Mechanism of formation of microstructure of thin-layer coating based on Portland cement

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Abstract. Coatings based on mineral binders with inorganic hollow microfillers are effective thermal insulation materials. However, they have poor physical and mechanical characteristics, and this prevents from their extensive practical use. The purpose of the work is to develop the composition of a thin-layer thermal insulation coating based on Portland cement with addition of a complex additive intended to improve its physical and mechanical properties. The use of this additive facilitated the additional on-surface synthesis of microspheres of crystalline hydrates in the form of aggregate gels, ettringite needles and laminar structures, as well as the compacting of the structure of a thin-layer thermal insulation coating with crystalline hydrates formed during the clinker alunate phase. These structural changes contributed to the improvement of physical and mechanical parameters of the thermal insulation coating.

1. Introduction
Coatings based on mineral binders with inorganic hollow microfillers [1-5] are promising thermal insulation materials. Such materials have high thermal insulation properties, but poor physical and mechanical characteristics, as well as high water absorption capacity and low adhesive strength due to their structure. Therefore, the development of a thin-layer thermal insulation coating based on mineral binders (aluminosilicate and glass microspheres) and having high thermal insulation properties and improved physical and mechanical characteristics is a task of high priority [6-8].

However, thin layers (1-2 mm) of such coatings based on mineral binders having sufficiently high physical and mechanical characteristics are quite difficult to produce, since most of the mixing water enters the porous mineral substrate (concrete, brick, etc.) and evaporates. Insufficient quantity of water impairs the hydration of the binder, and this reduces the coating's density and strength.
Development of the composition of a thin-layer insulation coating based on Portland cement and fillers consisting of hollow aluminosilicate and glass microspheres, which should have high physical, mechanical and thermal insulation properties, through modification of a binder using calcium salts and a water-retaining additive.

For the purpose of increasing the density and durability of a thin-layer thermal insulation coating based on Portland cement, the following scientific hypothesis was proposed: the improvement of physical and mechanical properties of a thin-layer thermal insulation coating based on a cement binder and fillers with hollow microspheres may be reached by microreinforcement of the cement matrix by ettringite needles formed on the microspheres and grown in the space of the cement matrix; such needles form a frame structure due to introducing additives of the second class and the third group (nitrates and calcium chlorides) and a water-retaining additive.

To select effective additives, works of the following scientists who worked on the development of additives for cements and the mechanism of their action were analyzed: V.B. Ratinov, F.M. Ivanov, M.M. Sychov, O.P. Mechedlov-Petrosyan, V.I. Babushkin, L.B. Svatovska, N.N. Shangina, P.G. Komokhov, V.G. Batrakov, A.M. Plugin, A. V. Usherov-Marshak, L.Y. Dvorkin, M.A. Sanitsky, P.V. Krivenko, R.F. Runova, V.L. Chernyavsky, A.A. Plugin, O.S. Shinkevich and others.

2. Main content of the work
The adsorption properties of hollow aluminosilicate microspheres in a cement composite material are largely determined by the balance of their acid-base centres, which also correlate with the sign of surface charge. In cement stone and mortar, to ensure the highest structural strength, a balance must be maintained between the positively and negatively charged surfaces of all dispersed particles and crystalline hydrates [9]. Introduction of aluminosilicate microspheres sized from 5 to 150 microns to the cement structure will have a positive effect on the formation of a denser structure both in the early stages and at a later time of hydration, because they will form electro-heterogeneous contacts not only with particles of cement and gypsum, but also with hydrates of the clinker aluminate phase [10, 11]. Improvement of physical and mechanical characteristics of a thin-layer thermal insulation coating was reached by micro-reinforcement with ettringite needles, and this proved the scientific hypothesis (figure 1, 2).

![Figure 1. Schematic representation of the reinforcement of the coating structure with ettringite needles (microfibers).](image-url)
Figure 2. Electron micrograph of the structure of a thin-layer thermal insulation coating with micro-reinforcing ettringite needles (proof of the scientific hypothesis).

