Research of composite binders with nanomodifiers for dry mixes

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Abstract. The article discusses the application of various mineral materials for the modification of Portland cement in order to obtain dry mixes. The main component in the composition of dry mixes is Portland cement, affecting its physical, mechanical and technological properties. To modify Portland cement, which is used to obtain dry mixes, various micro- and nano-additives were used: volcanic slag, microsilica, nanosilica. Mechanical parameters of modified Portland cement at various hardening periods are determined. The introduction of micro- and nano-additives positively affects the hydration process of Portland cement, which is confirmed by the study of the microstructure of the modified cement stone using scanning electron microscopy. It has been established that when using various micro- and nano-additives, the amount of low-basic calcium hydrosilicates changes, affecting the increase in the mechanical properties of cement stone. The use of volcanic slag and nanosilica allows to improve the technological and quality indicators of dry mixes. Studies of determining the angle of repose of the composition of composite binders based on Portland cement and volcanic slag, as well as the introduction of nanosilica in Portland cement show a significant change in this indicator indicating an improvement in the flowability of the material.

[1] Introduction
The main research in the design of dry building mixes is aimed at improving the processability and reducing the cost of their production through the use of composite materials of optimal structure based on cement, mixed composite binders, fine aggregate of optimal particle size distribution, finely divided fillers and chemical additives [1, 2].

The use of nanoscale modifiers for the modification of dry building mixtures not only actively affects the structure formation processes during cement hydration, but also improves the technological properties of the mixtures. The introduction of nanomodifying additives leads to a significant change in physical and mechanical properties [3-5].

[2] Materials
In studies to obtain dry mixes on cement and composite binders were used: Portland cement (OPC) CEM I 32.5 N; volcanic slag (VS) of the Khurai-Tsakir deposit (Baikal region), microsilica (MS), nanosilica (NS).

Microsilica is a by-product of the manufacture of silicon metal and ferro-silicon alloys. The process involves the reduction of high purity quartz (SiO2) in electric arc furnaces at temperatures in excess of...
2000°C. SF is a very fine powder consisting mainly of spherical particles or microspheres of mean diameter about 0.15 microns.

Nanosilica was obtained by evaporation and condensation for installation at the Institute of Theoretical and Applied Mechanics and the Institute of Nuclear Physics of the Siberian Branch of Russian Academy of Sciences (Novosibirsk city). Nanosilica contains more than 99% of amorphous silica, the content of inclusions, in mass. %: Al - 0.01, Fe - 0.01, Ti - 0.03.

[3] Results and Discussion
The introduction of nanomodifying additives leads to a significant change in physical and mechanical properties. For comparative analysis, experiments were carried out to determine the mechanical parameters of cement stone modified with micro- and nanosilica, volcanic slag (fig. 1).

![Figure 1. Mechanical properties of modified cement stone](image)

Theoretical studies and experimental results established that the optimal dosage of silica fume lies within 10%. Since the complete binding of calcium hydroxide lowers the pH of the pore fluid and thereby adversely affects the stability of the calcium silicate hydrogel and the corrosion resistance of the reinforcement. The kinetics of the set strength of the modified cement stone shows that when using volcanic slag, maximum values were obtained associated with pozzolanic activity and structure-forming action of slag. The indicators of micro- and nanosilica are somewhat lower, which is possibly associated with an irrational dosing interval. The mechanism of action of modifying additives is associated with a change in the structure of the composite.

Changes in the mechanical properties of modified cementitious compositions are associated with a change in its structure. Microphotographs of the chips of modified composites in comparison with the control non-additive composition showed a significant difference in the formed structure of the composites (fig. 2).
Figure 2. Microstructure (x500) of a modified cement stone at the age of 28 days: a – OPC, b – OPC+MS 10%, c – OPC+NS 0.1%, d – OPC+VS 10%

In the initial cement stone, due to the loose packing of cement particles, there are pores; during hardening, this space is filled with lime crystals of Ca(OH)2. The microstructure of the samples using VS, MS and NS is denser in comparison with the control composition. The introduction of mineral additives leads to a decrease in capillary porosity, and at the same time leads to an increase in the number of tiny gel pores that are part of the calcium silicate hydrogel.

The presence of silica with a defective crystal lattice in the high-level gas; leads to the creation of a high-density structure of cement stone due to the binding of portlandite and the additional formation of calcium hydrosilicates. The content of capillary pores decreases, with an increase in gel porosity. MS has a positive effect on the structure of the transition zone; the thickness is comparable with the size of cement grains. Thick matrix reinforcement is noted, which leads to an increase in the density and strength of the composite. It is worth noting that the structure with the introduction of NS showed a steady tendency to create a strong single conglomerate, there are volumetric germination of calcium hydrosilicates throughout the volume.

The use of nanoscale modifiers for the modification of dry mixes not only actively affects the structure formation processes during cement hydration, but also improves the technological properties of the mixtures.

One of the main technological properties of dry mortar is flowability. Providing a good indicator of the flowability of dry mixes will allow uninterrupted production process to be conducted under production conditions and intensified. To assess the manufacturability of powdered materials, which include Portland cement, as well as to predict the behavior of bulk materials in industrial production, their technological properties are determined: flowability, angle of repose. Studies of determining the angle of repose of the composition of composite binders based on Portland cement and volcanic slag
(fig. 3), as well as the introduction of nanosilica in Portland cement (fig. 4) show a significant change in this indicator indicating an improvement in the flowability of the material.

Figure 3. Change in the angle of repose of the composition of composite binders with volcanic slag: a - control (volcanic slag content - 0%), b - 5%, c - 10%, d - 20%

Figure 4. Change in the angle of repose of the compositions with nanosilica: a) OPC b) OPC + NS (0.5%), c) OPC + NS (1%), d) OPC + NS (3%)
Replacing part of Portland cement with volcanic slag leads to improved technological performance. The angle of repose with increasing volcanic slag content decreases by 20-30%, which indicates a better flowability of the material. The flowability of binders with nanosilica improves with an increase in nanosilica from 0.5 to 3%. Since the flowability of the material depends on the size and shape of the particles and is determined by the amount of internal friction between them, the introduction of nanopowder apparently reduces the amount of internal friction between the cement particles, thereby improving the flowability.

An important indicator of the quality of dry mortar is water retention capacity. Water retention capacity with an increase in slag content up to 20% lies in the range of 97-98%, which meets the requirements of standards (fig. 5). An improvement in the water-holding ability of compositions with volcanic slag and nanosilica is associated with a high specific surface area of the particles. Around the particles water shells form and the amount of “free” unbound water decreases. Particles of finely dispersed volcanic slag and nanosilica interact through a solvate shell formed on the surface, consisting of water adsorbed on the surface of the solid phase.

![Figure 5. Water-holding ability of the compositions of dry mixes using volcanic slag (a) and nanosilica (b)](image)

**Conclusion**

Thus, the conducted studies show that the composition of composite binders with volcanic slag is characterized by improved physical and mechanical and operational characteristics, the introduction of nanosilica in the composition of binders has a beneficial effect on the technological and mechanical properties of the composites. The study of the microstructure of modified cement composites showed a difference and favorable structure-forming effect of volcanic slag and nanosilica. The introduction of active mineral micro- and nano-additives leads to the creation of a dense structure and an increase in the number of neoplasms. The use of composite binders using volcanic slag and nanosilica allows to improve the technological and quality indicators of dry mixes.

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