Innovative Thermal Insulation Materials with Dual Properties

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Abstract. The paper presents the results of development and research of an innovative thin-layer thermal insulation material that protects the building from heat loss due to thermal radiation. The material is a dry mortar of cement binder and filler of hollow aluminosilicate microspheres. A thin-layer coating made from this optimally combines the functions of effective heat protection and external finishing warm plastering that is advantageous when reconstructing and restoring historical objects with a lavish decoration. The conducted studies have shown that aluminosilicate microspheres in the composite thermal insulation coating are also involved in the reflection of infrared radiation. The use of Class 2 admixtures made it possible to synthesize additional crystalline hydrates with the aluminate phase of clinker brick, which contributed to the strengthening of the cement composite at the micro- and submicrolevels. This was confirmed by electron microscopy. For the developed composition of the mineral thin-layer thermal insulation coating, the cost of the mixture is almost 3 times lower than for the known composition of the thermal insulation coating on the polymer binder. In addition, unlike polymer analogs, there are no restrictions in terms of temperature and service life. The thermal insulation coating may be applied both exteriorly and interiorly with no condensation being formed between the wall and the coating. Applying the developed thin-layer thermal insulation coating on a brick wall measuring 10 m by 10 m in the climatic conditions of Kharkiv allows reducing heat consumption by 0.188% per 1 m² per year.

Currently, the demand for thermal insulation materials shows a tendency for steady growth. Their varieties are growing rapidly. The domestic market offers a wide range of thermal insulation materials, including products made of mineral and glass fibers, products made of foamed polymers, cellular concretes and more. While thick-layer thermal insulation materials have been known for a long time now, liquid thermal insulation materials in thin layers require further research. This group of construction materials is relatively new; there is almost no equipment or methods for its study. Scientists Yu. M. Bazhenov, V. T. Yerofieiev, Ye. V. Korolov, Yu. V. Pukharenko, V. N. Sokiv and S. V. Fedosov are engaged in the development of high-performance thermal insulation materials by creating porous structures. The theoretical foundations of the structure formation in filled polymer
composite materials are explored in the works of A. N. Bobryshev, V. T. Yerofieiev, Yu. H. Ivashchenko, V. F. Stroganov, B. Muller. The works by D. V. Oreshkin and Ye. V. Korolev on the use of hollow microspheres in high-strength lightweight concrete, grouting and masonry mortars confirm their effectiveness as a light filler. Of great interest are studies of methods for determining the thermophysical characteristics of insulating materials and structures, considered in the works by M. O. Bakanov and V. H. Kotlov.

The transfer of thermal energy occurs spontaneously from one isothermal surface to another towards the equalization of temperatures from high to low temperatures. Heat transfer can be performed by convection, thermal radiation or thermal conductivity. Since heat transfer in solids is due to the movement of phonons (a phonon is a quantum of vibrational motion of the crystal atoms) or electron gas along the crystal lattice, metals with a large number of free electrons and a perfect crystal lattice exhibit the maximum thermal conductivity. Thermal insulation materials that are amorphous or submicrocrystalline structures have a small number of free electrons, so thermal energy is transferred as a result of phonon interactions. The vibrations in noncrystalline solids are anharmonic in nature owing to the attenuation of longitudinal elastic waves in the course of their propagation.

Most thermal insulation materials are multi-component systems; therefore, heat transfer in these depends on the thermal conductivity of the solid phase, on the convection and on the thermal conductivity of the gas in the pores and the radiation in these. The relative contribution of these components varies depending on the porosity level. New energy saving standards have forced to increase the requirements for thermal protection of buildings, which has increased interest in the development and production of new non-conventional materials. Of particular interest at present are thermal insulation materials made in the form of dry mortars from inorganic binder and mineral or organic filler, the so-called warm plasters (WP). These materials may simultaneously function as both thermal insulation and decoration. Their thermal insulation performance is only 1.5 times lower than that of recognized insulation materials such as expanded polystyrene and mineral wool, and 10 times higher than that of brick (the thermal conductivity of WP is 0.06 W/(m·°C), of foam is 0.039 W/(m·°C), of brick 0.65 W/(m·°C)). This means that 5 cm of plaster on the wall will replace 3 to 4 cm of foam or 51 cm of brick. Thermal insulating plasters are easy to use. These are dry mortars that are simply diluted with water before use. Insulation using WP is performed quickly and does not require particularly high qualification of the contractor. Cement, lime and gypsum are used as binders in WP. WP are adhesive to all materials; there is no need to use meshes when using WP. They are quite strong, and their durability is comparable to that of the base. However, WP are not always advantageous to be used as the only layer of insulation. To ensure the specified resistance to heat transfer of a brick wall with a thickness of 51 cm in climatic zone I in Ukraine, a 9 to 12 cm thick layer of WP should be laid. Under such conditions, WP are used as additional insulation. In climatic zone IV in Odessa and Kherson regions, a 2.5 to 5 cm thick layer of WP is enough. If the main structure of the wall is made of more energy-efficient material such as expanded clay concrete or shell rock, WP only will be enough in any climatic zone. As additional thermal insulation, WP are easy to apply on existing buildings, in particular when reconstructing and restoring historical objects with a lavish decoration. Plaster cannot be replaced when applying insulation on curved surfaces of facades, arches, architectural details, window slopes and sloping surfaces. If necessary, WP can be used as internal insulation, provided a vapor barrier be installed.

