many researchers who carry out experimental studies on development of theories giving the knowledge of structurization of silicate materials, as well as on modernization of the technology targeted at increasing some properties of the silicate brick. This allows creating a theoretical basis for further improving the technology of autoclave materials. As a result, new types of raw materials are used in the technology of silicate brick production.

An analysis of the data within the research studying the raw material base of autoclave hardening materials allowed theoretically substantiating and experimentally confirming the possibility of using instead of sand the clay rocks of an incomplete phase going in mineral formation processes [14–15]. Such clay rocks are widespread, and also in large quantities are simultaneously recovered in the extraction of ore minerals. The specificity of these rocks is the presence of thermodynamically unstable compounds, such as imperfect hydromica structure, mixed-layer minerals, finely dispersed weakly rounded quartz, as well as a small amount of montmorillonite and kaolinite. This raw material, which has the properties of natural nano-sized particles, allows to control the synthesis of neoplasms to obtain materials with the desired properties.

Clay rocks have a very diverse mineral composition and properties. In recent decades, when the modern research methods are used, the structures of clay minerals and their properties have been
studied in detail. It was found that the elementary layers and the spaces between them in the clay system are nano-scale and have a highly developed active surface [16–17]. The use of a specially selected alumino-silicate binder based on non-traditional clay raw materials in producing the silicate wall materials of hydrothermal hardening will help to achieve the necessary level of structurization and maximum level of some physical and mechanical properties of products not only at high pressures and temperatures, but also at temperatures up to 100 °C.

2. Methods and materials
For research, the Aeolian-eluvial-deluvial clay rock of the Quaternary age was used. These rocks are widespread in the region of the Kursk magnetic anomaly.

Visually, the mineral is unconsolidated (loose) rock of brown colour. It has a clay-silty structure. The size is dominated by silt and pelitic particles. By chemical composition, the rocks are classified as acidic with a high content of free silica (39.96 wt. %). In addition, a fraction of less than 0.005 mm also contains a significant amount of free quartz (33.60 wt. %).

The clay fraction of the rock is represented by Ca$^{2+}$ montmorillonite with $d_{001} = 14.81–15.87$ Å (fig. 1). These layers of the mineral structure are easily replaced by polar organic molecules; therefore, when saturated with ethylene glycol, the main interplanar distance increases. During calcinations at 600 °C for two hours, the reflections characteristic of $d_{001}$ decrease to 9.99 Å, due to the fact that interlayer water is easily removed at this temperature.

A series of reflexes of 9.99, 4.99 and 3.32 Å, the values of which do not change either after saturation with ethylene glycol or after calcination, indicate the presence of hydromica in the rock. The interplanar distances that are multiples of 7.14 Å, which disappear upon calcination within 2 hours, allows identifying kaolinite.

Quicklime clod lime with an activity of 87.34 % was used as an astringent component. As siliceous aggregate, quartz sand with a particle size modulus of 1.54 was used. The content of SiO$_2$ was 92.4 wt. %

The composition of the raw blends was determined based on the conditions of hydrothermal treatment:
• for hydrothermal treatment at elevated pressures and temperatures, raw blends were prepared with a content of 8 % active CaO, the content of aeolian-eluvial-deluvial clay rock in the raw material blend was changed from 5 to 70 wt. %. As a control, a calcareous sand blend was used. The molding moisture content of the raw material blend depended on the clay content and amounted to 7–10 %. The rock was added to the raw material blend in the form of a calcareous-sandy-clay binder, obtained by joint grinding of the rock and lime to a specific surface of 500 m$^2$/kg;
• for hydrothermal treatment under atmospheric pressure at a temperature of 95–0659 C, a mixture was used to produce the samples, including a pre-prepared aluminosilicate binder obtained by
co-grinding clay and lime, and as an aggregate, the original aeolian-eluvial-deluvial clay rock. The moisture content of the raw blend was 8–12 %.

All samples were obtained by semi-dry molding at a specific pressing pressure of 20 MPa. The phase composition of neoplasms was studied by x-ray and thermo-graphic analysis. The physical and mechanical properties of the samples were determined in line with the requirements of the regulatory documents.

