Physical and chemical research of the microstructure of the cement composite filled with aluminosilicate and glass microphases

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Abstract. Using the physical and chemical analysis, the possibility to obtain a dense and crack-resistant Portland cement-based composite material filled with aluminosilicate and glass microspheres and a complex additive which purposefully enhances each of the mentioned properties have investigated. During the molding of a composite material, in which particles of a filler and a binder have the same size in microns, micro-reinforcing fibrous additives will not be effective because their particles are larger than filler's particles. To specify the conditions for the formation of a micro-reinforcing layer of ettringite needles and for increasing the density of the cement matrix structure, relevant theoretical and experimental studies were carried out and a complex additive consisting of calcium nitrate and chloride, carboxymethylcellulose and plasticizer was proposed. Based on the physical and chemical analysis performed, it has been found that adding a complex additive facilitates the compacting of the cement matrix structure through the additional synthesis of crystalline hydrates: ettringite, calcium hydrochloroaluminate, calcium hydroxychloride, and calcium hydroxysilicates of the felt-like structure, which improves physical and mechanical properties of a Portland-based composite material.

1. Introduction
To obtain a dense and crack-resistant composite material based on a cement binder having a good substrate-gripping capacity, it is necessary to include certain additives purposefully enhancing each of the mentioned properties in its composition [1, 2]. During the molding of a composite material, in which particles of a filler and a binder have the same size (namely, a thermal insulation material based on Portland cement and fillers consisting of hollow microspheres), micro-reinforcing fibers will not be effective because the size of their particles exceeds several times the size of filler particles. To specify the conditions for the formation of a micro-reinforcing layer of ettringite needles and for increasing the density of the cement matrix structure, relevant theoretical and experimental studies were carried out.
and a complex additive consisting of calcium nitrate and chloride, carboxymethylcellulose and plasticizer was proposed [3-6].

2. Main content of the work
Structural transformations occurred during the hydration of a binder with the proposed complex additive were studied by the method of infrared spectroscopy (IRS) and with the use of an electronic microscope. This allowed us to reveal the nature of intermolecular and intramolecular interactions and to obtain information about the structure of compounds. Three samples in the form of a mixture solidified within 28 days were prepared for the study. Sample No. 1: Portland cement; sample No. 2: Portland cement with glass microspheres and a complex chemical additive; sample No. 3: Portland cement with aluminosilicate microspheres and a complex additive (Figure 1).

The infrared spectrum of sample 1 contains bands specific to certain components of clinker components. Bands specific to belite (840 cm\(^{-1}\)) and alite (880 to 950 cm\(^{-1}\)) are typical for cement. IR spectra of all three samples of cement have bands of aluminates in the range 450 to 550 cm\(^{-1}\) and bands of aluminoferrites in the range 600 to 700 cm\(^{-1}\), as well as valence vibration bands in the range 1000 to 1150 cm\(^{-1}\).

The IR spectrum of sample No. 2 shows the decreased absorption band at 500 and 1220 to 1260 cm\(^{-1}\). Increased absorption in the range of wavenumbers 1010 to 1100 cm\(^{-1}\) is explained by the presence of carbonates, hydrosilicates and ettringite, the band 1425 to 1450 cm\(^{-1}\) shows the presence of Ca(OH)\(_2\) or calcium hydrosilicates. The IR spectrum of sample No. 3 is similar to the spectrum of sample No. 2, but its band for 1500 cm\(^{-1}\) is more distinct, and this may show the presence of Ca(OH)\(_2\) or high-basic calcium hydrosilicates; this is also valid for the band 3423 available for all samples. Vibration bands 700 to 800 and 2928 cm\(^{-1}\) specific to calcite [7-8] are also present in spectra of samples No. 2 and No. 3.

All these spectral changes indicate that connections Si-O and Ca-O become damaged during the interaction of the mineral phases of clinker with water and a complex chemical additive.

Electron microscope images show most clearly the relative arrangement of structural elements in the cement composite material, the morphology of the phases, sizes and shapes of crystals and their binding [9-10]. To study structural features of a composite material in the process of its formation at the microlevel, a composition containing Portland cement, aluminosilicate and glass microspheres and a complex chemical additive was selected. The electronic photographs (Figure 2) show the microstructure of a composite material.
Figure 1. Infrared spectrum of the samples: a - sample No. 1, b – sample No. 2, c – sample No. 3.
The image shows that diameters of the hollow microspheres may range from 10 to 150 microns and that the microspheres may be bound with crystalhydrate structures of cement stone. The structure of the material is dense due to the well-balanced placement of microspheres of different diameters; there are no cavities and cracks. The selected fragment of the image clearly shows that a microsphere has a multi-chamber capsular structure giving the possibility to detect internal stresses and to effectively redistribute them between the cement matrix and the filler. This ensures increased strength parameters of a composite material and increased crack-resistance of a coating. Plates and blocks of calcium hydrosilicates and star-shaped aggregations of calcium hydrochloroaluminates (see in the center of the image) are being formed on the ettringite frame connecting microspheres with its needles: crystals of calcium hydroxychloride shaped as elongated prisms and calcium hydronitroaluminates shaped as hexagonal thin petals (Figure 3). Sometimes separate calcite cubes and lime plates may be formed.
the hydrated calcium aluminate phases form separate aggregations looking like elongated prisms mixed up with aggregations of hydrosilicates (darker clusters in the center and on the top left of the image) and lime (light blotched plates on the top left of the image).

**Figure 4.** Electron images of the microstructure of the reference sample of a composite material.

### 3. Conclusion

Therefore, based on the performed physical and chemical analysis, it has been found that adding a complex additive facilitates the compacting of the cement matrix structure through the additional synthesis of crystalline hydrates: ettringite, calcium hydrochloroaluminate, calcium hydroxychloride, and calcium hydrosilicates of the felt-like structure, which improves physical and mechanical properties of a Portland cement-based composite material.

### References

[1] Drukovanij M and Krivenko L 2007 Development and research of effective plaster solutions for thin-layer technology *Novi tehnologiyi v budivnictvi* **2**(14) 33-36

[2] Runova R 2015 Mineral binders for thin-layer technology of building materials *Visnik AB Ukrayini* **10** 57-60

[3] Plahotnikov K, Bondarenko O and Dedeniova O 2017 Possibility of using thermal insulation materials in thin layers in modern construction *Naukovij visnik budivnictva* **89**(3) 226-229

[4] Plahotnikov K, Dedeniova O, Diomina O and Bondarenko D 2018 Influence of water-retardant additives on adhesive strength of thin-layer thermal insulation coatings based on mineral binders *Naukovij visnik budivnictva* **91**(1) 152-156

[5] Plahotnikov K, Starkova O, Kostuk T and Bondarenko D 2018 Optimization of the content of additives in the composition of composite materials by methods of experimental-statistical modeling *Sistemi obrobki informaciyi* **1**(152) 68-73

[6] Demina O, Plugin A, Dedenyova O, Bondarenko D and Kostuk T 2017 Interaction of Portland cement hydration products with complex chemical additives containing fiberglass in moisture-proof cement compositions *Functional Materials* **24**(3) 415-419

[7] Plusnina I 1977 Infrared spectra of minerals (Moskow: Moscow State University)

[8] Nakamoto K 1966 IR Spectra and Spectra of Colloid Solutions of Inorganic and Coordination Compounds (Moskow: Mir)

[9] Rid S 1979 Electron probe microanalysis (Moskow: Mir)

[10] Gorshkov V, Timashov V and Saveliev B 1981 Methods for Physical and Chemical Analysis of Binders (Moskow: Vysshaya shkola)