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The Structure Formation of the Cellular Concrete with Nanostructured Modifier

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Abstract. In this work the peculiarities of phase formation of the cement stone at presence of nanostructured modifier of the silica composition were identified using the method of x-ray diffraction and raster electronic microscopy. Also the character of influence of modifier on the structure formation of the cement stone was defined. Polydisperse modifier with the presence of a highly active colloidal component, on the one hand, acts as a pozzolanic component, and on the other hand – as a submicron filler.

Introduction.

The modern level of building industry requires an application of the high-quality building materials with high exploitation characteristics. Increasing of the mechanical characteristics of the composites can be achieved through the use of different modifiers, including nanostructured ones. The opportunity of using the nanostructured modifier of the silica composition for increasing the strength characteristics of autoclaved materials due to the optimization of phase formation processes was approved by the number of works [1–7]. The purpose of the present research is analysis of the nanostructured modifier's influence on the process of the structure formation of cement stone. Usage of the nanostructured modifier is determined by the necessity of binding the extra portlandite, which is emerging because of cement hydration, and also by the decreasing of extra cement fraction in the production, which would stimulate the lowering of its cost. If there is an additional content of reactive silica in the form of nanostructured modifier in the system «cement – silica», equilibrium phase formation should shift to the area with the low ratio of CaO/SiO_2. This should decrease basicity of C-S-H(I) gel, from which phases, having the most similar basicity, can crystallize.

Experimental program. For studying the characteristics of mineral transformations in the system "cement – silica" a sample model with a ratio of cement/modifier=80/20 (%), hardening under normal conditions, was prepared. The modifier has obtained by means of a multi-stage prolonged grinding of quartz sand in the aquatic environment. The result is a slurry with a moisture content of 20 %, a specific surface area of 830 m^2/kg, characterized by polydispersity with peaks of particle sizes in the range of 5, 15–20, 50–70 μm, the presence of the particles of nanoscale level 10–50 nm up to 10%. The slurry also demonstrated a high activity towards the calcium hydroxide – the amount of absorbed CaO 81 mg/g.

For the quantitative measurement of mineral phases in the modified binder the quantitative x-ray phase analysis on the basis of full-profile Rietveld method was applied. Radiographs of the samples were obtained on x-ray workstation ARL 9900 using radiation x-ray tube with co-anode (the interval of angles of diffraction 2θ = 8-80, scanning step of 0.02, filtration β-radiation) applied. The preparation of samples for analysis was carried out by the traditional method of grinding in an agate mortar in ethanol medium. The X-ray diagnosis had been carried out using the diffraction data base

PDF-2 with the help of the program Crystallographica Search Match. Simulation of the diffraction spectra was held due to a full-profile methods DDM 1.95 c.
The microstructure was studied using high resolution scanning electronic microscopy (SEM) TESCAN MIRA 3 LMU (Poland). The survey of the samples occurred in the high vacuum. The samples of the elaborated products went through the process of sputtering of graphite materials beforehand. After the formation of the fresh cleavage, the samples were placed in an alcoholic solution to stop the hydration processes in purpose of fixation of morphological structure of tumors, conforming to the certain period of hardening.

Results and discussions.

According to the obtained data, the radiograph failed to capture the most intense reflection (002) of 14Å-tobermorite (figure 1). This result is connected with the peculiarities of to x-ray optics scheme of the goniometer of the x-ray workstation WorkStationARL 9900, as this silicate hydrate peaks are outside of the station's work measurement. In this case, the radiograph revealed a number of weak reflections, which could belong to this silicate hydrate. The comparatively low content of suolunite can be explained by the factors, mentioned above.