MicroSizer 201 was used to determine the particle size distribution of materials. In order to determine the material composition of the clay rocks used, as well as the emerging composition of the neoplasms, X-ray phase analysis (model diffractometer – ARL XTRA) and differential thermal analysis (Derivatograph Q – 1500 D) were used in this research. For scanning electron microscopy (SEM), a MIRA 3 LM scanning electron microscope was used.

3. Results

For autoclaved samples, the compressive strength, average density and water absorption were determined (fig. 2). The experimental data showed that the clay rock has a positive effect on increasing the strength of silicate materials. The optimal content of loam, corresponding to the maximum strength of the samples, is 20–30 wt. %. The strength of the samples increases from 20 to 32 MPa (1.6 times). When the rock content is in the amount of 5 wt. %, there is a slight decrease in strength. The average density increases from 1780 to 1980 kg/m$^3$ with a rock content of 30 wt. %. The minimum water absorption (9.3%) corresponds to a rock content of 20 wt. %

There were carried out some microscopic studies of calcareous and sandy samples with a clay rock content of 30 wt. %. It has been established that on the surface of quartz grains of calcareous-sandy images and at the contacts between them, there are some substances, indistinct and smudgy by nature (difficult to identify). Cementing compounds are formed by the reaction of lime with fine and coarse aggregate quartz. Grains of quartz in samples with clay content are evenly distributed in the total amorphous mass.

The surface of many small particles of quartz is subject to corrosion and is surrounded at the edges by a gel-like film of neoplasms.

![Figure 2](image_url)

**Figure 2.** Physico-mechanical properties of silicate materials of autoclave hardening depending on clay content (active CaO content 8 wt); 1 – compressive strength; 2 – average density; 3 – water absorption

From the data presented, it can be concluded that in the lime-sand blend in the presence of clay minerals, the formation of a cementitious compound occurs mainly due to the interaction of calcium hydroxide with clay minerals and partially finely divided quartz. Coarse quartz with lime practically does not react.

The cementitious compound of calcareous (control) samples is represented by low-basic calcium hydro-silicates of the CSH (B) group, detected by the exothermic effect at 835–1659 °C in the thermo-gram and reflections of 3.04, 2.80, 1.82 Å in the X-ray diffraction pattern (fig. 3).
Calcium hydrosilicates CSH (B) are also formed in samples based on a calcareous binder. The shift of the exothermic effect to higher temperatures (870–880 °C) is probably associated with an increase in the basicity of calcium hydrosilicates.

With a content of 5 wt. % of loam in the raw blend shows the hydrogranates formation, the amount of which increases with increasing rock content that can be judged by the increase in the intensity of the endothermic effect at 340 °C and reflections of 5.00, 2.75, 2.00 Å, increases (fig. 3).

The data allow us to conclude that the maximum permissible content of sand-clay rock in the raw material blend determines the amount of clay component of the rock and the content of lime.

The increase in the samples strengthening occurs as a result of the formation of a stronger microstructure of the cementitious substance due to an increase in the packing density of the material, as well as the synthesis of hydrogranates. Isometric crystals and hydrogranate plates have a small specific surface and are microfiller, which is cemented by a submicrocrystalline gel phase from low-basic calcium hydrosilicates. An increase in average density and the formation of denser packaging associated with this leads to a decrease in water absorption. This is confirmed by the fact that the samples with the maximum average density correspond to the minimum water absorption (fig. 2).

To obtain hydrothermal silicate materials under atmospheric pressure, aeolian-eluvial-deluvial clay rock of the Kursk magnetic anomaly region was used as in previous experiments.

To conduct an experiment, a raw blend was prepared with a percentage of CaO of 15 wt. % (table 1). The samples were obtained by pressing, where the pressing pressure was 20 MPa. The moisture content of the raw blend depended on the composition, and was in the range of 8–12 %. After 2 days, the samples were tested to identify a compressive strength. Part of the samples of each composition withstood 1 year in a tap water. After that, the samples were tested for tensile strength in compression in a water-saturated state. The results are shown in table 2 and 3.

