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COMPOSITE PERFORMANCE IMPROVEMENT BASED ON NON-CONVENTIONAL NATURAL AND TECHNOGENIC RAW MATERIALS

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Abstract

The study of rational nature use problem, the use of natural and environmentally friendly man-made materials, the introduction of new modern, energy-efficient and resource-saving technologies during the creation of building materials is one of the most important tasks. The solution to this problem is possible by the creation of new closed technological circuits with the full use of all the by-products at all stages of production. One of the main technical and economic indicators of any technology is the conversion of raw materials into useful products. However, in practice, a large proportion of the raw materials is converted into waste that is directed mainly to dumps, causing a significant damage to the economy and ecology.

The modern development of technological mineralogy is inconceivable without a complex processing, where all products are processed into a commodity, which excludes the notion of "main" and "additional" product. One of the main trends concerning a complex use of rocks is the use of it for the obtaining of building materials. The clay rocks unconventional for building industry can be considered among the possible sources of raw materials to produce building materials. One of the important quality criteria for the construction of composites is their durability, which is determined by the ability of a material to resist the action of the complex atmospheric and other factors. The study of non-traditional and technogenic raw material effect on the durability of building composites is an urgent task.

Keywords: Clay rocks, aluminosilicate raw materials, durability, x-ray amorphous material, heat and humidity treatment, structure formation, building materials.

Introduction

The study of rational nature use problem, the use of natural and environmentally friendly man-made materials, the introduction of new modern, energy-efficient and resource-saving technologies is aimed at the solution of an urgent important problem to improve the production efficiency of new building composites.

The forefront is presented by the problems of energy-saving technology development and introduction for the production of building materials, which corresponds to the modern trends of "green" technology development that preserve the environment and provide a comfortable environment for human life [1-5].

The increasing pace of civil, industrial, transport and other sectors of construction in many countries, led to the rapid development of building material production industry. The industry of building materials is the major consumer of energy. In order to produce the energy a large amount of hydrocarbons is used, during the combustion of which a lot of carbon dioxide and other harmful substances that have a negative impact on the biosphere is released into the atmosphere. The share of the construction material industry accounts for approximately one-third of global energy consumption and 36% of carbon dioxide emissions (CO2). According to the statistics the world CO2 emissions amounted to 34 billion of tons and were 50 % higher than in 1990. According to the data announced at the World Economic Forum (IWR) in Münster, if the current trend preserves the volume of global carbon dioxide emissions will be increased by 20% in 2020 and will make more than 40 billion tons. Let’s compare: in 1990 the volume of global carbon dioxide emissions barely reached 22.7 billion tons.

In order to deal with greenhouse gas emissions the following measures are necessary today: the complete rethinking of the production process, to follow the path of sustainable production, which involves the use of advanced "green" technologies to preserve the environment and create a comfortable environment for human habitation. Unfortunately, many new plants are constructed in such a way to ensure the qualitative characteristics of only the main product, the rest is left without a proper attention. In order to reduce the adverse impacts on the environment, as well as to save fuel resources one should strive to the reduction of energy consumption through the use of new types of non-traditional raw materials.

Currently, each year more than 10 billion tons of building materials is produced all over the world. A significant part of the traditional natural resources, the reserves of which are limited, could be replaced by industrial waste. The specifics of this kind of raw materials is the significant difference from traditionally used rocks, mineral composition and structure. Clay rocks may be considered among the possible sources of raw materials to produce the building materials for the construction industry, which are the products of one of the final phases of aluminosilicate rock weathering, hundreds of million tons of which fall within the area of mining operations during the extraction of ferruginous quartzite. The pelitic fraction of these rocks is presented by thermodynamically unstable compounds such as mixed minerals, fine poorly rounded quartz, imperfect hydromica, Ca2 + montmorillonite, kaolinite, as well as X-ray amorphous minerals. These thermodynamically unstable compounds that have the properties of natural nanosized particles, allow to change the morphology of new formations and optimize the structure of the cementitious compound. The modern analysis of non-traditional clay raw materials concerning its application with the use of the latest scientific achievements, will give a serious impetus to the development of new types of building materials and production technologies [6-17].

Further evaluation, the development and the utilization of mineral resource base is related with the creation and the use of high technologies. Each of technogenic deposits is a unique one, and requires new methods of their evaluation and the industrial use of construction materials [18-26].

