Impact of zeolite-based nanomodified additive on the structure and strength of the cement stone

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Abstract. Portland cement is the main binder in the building materials industry; its properties strongly influence properties of mortars and concretes. Some regions experience difficulties with delivery and storage of Portland cement, raising the need to develop an effective additive from the available raw materials. Such materials for the Republic of Sakha (Yakutia) are zeolite-containing rocks. Studies have shown that introducing of dibutylphthalate to the composition of modified additive during mechanochemical activation leads to achievement of up to 11% of total amount particles with the size of 3-30 nm. After introducing 0.5% of the obtained additives, the compressive strength of cement-sand slurry samples increases up to 28%. Positive effect of additives introduction is also observed at high flow rate of water (W / C = 0.7). Gaining strength reaches 23%, allowing the efficient use of additive for movable mixtures with enhanced strength properties. In general, the proposed supplement allows reducing the water flow in the solution without decreasing its mobility, and increasing strength properties, which makes it possible to obtain a whole class of solutions of modified cement binder. The market value of the developed additives is 18 rubles per 1 kg, making sound competition in the market of modifying additives.

1. Introduction
Materials and products based on Portland cement are an integral part of the entire building complex. Among them there are solutions as well as heavy concrete. On the vast territory of the Republic of Sakha (Yakutia), with poor infrastructure, the only cement plant cannot perform high-quality supply of raw materials to the remote districts. This problem hardly provides an opportunity to accomplish monolithic building, while the demand for it keeps on increasing every year (the construction of bridges, schools, kindergartens, cottage low-rise construction, etc.).

In the manufacture of precast concrete products and structures, an urgent task is to reduce consumption of expensive Portland cement without losing strength. For this purpose, the existing plants producing concrete products use classical additives such as superplasticizer-3, sodium formate, the PFM-NLK. Modern additives such as “Superplast” are not in high demand, as their use may considerably increase the cost of production.

One way to improve the performance properties of concrete is the introduction of active mineral additives (AMD) to the mixture. AMD-additives provide hydrolicity of the binder and the existing structure of resistance over time. Mechanism of action of a hydraulically active additive is mainly caused by their chemical interaction with the lime, formed by hydrolysis of C₃S during cement hydration. At the same time type C-S-H(B) low-basic calcium hydrosilicates are basically formed, calcium hydroaluminates and hydroferrites, which increase the gel component of the cement paste, improve strength and deformation properties of concrete. As minerals siliceous components can be
used - natural AMD of sedimentary or volcanic origin, artificial additives (glinite, opus signinum, pulverized waste generated during burning of expanded clay), burnt rock, ash and slag, as well as inert additives (coal dust, sand, glass, etc.) [1].

In the production of building materials zeolite is used as an active mineral supplement since 1960s. This is due to the fact that zeolite is an effective material for reducing the flow of cement (15-30 %) for the production of light and heavy concrete, and as for preparation of solutions it can completely replace lime. This increases water-holding capacity of mortar and crack resistance. Portland cement additive zeolite in amount of more than 15 % provides excellent corrosion resistance of cement compositions relative to the chloride and sulphate brines. [2]

Extensive exploration showed that zeolites are widespread in nature, and some sedimentary rocks contain almost monomineralic layers, in which the original volcanic rocks 95% turned to a particular zeolite mineral. Some zeolites deposits can easily be explored as overlie the shallow or surface. Natural zeolites may not replace synthetic in those areas where raw material is of high purity, however, they are of interest to the industry in those cases where there are large amounts and, therefore, low cost of natural minerals are more important than the feed purity. [3]

Great possibilities of using natural zeolites in Yakutia, associated with the development of the field Honguruu, which were first discovered in Yakutia by K.E. Kolodeznikov, the employee of Yakut branch of Russian Academy of Sciences in 1978 in Honguruu settlement of Republic of Sakha (Yakutia). Zeolite materials of this deposit according to the data, are different from other known in CIS and Russian deposits of this type and characterized by high content of mineral clinoptilolite of Haylandite series (70-98%), with predominance of the chemical composition of the aluminosilicate sodium-calcium form.

The presence of local raw zeolite rocks in the Republic of Sakha (Yakutia) determines the feasibility of establishing effective integrated additives obtained by AMD mechanochemical activation - from fine zeolite rocks and plasticizing component capable of increasing the physical, mechanical and performance properties of cement-sand mortar and heavy concrete for severe climatic conditions.