![Figure 3. X-ray diffraction patterns of samples: 1 – calcareous; loam content, wt. %; 2 to 5; 3-30](image)

**Table 1. Compositions of raw blends based on a calcareous binder**

| Composite No. | Lime content in raw materials blend, wt. % | Lime ration: clay in a binder | Specific surface of a binder, m²/kg |
|---------------|------------------------------------------|-----------------------------|---------------------------------|
| 1             | 15                                       | 1 : 1                       | 1000                            |
| 2             | 15                                       | 1 : 1.5                     | 950                             |
| 3             | 15                                       | 1 : 2                       | 700                             |

The physicomechanical parameters of silicate samples indicate that the studied raw materials actively interact with lime under steaming conditions at a temperature of 90–95 °C.
This time as well, the physicochemical processes are going that lead to the synthesis of a complex binder, forming a strong frame. According to the differential thermal and x-ray phase analysis, the neoplasms are represented mainly by weakly crystallized calcium hydrosilicate compounds — CSH (B) and C₂SH₂.

Table 2. Physico-mechanical properties of silicate materials based on an aluminosilicate binder

| Physico-mechanical properties | Composite No. |
|------------------------------|---------------|
|                              | 1  | 2  | 3  |
| Compressive ultimate strength, MPa | 22.58 | 21.8 | 21 |
| Softening coefficient         | 0.8 | 0.85 | 0.9 |
| Average density, kg/m³        | 1815 | 1825 | 1800 |
| Water absorption, %           | 11.6 | 9.8 | 9 |

The test results of the samples cured for 1 year in water (table 3) showed a significant increase in strength compared to the samples that were not subjected to long-term storage in water.

Table 3. Compositions of raw blends based on a calcareous binder

| Physico-mechanical properties | Composite No. |
|------------------------------|---------------|
|                              | 1  | 2  | 3  |
| Compressive ultimate strength, MPa | 34.7 | 32.5 | 32 |
| Softening coefficient         | 0.73 | 0.8 | 0.8 |
| Average density, kg/m³        | 1830 | 1820 | 1810 |
| Water absorption, %           | 10.2 | 9.5 | 8.8 |

This is due to the fact that the rock-forming minerals, in particular, its nanodispersed component, provide the synthesis of a cementing compound with hydraulic properties. The cementitious compounds are likely to possess these properties both due to the synthesis of highly basic compounds, which undergo further hydration, and due to recrystallization of gel-like calcium hydrosilicates that leads to densification of the neoplasm structure.

In the microstructure of the original sample there is an accumulation of globules up to 0.5 μm in size, which are connected by a network of neoplasms, which are weakly crystallized low-basic calcium hydrosilicates (fig. 4).

Neoplasms also cover the surface of the aggregate. A crystallization structure was formed here, providing high strength and water resistance.

The chemical composition of the globules of the original sample was studied by energy dispersive x-ray spectroscopy. According to the emission spectra, the elemental composition of the globules was calculated. The main elements that make up the globules are wt. %: O – 33.57–44.42; Ca – 28.2-40; Si – 12.44-24.63; Al – 7.37-10.92. It follows that the globules are formed mainly due to the interaction of lime with clay minerals and the X-ray amorphous phase and as a result, they are the amorphous aluminates and calcium hydrosilicates. It can be concluded that globules are intermediate compounds formed during the synthesis of neoplasms from the finely dispersed part of the rock-forming minerals, and, above all, the clay component and lime.

The microstructure of the sample after a year of storage in water is significantly different from the original sample, which was not subjected to long-term storage in water (fig. 5).
The globules in the structure of the cementitious compound are practically absent. At the same time, the number of weakly crystallized calcium hydrosilicates increases, which, forming a continuous grid, almost completely fill the pores, cover the surface of the filler and fasten its grains together. Consequently, the globules exhibit thermodynamic instability and the formation of weakly crystallized calcium hydrosilicates based on them continues after hydrothermal treatment of products. In the water environment, the process of calcium hydrosilicates formation continues over time, which leads to the formation of a more durable microstructure of the cementitious compound. In addition, weakly crystallized calcium hydrosilicates are an unstable phase, capable of undergoing recrystallization in time, and especially in the water environment, which also leads to a change in the structure of the cementitious compound. Probably, these processes provide the hydraulic properties of the silicate materials.