Durability is one of the important quality criteria for construction composites on the basis of clay raw materials, which is determined by the material ability to resist the complex action of atmospheric and other factors in operating conditions. Despite high technical and economic parameters of construction composites, the problem of their durability exists. As the resistance to adverse factors is determined mainly by the composition of the cementing compound, and the presence of clay minerals in a raw mixture can negatively affect the strength of the cementing binding element the durability for such materials becomes a very important factor.

Main part

The purpose of this work is the study of non-autoclave silicate materials durability based on man-made clay raw materials and the obtaining of efficient wall building materials according to energy-efficient technology.

The sand-clay rock of the Kursk magnetic anomaly was used as a natural nanoscale material for studies. The granulometric composition of the rock is shown in Table 1.

Table 1: Granulometric composition of the rock

Fraction content, wt. %, size of sieves, mm								
More than 0,315	0,315–0,20	0,20–0,125	0,125–0,10	0,10–0,05	0,05–0,04	0,04–0,01	0,01–0,005	Less than 0,005
1,3	2,95	5,10	6,35	12,90	5,82	42,95	5,70	16,93

According to granulometric content and the number of plasticity (6) the rock can be characterized as a silty loam. According to an infrared and X-ray analysis the clay fraction of the rock is presented by nanoscale minerals: montmorillonite, hydromica, kaolinite and the formations of mixed layers. The lump quicklime of JSC "Stroymaterialy" (Belgorod) was used as a lime component. The lime activity made 78.3 wt. %, the quenching temperature was 97.5 C, the quenching period made 4 minutes 30 seconds. The samples were prepared by dry compaction method. The raw mixtures were prepared with the lime content of 5, 8, 10, 12 and 15 wt. %. The molding mixture humidity was 10%. The compaction was carried out using the laboratory press at the pressure of 20 MPa. The samples were subjected to hydrothermal treatment in a steaming chamber at 90-95 C according to the mode of 9 + 1.5 + 1.5 hours. The maximum compressive strength, an average density, water absorption and the softening ratio was determined for obtained samples. In order to evaluate the effect of water impact on the strength properties of the obtained material the samples of each composition were kert in tap water for 1 year. The results are shown in Table 2 and on Fig. 1.

Table 2: Physical and mechanical characteristics of samples based on clay sand.

Physical and mechanical characteristics	Lime content, wt. %				
	5	8	10	12	15
Maximum compressive strength, MPa	17,80	18,60	22,58	17,50	16,70
Maximum compressive strength for water saturated samples, MPa	14,00	14,4	18,35	17,46	15,73
Softening ratio	0,79	0,78	0,81	0,99	0,94
Average density, kg/m3	1880	1855	1850	1815	1755
Water absorption, %	13,03	13,20	13,85	14,26	16,76
The compressive strength of saturated samples after 1 year storage in water, MPa	22,10	25,24	28,10	34,71	29,45

The increase of lime content from 5 to 10 wt. % increases the strength of the samples from 17.8 to 22.58 MPa (see. Fig. 1, curve 1). The increase of the lime content up to 15 wt. % reduces the strength to 16.7 MPa. The maximum strength of the samples in water-saturated condition (18.35 MPa) also corresponds to the lime content of 10 wt. % (See. Fig. 1, curve 2). The softening ratio makes 0.78-0.99, which demonstrates the high water resistance of the obtained material (see Table 2). The average density with lime content increase decreases from 1880 to 1755 kg/m3, the water uptake increases from 13.03 to 16.75 %.

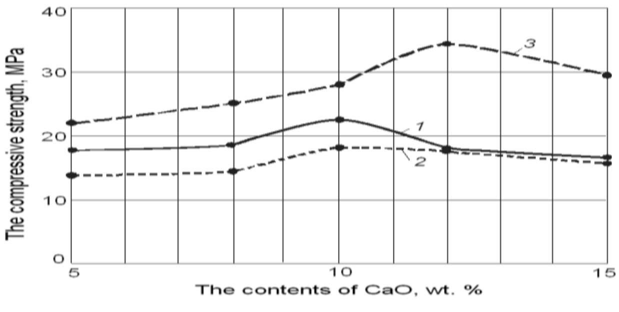

Fig. 1. Maximum compressive strength of the samples according to the content of lime:

1 - the samples after 2 days of keeping at room temperature;

2 - the water-saturated samples;

3 - the water saturated samples after 1 year storage in water

The test results of water saturated samples kept for 1 year in water, showed the significant increase of strength as compared with water-saturated samples that were not subjected to long-term storage in water (see. Fig. 1, curve 3). The maximum strength of 34.71 MPa is reached by the samples with the lime content of 12 wt. %. At that the strength increased two times as compared with the samples without the long-term storage in water (see Table 2). This is due to the fact that the rock forming minerals and, in particular, its component nanoscale element provide the synthesis of cementitious compound with hydraulic properties.

