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To cite this article: A A Volodchenko *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **463** 032016

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Influence of Composition of Technogenic Materials-sourced Aluminosilicate Binder onto Structural Formation and Performance Properties of Construction Composites

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Abstract. Analysis of data from studies of aluminum silicate binder-based construction composites allowed giving theoretical justification and then experimentally confirming a possibility to control synthesis of new growth to obtain composites with predefined characteristics by means of using shales of incomplete clay synthesis of various genesis. Employing aluminosilicate rocks of incomplete clay synthesis, which contain thermodynamically-unstable compounds make it possible to shift from traditional raw materials to production of composite materials on the basis of natural polyfunctional raw material, thus allowing to accelerate synthesis of new growth, change its morphology, optimize microstructure of binding materials and as a result, to improve performance properties of final products. Improvement of performance properties of silicate materials and reduction of their energy content are provided by producing hydrogarnets and other $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ compounds in the binding material under condition of hydrothermal treatment without additional pressure.

1. Introduction

Currently there is a trend to develop future construction materials by employing new types of raw materials which were previously deemed unfit for production of such construction materials. Development of research equipment allows opening new prospects for application of non-traditional raw materials, including with the use of nature-like technologies [1-5]. So, for instance, production of common silicate wall materials is based on a traditional technology that uses autoclave treatment of products and employs lime and quartzite sand as raw materials. However, it is difficult to obtain energy-efficient products with high hollow ratio due to a low strength of adobe and sub-optimal structure of the matrix. Solution of this problem is linked to a new approach to silicate material production technology, which lies in switching from traditional raw materials to production of composite aluminum silicate binders with non-traditional shales of incomplete clay formation.

In the traditional silicate material production technology, there is a chemical reaction between the components of the raw mixture where calcium hydrosilicates are formed: CSH(B) , $\text{C}_2\text{SH(A)}$, C_2SH_2 , tobermorite $\text{C}_5\text{S}_6\text{H}_{5-2}$ and less often eakleite $\text{C}_6\text{S}_6\text{H}$. Dissolution of the components and synthesis of calcium hydrosilicates happens under high temperature in the traditional technology, thus determining increased energy content of the silicate material production. Reduction of the energy consumption in production is possible by use of silica-containing raw materials with high activity, which is determined by reduced solution temperature of the silica. Selection of such raw material is possible only when



taking its genesis into account, as well as structural and textural features and mineral composition. Improvement of performance properties of silicate materials and reduction of their energy content are provided by producing hydrogarnets and other $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ compounds in the binding material. That is why aluminosilicate mixes provide silicate materials with various properties.

Employing non-traditional and technogenic shale materials in production of building materials make it possible to shift from traditional raw materials to production of composite materials on the basis of natural non-traditional shale material, thus allowing to accelerate synthesis of new growth, change its morphology, optimize microstructure of binding materials and as a result, to improve performance properties of final products [6-8]. Shales of incomplete clay formation contain highly dispersed components: shale minerals, X-ray amorphous phase and fine quartz. Quartz's surface is largely corroded. Natural processes performed a part of work in rock destruction, thus allowing reducing energy costs for milling the aluminum silicate binder [9-11].

One of the significant differences in interaction of Ca(OH)_2 with quartz and shales is that the latter have ion-exchange qualities due to the presence of hydroxyl group on silicon atoms. Silicon-oxygen surface $[-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-]$ does not have such properties. When considering processes happening under hydrothermal conditions, the most important ones are adsorption and cation exchange at the shale surface. Obviously, the $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system is largely characterized by ion exchange processes. Due to a dynamic equilibrium on the shale mineral surface in autoclaving, the hydroxyl groups may leave the active positions by breaking the bonds on the surface of the crystalline structure and consolidating on the surface, while the Ca^{2+} ions may adsorb at these active positions. It leads to structural destruction of the shale with formation of calcium hydrogarnets and hydrosilicates. Thus, one may conclude, that when using shales of unfinished clay formation with thermodynamically-unstable compounds as a raw material for production of aluminosilicate binder, it is possible to obtain efficient silicate materials under hydrothermal treatment without applied pressure.

2. Materials and methods

As binding components, lumped quicklime produced by Belgorodstroy material following GOST 9179-77 was used. This work used aeolian-eluvial-glacial Quarternary shales from deposits of Kursk Magnetic Anomaly.

Grain size distribution of materials was determined with MicroSizer 201 unit, which allows detecting particles sized from 0.2 to 600 micron.

Mineralogical composition of raw materials and synthesized new growth was studied with X-ray diffraction analysis. The studies were performed at X-ray diffraction meter – ARL X'TRA. Thermo Fisher Scientific. Additionally, differential thermal analysis was used to identify new growth products and mineral composition. The studies were performed with a Derivatograph Q – 1500 D. Scanning electron microscopy (SEM) was performed with a MIRA 3 LM microscope.