4. Conclusion
Thus, using aluminosilicate raw materials which are represented by clay rocks, non-traditional for the construction industry; it is possible to obtain high-hollow silicate wall composites with improved properties, both in autoclave synthesis and in heat and moisture treatment. The use of pure quicklime or a specially prepared binder, as a binder component, in order to obtain composites with higher properties depends on the specific rocks used and their composition.

The studies have established the influence of operating conditions on the structurization mechanism of the composites based on unconventional clay raw materials. We identified that initially, when clay minerals and finely dispersed quartzas interact with lime, under conditions of heat and heat treatment, intermediate compounds are formed, in a shape of the globules, which are amorphous hydroaluminates and calcium hydrosilicates. Further, based on them, a spatial network of neoplasms is formed,
consisting of weakly crystallized calcium hydrosilicates, as well as aluminum-substituted calcium hydrosilicates and hydrogranates. After prolonged use in humid conditions, these neoplasms recrystallize, thus compacting the structure at the nano, micro, and macro levels.

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**References**
[1] Suleymanova L A, Lesovik V S, Kara K A et al 2014 Energy-efficient concretes for green construction Res. J. of appl. Sci. 9(12) 1087–90
[2] Dmitrieva T V, Strokov V V and Bezdrodykh A A 2018 Influence of the genetic features of soils on the properties of soil-concretes on their basis Construct. Mater. and Products 1(1) 69–77
[3] Kuprina A A, Lesovik V S, Zagorodnyk I H and Elistratkin M Y 2014 Anisotropy of materials properties of natural and man-triggered origin Res. J. of Appl. Sci. 9(11) 816–9
[4] Murtazaev S-A Y, Zaurbekov A Kh, Saydumov M S et al 2018 Impact of technogenic raw materials on the properties of high-quality concrete composites Advances in Engineering Research 177 275–9
[5] Pucharenko J and Morozov V 2013 Structural model and strength predicting of fiber-reinforced concrete World appl. Sci. J. 23 111–6
[6] Elistratkin M Yu and Kozhukhova M I 2018 Analysis of the factors of increasing the strength of the non-autoclave aerated concrete Construct. Mater. and Products 1(1) 59–68
[7] Pukhareenko Yu V, Letenko D G, Nikitin V A and Morozov V I 2017 Obtaining the nanomodifier for cement composites based on the “dealton” carbon nanotubes Mater. Phys. and Mechan. 31 59–62
[8] Lesovik V S and Volodchenko A A 2015 The problem of technogenic metasomatose in materials science Bull. of BSTU named after V G Shukhov 4 38–41
[9] Murtazaev S-A Y, Salamanova M, Zaurbekov S et al 2016 Composite Binders with the Use of Fine Raw Materials of Volcanic Origin Int. J. of Appl. Enginner. & Sci. Ed. 1(18) 12711–6
[10] Strokov V V, Sumin A V, Nelubova V V and Shapovalov N A 2015 Modified binder with application of nanostructured mineral components Bull.of BSTU named after V G Shukhov 3 36–9
[11] Pukhareenko Yu V, Letenko D G, Nikitin V A and Morozov V I 2017 Obtaining the nanomodifier for cement composites based on the “dealton” carbon nanotubes Mater. Phys. and Mechan. 31 59–62
[12] Klimesch Danielle and Ray Abhi 2002 Evaluation of phases in a hydrothermally treated CaO-SiO2-H2O system J. of Thermal Anal. and Calorimetry 70(3) 995–1003
[13] Bernstein S and Fehr T K 2012 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 Characterizat. of Mater. 58(2-3) 84–91
[14] Volodchenko A A, Lesovik V S, Volodchenko A N and Zagorodnjuk L H 2015 Improving the efficiency of wall materials for “green” building through the use of aluminosilicate raw materials Int. J. of Appl. Engineer. Res. 10(24) 45142–9
[15] Volodchenko A A, Lesovik V S, Volodchenko A N et al 2016 Composite performance improvement based on non-conventional natural and technogenic raw materials Int. J. of Pharmacy and Technol. 8(3) 18856–67
[16] Olad Ali 2011 Polymer/Clay Nanocomposites Advances in Diverse Industrial Applications of Nanocomposites, InTech 113–38
[17] Kiliaris P and Papaspyrides C D 2010 Polymer layered silicate (clay) nanocomposites: An overview of flame retardancy Progress in Polymer Science 35 902–8