2. Materials and methods
Complex additive based on zeolite is obtained by modifying natural zeolites and plasticizing additives. Due to its chemical and mineralogical composition, zeolite is able to be dispersed to the value of the specific surface of 2,500 kg/m² without plasticizers. Such indicators of specific surface were obtained by mechanical activation of zeolites in a planetary mill “Activator-25”, developed at the Institute of Solid State Chemistry and Mechanochemistry, Novosibirsk Branch of the Russian Academy of Sciences.

As seen from the graph (see Figure 1), during grinding over 5 minutes a decrease in specific surface is observed due to the increased fineness of the particles and their self-aggregation. To prevent this phenomenon, plasticizer was introduced.

![Figure 1. Graph showing dependence of specific surface value of grinding time period.](image-url)
As a plasticizer, common liquid plasticizer was used - dibutyl phthalate (DBP), GOST 8728 (Russian State Standard). Owing to this, the activity of zeolite does not fall in time and joint mechanochemical activation allows you to receive nanofraction. When activated, the particle size of zeolites reach an average of 1.3 microns with 11 % of the total amount of the particles having sizes of 3-30 nm, i.e. with the first approximation it can be considered as an additive nanomodificator that is supported by studies of the sample with a laser particle size analyzer of HORIBA brand (Figure 2).

Further, the complex additive was prepared in different proportions of zeolite and dibutyl phthalate (DBP): 1:0.2; 1:0.6; 1:1, respectively.

3. Experimental
The prepared additive was mixed in different quantities of the cement-sand mortar. The additive prepared in a ratio of 1:0.2 is light green-tinted powder. Under laboratory conditions three standard samples of cement-sand mortar preparation time is 3 minutes. An additive prepared in a ratio of 1:0.6 has a high viscosity and dark green color. For obtaining a homogeneous suspension in water additive requires more time as compared to other ratios. Under laboratory conditions for the preparation of three standard test-beams of cement-sand mortar, slurry preparation time is 5 minutes at water temperature of 15°C. At higher water temperature during preparation, time of the aqueous slurry is significantly reduced.

Additives prepared in a ratio of 1:1, have average viscosity and they are more fluid compared with the above-described compositions of additives. Color of additives is green. Total suspension preparation time for obtaining three standard cement-sand mortar test-beams in the lab conditions is 1.5 minutes.

The density of cement-sand mortar does not depend on the amount of introduced complex additive; there is no definite relationship. The densest packing of the sample is provided at a ratio of zeolite and DBP 1:0.2, respectively, and the amount of injected additive is 5%. A lowest value is reached at a ratio of 1:0.6 and in the quantity of 15%.

The maximum value (22 MPa) of compressive strength of cement-sand mortar samples is achieved with an integrated flow additive 25% and the ratio of zeolite and DBP 1:1. This is due to the fact that the composition increases the amount of DBP and consequently decreases the amount of zeolite. Also, increasing the tensile strength is observed even at 5 % of complex additive administration that shows structural changes in the cement-sand mortar, which results in improved strength properties of the materials (see Figure 3).
The results obtained are confirmed by studies of the microstructure of cement paste solution with the scanning probe microscope “NtegraPrima” NTMDT (Figure 4).

5% of the additive 15% of the additive 25% of the additive

100 times

1000 times

10 000 times

**Figure 4.** Micrograph structure of cement-sand mortar with nanomodified additive based on zeolite in the ratio of 1:1.

Analysis of the cement stone micrographs reveals that increase of its compressive strength while introducing additives in the amount of 5 to 25% is due to thickening of the structure. In the former case, the direction of new formations orientation, and in the second - the formation of the zeolite structure, which completely fills all of the intercrystalline space.

Even with introduction of the additive in the amount of 0.5%, increase in the compressive strength of the samples of cement-sand mortar is 28%. There is a positive effect of the introduction of additives at high flow rate of water (W/C = 0.7). Gaining strength in this case reaches 23%, which allows the possibility of efficient use of the additive for movable mixtures with enhanced strength properties.

Increasing the amount of additives and decrease in the flow of water in the composition of the cement-sand mortar causes increase of flexural strength. This is due to the fact that increasing the amount of additive increases the amount of plasticizing component which imparts organic features to the material; they are characterized by high tensile bending loads.

4. Conclusions
In general, the proposed supplement allows to reduce water flow of the solution without decreasing its mobility, as well as to increase the strength properties, which makes it possible to obtain a whole class of solutions of modified cement binder.

The market value of the developed additives is 18 rubles per 1 kg, which can make sound competition in the market of builders.
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