The performed literature data analysis has confirmed the unique character of plasters and thermal insulation coatings that work based on the principle of reflective thermal insulation. It is recommended for both outdoor and indoor application. One may insulate everything that needs to be plastered and painted. These materials function both as thermal insulation and a leveling and finishing plaster. No special construction skills are required for installation. Therefore, the development of a thin-layer thermal insulation coating with high thermal and physical and mechanical properties based on the mineral binder and fillers from hollow microspheres with a reflective power is a priority at present.

The research objective is set to justify and develop the composition of a thin-layer thermal insulation coating on cement binder and fillers of aluminosilicate and glass hollow microspheres with
high physical and mechanical and thermal insulation properties, particularly by means of reflecting infrared radiation by modifying the binder.

Thin-layer cement-based compounds quickly lose moisture from the surface owing to the evaporation and absorption of moisture by porous substrates. As a result, the hydration processes are insufficient and such material after curing has low physical and mechanical properties.

The main objective for improving the properties of the thin-layer coating is to increase the number of crystalline hydrates in the composition of cement stone, as well as to adjust the curing time and rheological properties, which may be done by using chemical admixtures. This effect can be produced, for example, by plasticizers, water-retaining admixtures, and salt solutions.

Chemical admixtures on the basis of cement components were classified in terms of the mechanism of their action by V.B. Ratinov and F.M. Ivanov [1]. Class 2 admixtures interact with aluminum- and iron-containing phases of cement with the formation of poorly soluble hydrated double salts. Their specific feature is that they all participate in the addition reactions that occur in solutions and crystallize as hydrated double salts from supersaturated solutions.

This effect is exerted by sulfate-, chlorine- and nitrate-containing admixtures, which lead to the formation of crystalline hydrates such as ettringite or other hydrated calcium sulfoaluminates, hydrated calcium oxychlorides, hydrated calcium aluminates and hydrated calcium nitroaluminates, which have, as noted, an equilibrium surface potential [2, 3].

In the microstructure of the cement paste there are cement particles with a predominant fraction by weight of 50 μm, which are the structural elements of the microstructure of the cement dough and cement stone.

Cement particles are represented by four main minerals: alite C₃S, belite C₂S, tricalcium aluminate C₃A and tetracalcium aluminoferrite C₄AF.

A clear idea of the structural elements of cement stone can be obtained from electron microscopic images (EMC).

According to the paper [4], on the surface of C₃S there are flat hexagonal formations of Portlandite Ca(OH)₂, which grow from the bumps of growth in the form of cone-shaped crystals measuring 200-300 nm (2000-3000 Å). In the volume between the cement particles there are larger prismatic crystals of portlandite. Ettringite 3CaO·Al₂O₃·3CaSO₄·31H₂O in free space has the form of individual long needle-shaped or prismatic crystals up to 10 μm and more, the thickness of which is up to 1-2 μm. In cement stone, the size of ettringite crystals is an order of magnitude smaller; the size of its blocks is up to 1 μm (1000 nm) at a thickness of 100-200 nm (1000-2000 Å). It is believed that these differences in the size of ettringite in the free water space and in the cement paste are due to the thickness of the aqueous layer between the cement particles in the cement paste during its mixing. The thickness of this layer averages 1-3 μm depending on the water-cement ratio.

The blocks of hydrated calcium monosulfoaluminate (CMS) 3C₃O·Al₂O₃·CaSO₄·19H₂O have the shape of thick hexagonal plates; the size of the blocks is less than 1 (one) μm. The blocks of hexagonal hydrated calcium aluminates (HCA) 4C₃O·Al₂O₃·13H₂O are similar in shape [5].

Hydrated calcium aluminates 3C₃O·Al₂O₃·4H₂O are cubic in shape [5]; their size does not exceed 1 (one) μm.