The initial sample micrograph (Fig. 2a), containing 10 wt. % of lime, demonstrate the accumulation of globules up to 0.5 microns, which are connected with the mesh weakly crystallized low-basic calcium hydrosilicates. The globules represent probably the intermediate compounds formed during the synthesis of new formations made of fine disperse part from rock-forming minerals of sand and clay rocks, and especially from clay minerals and lime. New formations also cover the surface of the filler. The formation of crystal structures takes place here. This provides a high strength and water resistance for obtained material.

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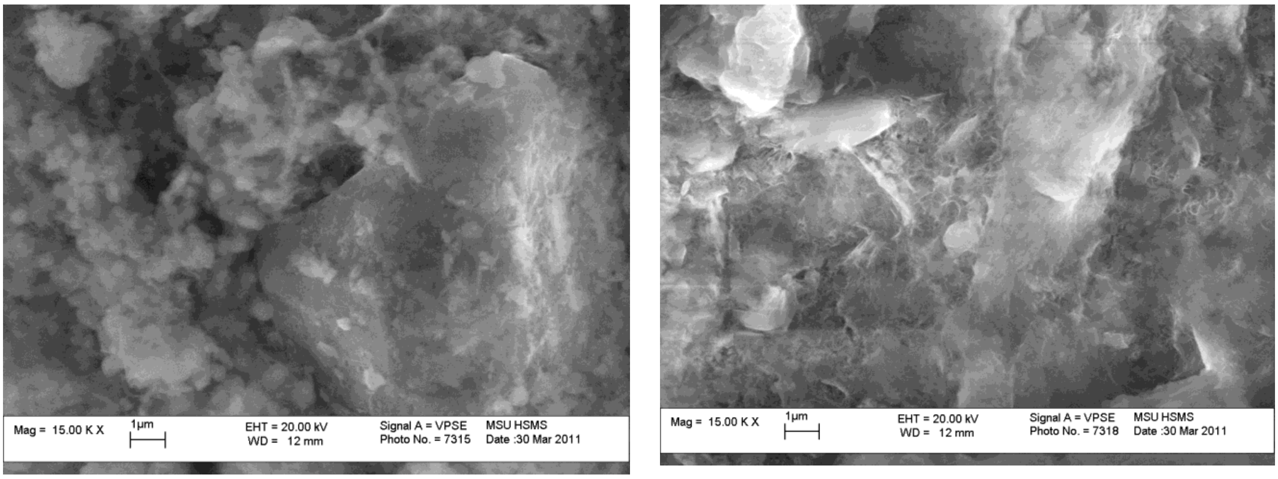

Fig. 2. The microstructure of samples based on loam containing 10 wt. % of lime, SEM:

a - the original sample; b - after a year of storage in wate

The microstructure of the sample after year of storage in water differs significantly from an original sample (see. Fig. 2b). The amount of globules becomes much smaller. At the same time the amount of weakly crystallized calcium hydrosilicates also increases, which form a continuous grid and fill the pores almost completely, cover the filler surface and bond its grains between each other. It can be concluded that the globules are intermediate compounds formed during the synthesis of new formations made of rock forming minerals, primarily of a clay component and lime. In the aqueous medium the process of calcium hydrosilicate formation continues in time, resulting in the formation of more durable microstructure of the cementitious compound. Besides, the weakly crystallized calcium hydrosilicates represent an unstable phase capable of recrystallization in time, and especially in an aqueous medium, which also leads to the change of a cementitious compound structure. Probably these processes provide the hydraulic properties of the obtained silicate materials.

The above stated results of the experiments used the powdered quick lime as a binder. In order to intensify the synthesis of new formations in further experiments the part of sand and clay rock was subjected to the co-milling with lime. The raw mixture was prepared by mixing the obtained lime-sand-clay binder (LSCB) with the original sandy loam. The total content of lime in the raw mix was 10 wt. %. The compositions with LSCB were used in the experiments in which the ratio of lime to a sandy loam was 1:1, 1:1.5, 1:2, 1:2.5. The samples were molded from the raw mixtures at the humidity of 12% and the pressure of 20 MPa. The samples were subjected to a hydrothermal treatment in the steaming chamber at the temperature of 90-95 C according to the mode 1.5+9+1.5 hours. The maximum compressive strength, average density, water absorption, softening ratio, frost resistance were determined for obtained samples and exposed to alternative wetting and drying. The results are shown in Table 3 and on Fig. 3.