The choice of a complex chemical additive (CaCl₂, CaNO₃) made it possible to additionally synthesize crystalline hydrates in the form of CSH aggregate gels, ettringite needles and laminar structures C₄AH₁₃ on the surface of microspheres, as well as to compact the structure of a thin-layer thermal insulation coating formed during the clinker aluminate phase [12] that is proved by the results of electron microscopic studies (figure 3, 4).

Figure 3. Electron micrograph of a glass microsphere in the structure of a composite material: a – a microsphere is covered with ettringite fibres, b – enlarged surface of a microsphere with newly formed crystalline hydrate structures.
Figure 4. The compacting of the structure of a thin-layer coating with aluminosilicate and glass microspheres with cubes and prisms of crystalline hydrates formed during the clinker aluminate phase.

Following from the results of experimental studies with the use of the method of mathematical planning of the experiment, a rational ratio of methylcellulose and a complex chemical additive in a composite material based on Portland cement was determined: from 0.05% to 0.09 % of the cement content, and the content of a complex chemical additive ranged from 1% to 2.8%.

The results of theoretical studies have been experimentally proved and the physical and mechanical characteristics of samples of a thin-layer thermal insulation coating have been determined.

Figure 5 shows the results of testing of thin-layer thermal insulation coating samples: its compressive strength, flexural tensile strength, adhesive strength, vapour permeability.

Figure 5. Results of testing samples of a thin-layer thermal insulation coating.

3. Conclusion
Based on the analysis performed, it was discovered that adding a complex additive facilitates the compacting of the structure of the cement matrix through the additional synthesis of crystalline
hydrates: ettringite, calcium hydrosilicates of the felt-like structure, calcium hydrochloroaluminate, calcium hydroxychloride, and this facilitates the improvement of physical and mechanical properties of a thermal insulation coating.

References
[1] Plakhotnikov K V, Bondarenko D O, Dedenyova O B 2017 The possibility to use thin-layer thermal insulation materials in modern construction Scientific Bulletin of Construction 3(89) 226-229
[2] Zaharchenko P V, Piven N M 2009 Study of the processes of structure formation in thin-layer coatings Building materials and products 5(6) 27-28
[3] NETZSCH-Gerätebau 2016 Thermal Insulation Materials. Material Characterization, Phase Changes, Thermal Conductivity (Germany) p 23
[4] Yurkov A L 2008 Properties of Heat-Insulating Materials Refractories and Industrial Ceramics 46 170-174
[5] Ryzhenkov A V, Pogorelov S I, Loginova N A, Belyaeva E V and Plestsheva A Y 2015 Syntactic Foams Efficiency with the Use of Various Microspheres for Heat Supply Equipment and Pipelines Heat Insulation Modern Applied Science 9(4) 319-327
[6] Liang J Z and Wu C B 2012 Effects of the glass bead content and the surface treatment on the mechanical properties of polypropylene composites Journal of Applied Polymer Science 123(5) 3054-3063
[7] Valášek P and Müller M 2013 Polymeric composite based on glass powder - usage possibilities in agrocomplex Scientia Agriculturae Bohemica 44(2) 107-112
[8] Ku H, Trada M and Wong P 2010 Tensile Tests of Phenol Formaldehyde Glass-Powder-Reinforced Composites: Pilot Study Journal of Applied Polymer Science 116 10-17
[9] Plugin A, Kostuk T and Babushkin V 1999 Strength control of fine-grained concrete immediately after forming based on the electro-surface properties of its components Naukovij visnik budivniictva 7 63-67
[10] Babushkin V, Plugin A and Kostuk T 1998 The effect of active surface centers on the strength of freshly formed fine-grained concrete Naukovij visnik budivniictva 5 85-88
[11] Plugin A A, Savchuk Y, Liutyi V, Kostiuk T and Bondarenko D 2018 Penetrating Fine-Clinker and Clinkerless Cement-Based Waterproof Compounds 20 Internationale Baustofftagung (Weimar: Bauhaus-Universität) 2 1063-1071
[12] Demina O, Plugin A 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