Method of sample production depended on the raw mix composition. If only ground quicklime was used as a binder, then the mix was prepared by mixing the raw components in a necessary ratio.

The mix including a pre-produced binder (pre-milled shale and binder) was mixed with the basic rock or a component with the same silica content and was also moistened with water. After forming, the samples were placed into a curing room and treated with steam curing at a temperature of 90–95 °C following the procedure: 1.5 h.+9 h. +1.5 h.

3. Main part

To resolve the task of creating efficient composites using aluminosilicate binder, we used shale which is highly characteristic of Kursk Magnetic Anomaly, with high aluminosilicate content.

Pellite fraction in the shale constitutes 22.63 %wt. Alevrite and pellite particles prevail. Chemical analysis shows that the rock has high silica content and pertains to acidic rocks. When studying the shale by X-ray diffraction and differential thermal analysis, it was found that the rock contains montmorillonite, kaolinite, hydrous mica and mixed lattice compounds.

Microstructural studies revealed, that the structure is skeletal. There is a multitude of microscopic particles as aggregates, as well as shale particles. Chrystal habit of the particles is plates, as well as foliated and bidirectional elongated forms. The particles form microaggregates by chaotically interconnecting (by means of mechanical bonds). However, there are aggregates with quite well-oriented particles (shale minerals) throughout. From this, one may conclude, that the studied rock has a multi-component (multi-mineral) composition. In addition, there are nanoscale particles observed in the rock, which may determine high characteristics of the products.

Presence of nanodisperse aluminosilicate particles in the studied raw material, as well as fine activated quartz under alkaline condition lead to formation of tobermorite hydrosilicates of various base-to-silica ratio and calcium hydroaluminosilicates. At normal temperatures such reactions are slow, however they accelerate significantly with increased temperature and humidity. These compounds have higher binding properties than, for example, CaCO_3 and Ca(OH)_2 . Thus, fine component of the shale acts as an active hydraulic additive, and lime automatically converts into a hydraulic binder. Under conditions of increased temperature in hydrothermal treatment, the binder formation processes proceeding in interaction between the quicklime and shales are significantly accelerated, thus providing the building materials with improved physical and mechanical properties.

The goal of this research is to study influence of the aluminosilicate binder composition onto the structure formation processes in the composites obtained.

For the experiment, a raw mix was prepared, containing 15%wt of CaO (Table 1). Samples were produced by compaction with the pressure of 20 MPa. Humidity of the raw mix depended on its composition and was in the range of 8-12 %. After 2 days, the samples were tested for ultimate compression strength. A portion of samples of each composition was held submerged in tap water for 1 year. After that, the samples were tested for ultimate compression strength in water-saturated state. The results are shown in Tables 2 and 3.

Table 1. Composition of raw mixes on the basis of lime and shale binder.

no. of composition	Lime content in the raw mix, %wt	Ratio between lime and shale in the binder	Specific surface of the binder, m ² /kg
1	15	1 : 1	1000
2	15	1 : 1.5	950
3	15	1 : 2	700

The obtained physical and mechanical properties of silicate samples show, that the studied raw material actively interacts with quicklime under steam treatment condition under the temperature of 90–95 °C. At that, physical and chemical processes proceed, leading to synthesis of a complex binder, which forms a strong skeleton frame. Differential thermal analysis and X-ray diffraction analysis reveal, that new growth is largely formed by dyscrystalline compounds of calcium hydrosilicate: CSH(B) and C_2SH_2 .

The results of testing for the samples held under water for 1 year (Table 3) have shown a significantly improved strength in comparison with the samples not held submerged.

Table 2. Physical and mechanical properties of aluminosilicate binder-based silicate materials.

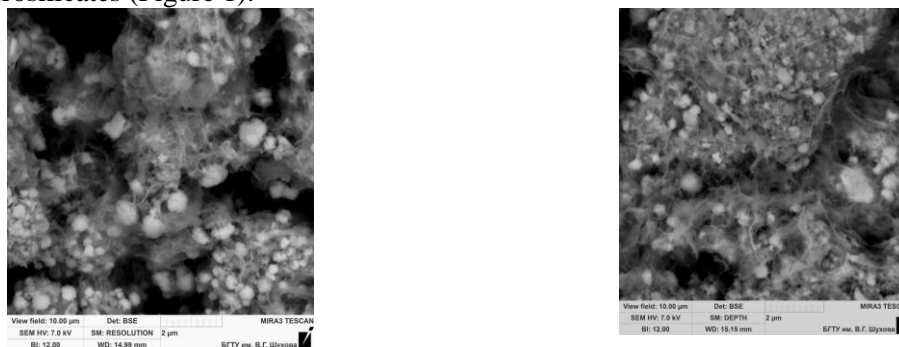
Physical and mechanical characteristics	Composition number		
	1	2	3
Ultimate compressive strength, MPa	22.58	21.8	21
Softening factor	0.8	0.85	0.9
Average density, kg/m ³	1815	1825	1800
Water uptake, %	11.6	9.8	9

Table 3. Physical and mechanical properties of aluminosilicate binder-based silicate materials after held submerged in water for 1 year.