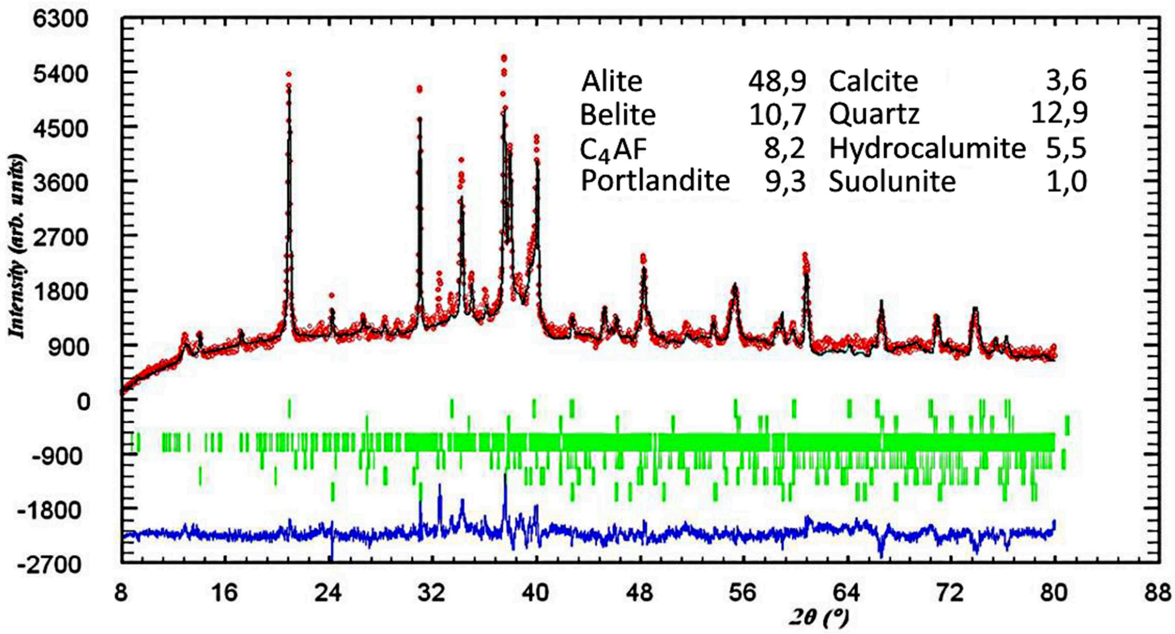


Fig. 1. The radiograph of the model age 7 days

X-ray diagnostics (qualitative XRD), held on the diffraction data base PDF-2, showed that the main components of the experimental and control sample of a cement stone composition (hardened cement stone) are clinker components (C_3S, C_2S and C_4AF) and the portlandite. There were no reflections, identified as C-S-H, detected, probably because of their cryptocrystalline (amorphous) state.
To assess the nature of the processes of hydration of the binding composition «cement–nanostructured modifier» we carried out a full-profile quantitative XRD of abovementioned binding composition and the control sample of the cement stone in 1, 3, 7, 21 and 28 days of hardening.
The analysis of the obtained data on the change of the concentration of portlandite (Fig. 2 a) allows to conclude that a certain amount of portlandite was binded by the reactive colloidal silica in the composition of a complex binder. Similar dependences of the variation of the portlandite concentration in binding systems with active silica are given, in particular, by the authors of [8].

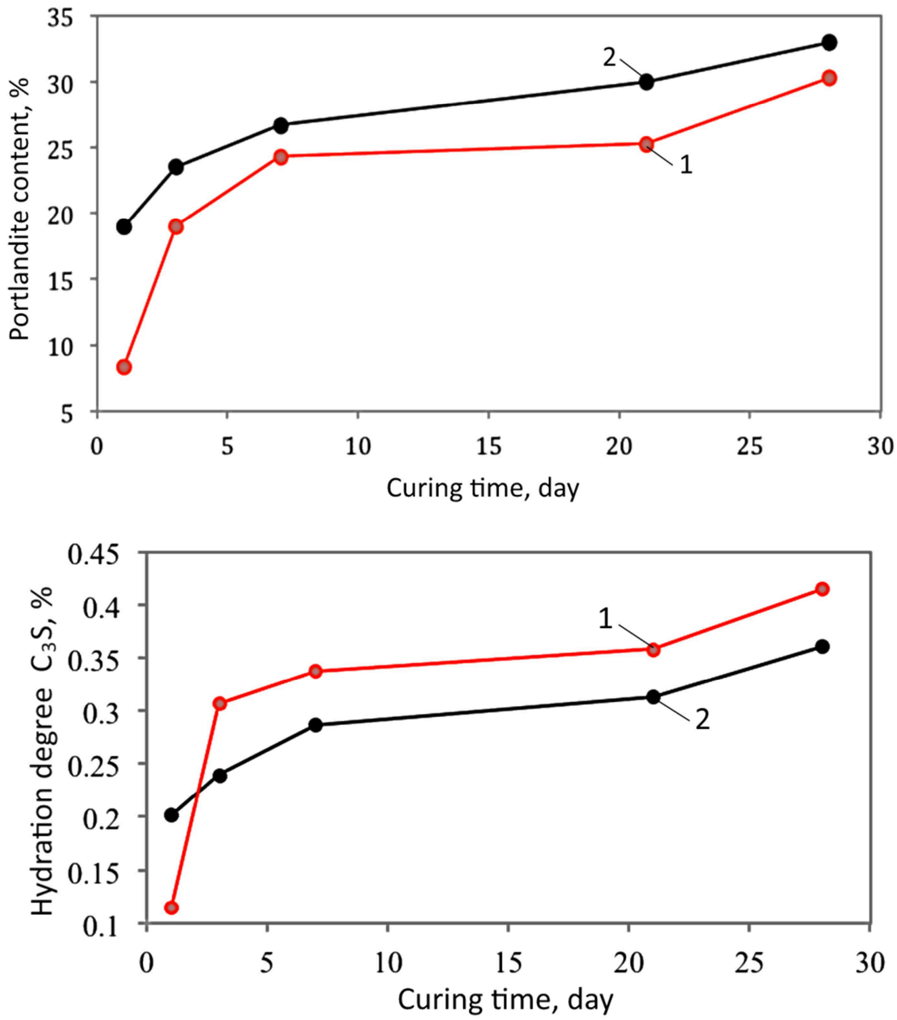
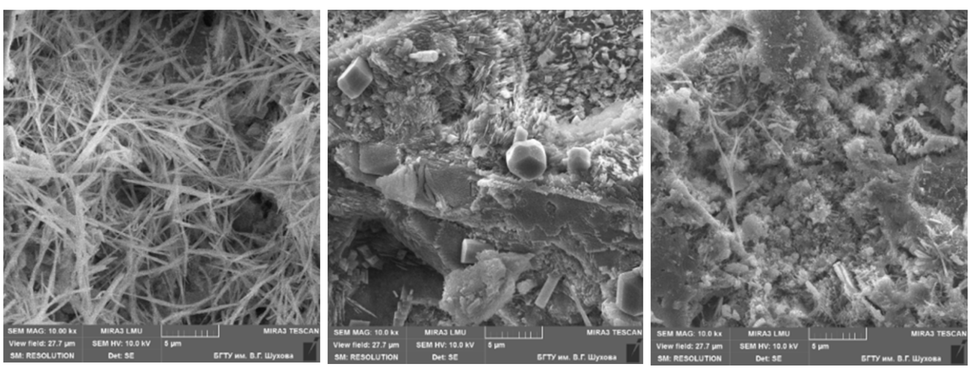