The change of lime-sandy loam ratio from 1:1 to 1:2.5 results in a slight increase of sample strength only, from 18.9 to 20.2 MPa (see Table 3 and Figure 3). It should be noted that the sample strength for which only ground lime was used as a binder makes 22.58 MPa (see Table. 2). It can be concluded that the use of LSCB as a binder instead of ground lime does not increase product strength, and even decreases it slightly.

It can be assumed that the content of nanosized minerals in the original clay loam is sufficient to form a solid microstructure of cementitious material and the increase of fine disperse element due to the additional milling of the rock part leads to the formation of new formation composition, reducing the strength characteristics of the material.

Table 3: Physical and mechanical properties of LSCB based silicate materials.

Physical and mechanical properties	Lime:clay loam ratio in a binder			
	1:1	1:1,5	1:2	2,5
Maximum compressive strength, MPa	18,90	19,60	20,02	20,20
Maximum compressive strength of water saturated samples, MPa	14,40	14,24	15,84	14,24
Softening ratio	0,76	0,73	0,79	0,71
Average density, kg/m^3	1890	1900	1910	1855
Water absorption, %	10,63	10,07	10,87	10,85
Maximum compressive strength after 100 cycles of	28,20	30,28	34,17	32,85

alternate wetting and drying, MPa				
Maximum compressive strength after 100 cycles of alternate wetting and drying in water-saturated state, MPa	19,91	23,67	23,67	23,67
Softening coefficient of samples after weathering test, %	0,71	0,78	0,70	0,73
The loss of strength after 15 cycles of alternate freezing and thawing, %	0,78	0,81	0,73	0,77

During the grinding of sandy loam in raw mixture the content of fine dispersed quartz is increased, by which more weakly crystallized calcium hydrosilicates are synthesized in steaming terms, i.e. the share of gel like formations is increased. At that the optimum ratio between the crystalline and the gel like component is disrupted, which leads to strength reduction.

The average density of samples at the change of lime - sandy loam ratio from 1:1 to 1:2 increases from 1890 to 1910 kg/m3, and then it is reduced to 1855 kg/m3. At that, the average density for all these compositions is higher than for the samples in which the ground lime was used as a binder (see Table. 2 and 3). Accordingly, the water absorption decreases by increasing the packing density of the material. The values of the softening coefficient (0,71-0,79) indicate a good water resistance of the obtained samples (see Tab. 3).

The tests for frost resistance showed that the resulting silicate materials may withstand 25 cycles of alternate freezing and thawing. According to this indicator of frost resistance the silicate bricks correspond to ordinary ones.

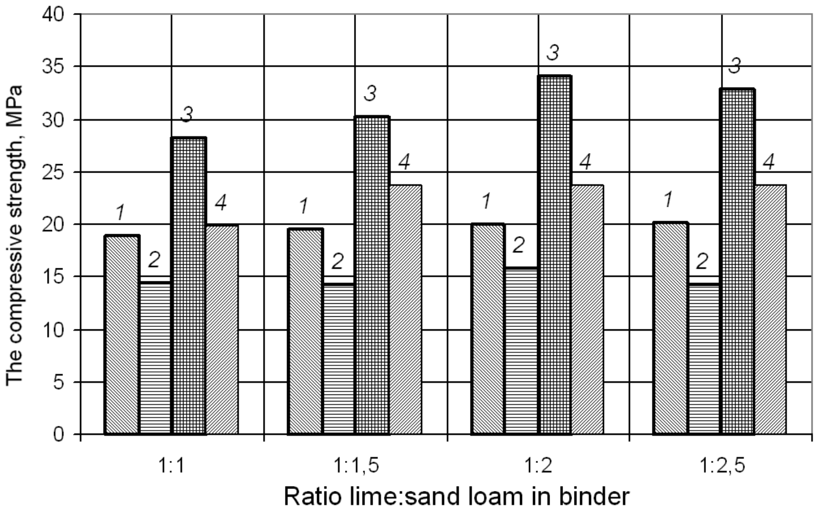

Fig. 3. The maximum compressive strength of the samples based on LSCB depending on a binder composition:

1 - after steaming; 2 - water-saturated; 3 - after 100 cycles of alternate wetting and drying; 4 - after 100 cycles of alternate wetting and drying in water-saturated condition

After the test of alternating wetting-drying the sample strength increased substantially (see. Tab. 3 and Fig. 3). The strength increase made from 49.2% (for LSCB composition 1:1) to 87.7% (for LSCB composition 1:2). Consequently, the optimal ratio of lime to sandy loam in a binder makes 1:2. The softening factor of samples after the test on alternate wetting-drying made 0,73-0,81.

The microstructure of samples with LSCB composition 1:1 was studied by the scanning electron microscope (Figure 4.).

The new formations are presented by weakly crystallized low-basic calcium hydrosilicates, forming a solid grid that covers the surface of the filler and binds its grains together. The globules are observed in grid surface nodes (see Fig. 4a).

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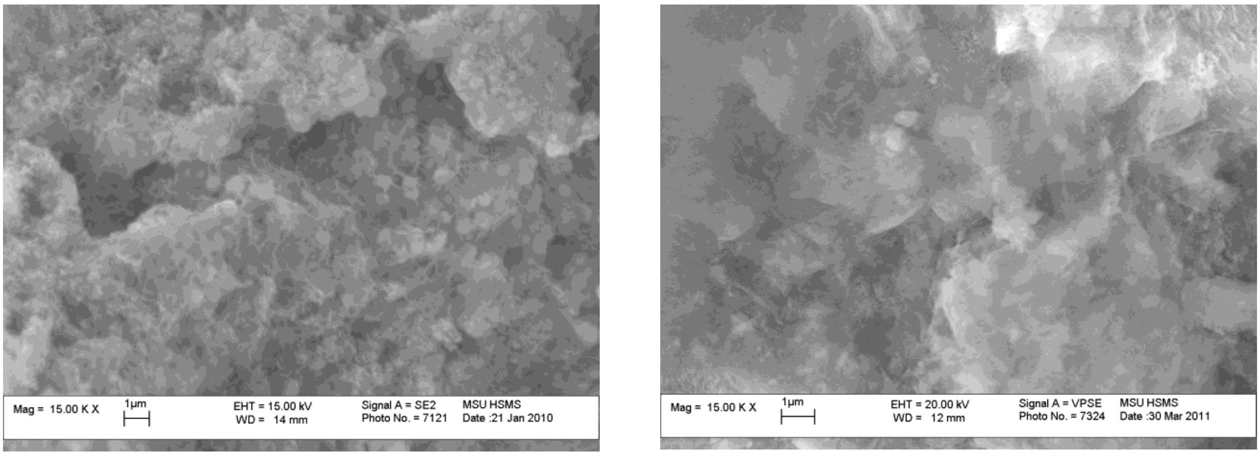

Fig. 4. The microstructure of the sample based on LSCB composition 1:1 SEM:

a - the original sample; b - after 100 alternate wetting and drying cycles

A large number of observed gel like phase confirms the abovementioned assumption about sample strength reduction on the basis of LSCB samples by disrupting the optimal balance between gel like and crystalline component in the composition of the cementitious compound.

The sample microstructure after 100 cycles of alternate wetting and drying cycles varies considerably (see Fig. 4b). The globules in the structure of new formations are practically absent. There are the areas with dense formations, the space between which is filled with the grid of weakly crystallized low-basic calcium silicates. The structure of the cementitious compound becomes more dense.

Summary

The improved composite strength after alternative wetting and drying is associated with the hydraulic properties of the obtained material. Obviously, at the obtaining of samples in water the subsequent recrystallization and hydration of new formations had a greater effect on the material strength increase than the destructive action at alternate wetting and drying.

Conclusions

Thus, on the basis of the studied raw material one may obtain weatherproof silicate materials without an autoclave, the strength of which can be increased during an operation even at the expense of the cementitious compound hydraulic properties. Frost resistance makes 15 cycles, which corresponds to the performance of an ordinary brick. The use of LSCB as a binder instead of ground lime somewhat reduces the strength characteristics of silicate materials. The optimum ratio of lime to sandy loam in the binder makes 1:2. The selection of LSCB or ground lime as a binder to obtain the high strength properties of silicate materials will depend, probably, on the material composition of the used sand and clay rocks.

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