Physical and mechanical characteristics	Composition number		
	1	2	3
Ultimate compressive strength, MPa	34.7	32.5	32
Softening factor	0.73	0.8	0.8
Average density, kg/m ³	1830	1820	1810
Water uptake, %	10.2	9.5	8.8

This is due to the fact, that rock-forming minerals, and particularly its nanodisperse component provide synthesis of a cementing compound with hydraulic properties. The cementing binders probably have such properties due to synthesis of highly basic compounds that undergo further hydration, and due to recrystallization of gelled calcium hydrosilicates, which leads to compaction of structure of the new growth.

In the microstructure of the original sample, one may see accumulation of globules with the size of up to 0.5 micron, which are interlinked with a net of new growth, which is dyscrystalline low-basic calcium hydrosilicates (Figure 1).

**Figure 1.** Microstructure of composite, SEM.

The new growth also covers the surface of aggregate. Here, a crystalline structure providing high strength and water resistance has been formed.

Chemical composition of the globules for the original sample was studied with energy dispersive X-ray spectroscopy. Elemental composition of the globules was calculated from emission spectra. The main elements composing the globules are, %wt: O – 33.57–44.42; Ca – 28.2–40; Si – 12.44–24.63; Al – 7.37–10.92. In addition, there are trace amounts of Mg and Fe. These elements are also the main elements in the composition of shale minerals. Thus, the globules are mainly formed by interaction between the quicklime and shale minerals and X-ray amorphous phase and they are amorphous calcium aluminates and hydrosilicates. The reaction takes place in the liquid phase. In these amorphous compounds, cohesion forces are significantly more pronounced than adhesion to the neighboring components of the mix. That is why the primary new growth takes the globular form due to high surface tension. One may conclude, that the globules are intermediate compounds being formed during the new growth synthesis from the fine components of the rock-forming minerals, primarily clay component and quicklime.

Microstructure of the sample that underwent one year of storage submerged under water significantly differs from that of the original sample that did not undergo such treatment (Figure 2).

There is almost complete absence of globules in the structure of the binder. At the same time, the amount of dyscrystalline calcium silicates is increased; they form a compact lattice, almost completely filling the pores, covering the aggregate surface and holding its grains together. Thus, the globules show thermodynamic instability and formation off dyscrystalline calcium hydrosilicates on their basis continues after the hydrothermal treatment as well.

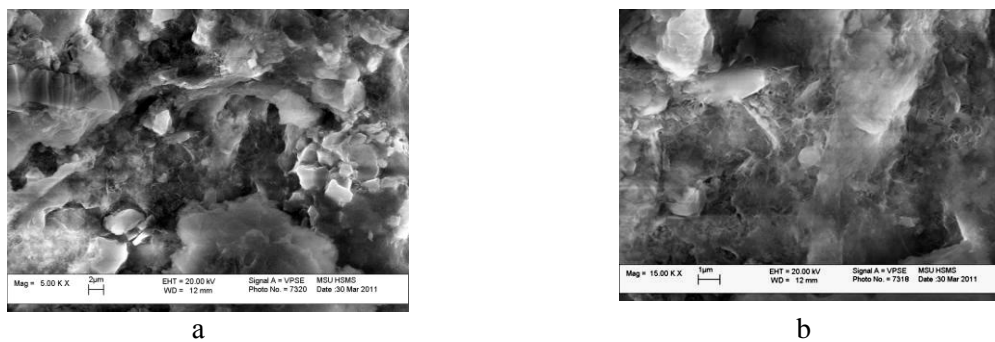


Figure 2. Microstructure of composite after one year of storage submerged in water, SEM: a – $\times 5000$; b – 15000 .

In the aqueous medium, the process of calcium hydrosilicate formation continues, leading to creation of a more robust binder microstructure. Besides that, dyscrystalline calcium hydrosilicates are an unstable phase, which may with time and especially in the aqueous medium, undergo recrystallization, which also leads to changes in structure of the cementing compound. These processes probably determine hydraulic properties of the silicate materials obtained.

4. Conclusion

The research revealed structural formation mechanism of aluminum silicate binder composites produced from non-traditional natural and technogenic raw material under hydrothermal conditions without applying additional pressure. Initially, on interaction of shale materials and fine quartz with lime, intermediate compounds in the form of globules are formed; they are amorphous calcium hydroaluminates and hydrosilicates. Then, they serve as a base for formation of a spacial new growth lattice, consisting of dyscrystalline calcium hydrosilicates, as well as aluminum-substituted calcium hydrosilicates and hydrogarnets.

5. Acknowledgments

The paper has been prepared under the scholarship of the President of Russian SP-3717.2018.1 for the years 2018-2019, using equipment of High Technology Center at BSTU named after V.G. Shoukhov

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