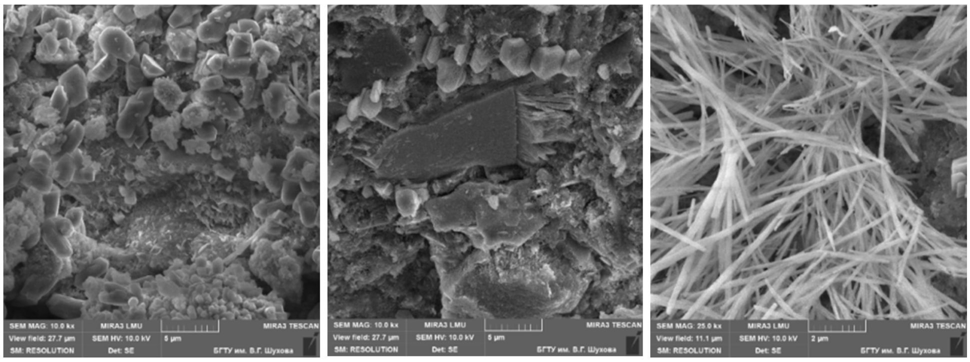
Fig. 2. Alteration of the normalized portlandite content (a)
and the normalized hydration degrees of C_3S (b)
during the hardening of composite binder (1) and cement (control sample) (2)

However, this ratio of the concentrations of portlandite in the hardened composite binder may occur in the case of slowdown of hydration, particularly tricalcium silicate, when included in the cement system a colloidal silica – a (weak) acid component. To confirm this fact, we calculated the degree of hydration of C_3S, defined on the basis of quantitative x-ray fluorescence analysis-definitions of concentrations of C_3S at various stages of hardening of the composite and the control binders, and a certain quantitative XRF content of C_3S in cement (Fig. 2 b). According to the data obtained, it can be confirmed that the hydration of composite binder accelerates due to linking the part of the portlandite by the nanostructured modifier's active substance.



a *b* *c*

Cement (control sample)



d *e* *f*

Composite binder

Fig. 3. Binder microstructure in different curing time:
a, d – 1 day; b, e – 3 days; c, f – 7 days.

The analysis of the microstructure of the system «cement–NM» (figure 3) showed that on the 1st day in the composition of the control samples the filamentous crystals dominated, and in the modified cement stone – rhombohedral did. By the 3rd day the flattened tabular tumors were observed in the modified samples. To the 7th day, the entire mass of the control samples composed flake-like clusters, at that time there were clusters of newly-formed substances with typical morphostructures in the modified binder. After 14 days of hardening, the picture changed quite noticeably for samples of both compounds: there were no both filamentous and prismatic tumors.

Conclusions.

We studied the mechanism of the influence of the nanostructured silicate composition modifier on the phase and structure formation of cement stone, which illustrates the fact that the polydispersity composition of the modifier with the presence of a highly active colloidal component, on the one hand, acts as an active pozzolanic component, and on the other hand – as a submicron filler.

On the basis of the full-profile calculations of diffraction data it can be concluded that, comparing with the control sample, the decrease of the intensity of portlandite reflections in the later stages of hardening of experimental composition, was connected with the silification of C-S-H(I) gel in the cement stone active colloidal silica, which leads to the formation on its basis of crystalline calcium silicate hydrate – suolunite and alteration of the morphological structure of C-S-H(I) gel with the change of fiber shape on small scales.

The microstructural study together with the data of x-ray diffraction allow to claim, that the silicate nanostructured modifier in the composition of cement definitely affects the changes in the overall pattern (kinetics) of the phase formation, also having a certain impact on the recruitment strength of the modified cement stone.

Acknowledgements.

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