In free space, the singularity of the growth of ettringite in the form of thin needle-shaped crystals is also manifested on the surface and in the layers of cement grains [4]. This suggests that ettringite can developed on the surface of glass microspheres by forming a kind of lattice, which serves as a structure that binds the individual microspheres during the first hours of cement hardening. The conducted studies using electron microscopy confirmed the suggested scientific hypothesis (figure 1).
Hydrated calcium silicates in the form of thin felted structures will develop on aluminosilicate microspheres and serve as a basis for the synthesis of the hydroaluminate phase (figure. 2), which is confirmed by studies using electron microscopy.

As a result of experimental research and application of the mathematical planning method of the experiment, a rational composition and rational ratio of aluminosilicate and glass hollow microspheres, a ratio of Portland cement and hollow microspheres, carboxymethyl cellulose (Walocel with a molecular weight of 15,000) and a complex chemical compound were selected, which included
a plasticizer, calcium nitrate and calcium chloride in the range of 0.05% to 0.09% and 1% to 2.8% of
cement, respectively.

Chemical admixtures in the form of water-soluble compounds, just as Class 2 admixtures such as
calcium chlorides and calcium nitrates, are capable under certain conditions to react with tricalcium
aluminate and tetracalcium aluminoferrite with the formation of poorly soluble hydrated double salts.
This is due to the fact that the joint presence in the concrete of two or more of these admixtures induces a “competition” between these for the right to participate in the reaction with calcium
aluminates $3\text{CaO} \times \text{Al}_2\text{O}_3$ and calcium aluminoferrites $4\text{CaO} \times \text{Al}_2\text{O}_3 \times \text{Fe}_2\text{O}_3$.
The admixture, which with these components of cement forms the most poorly soluble salts promotes the greatest
supersaturation and, as a result, crystallizes with the maximum speed, wins the competition. Hydrated
calcium sulfoaluminate has similar properties in cement; it crystallizes upon interaction between
aluminum in the composition of cement and calcium hydroxide and sulfates (gypsum in Portland
cement) (figure.1).

As long as these reactions go on, other admixtures introduced into the concrete with mixing water
such as $\text{CaCl}_2$ and $\text{Ca(NO}_3\text{)}_2$ wait, i.e. remain in the electrolyte of the cement paste in the form of the
corresponding ions, which accelerates the hardening of silicate components (e.g. felted formations of the
CSH phase) (Ref. figure.2) by changing the solubility of calcium silicates. These admixtures act as
Class 1 admixtures, which do not contain any ions of the same name with cement and accelerate
hardening by changing the ionic force of the solution. Since cement must contain gypsum, any of the
above admixtures does not react with the aluminum-containing components of the cement until the
gypsum is almost completely bound to the poorly soluble hydrated calcium sulfoaluminate. Further
interaction with calcium nitrate and calcium chloride is possible, if after the formation of hydrated
calcium sulfoaluminate in the solution of cement paste there remain tricalcium aluminate and
tetracalcium aluminoferrite with the synthesis of calcium hydrochloro- and hydronitroaluminates, as
evidenced by the calculated negative Gibbs free energies, -$307.1$ and -$280.2$ respectively.

A Seek thermal imager was used to determine the reflection efficiency of infrared radiation of the
thermal insulation composition based on modified Portland cement and fillers made of aluminosilicate
and glass microspheres. The Seeks wavelength spectral range operates in the wavelength range of 3.5
to 5.5 $\mu$m or 8 to 13.5 $\mu$m. To set up the experiment, a plastic container was used, on one part of the
outer surface of which a composite thermal insulation material was applied. The other part of the outer
surface of the container remained uncovered. The container was filled with water heated to a certain
temperature. The temperature on the test surface was determined using a thermal imager. The
temperature of the water poured into the container was 78°C; the outside temperature on the surface of
the plastic container was 73°C; the temperature on the surface of the thermal insulation layer with a
thickness of $1 \text{ mm}$ was 51°C, and on the layer with a thickness of $2 \text{ mm}$ was 28°C (figure. 3).

According to the obtained measurement results, it can be concluded that thin-layer coatings on the
base of Portland cement filled with aluminosilicate and glass microspheres quite effectively reflect
heat fluxes even at a thickness of $1-2 \text{ mm}$. The thermal conductivity coefficient of the thin-layer
coating was calculated, which, depending on the content of components, ranged from 0.033 to 0.067
$\text{W/(m}^\text{°C})$.

A composite material was obtained in the form of a dry mortar with physical and mechanical
properties and performance shown in Table 1.

To determine heat savings owing to the use of a thin-layer thermal insulation coating from the
developed dry mortar, calculations were performed on the heat transfer resistance of the enclosing
structure with reference to the thermal insulation (TI) coating containing glass microspheres according
to the proposed method [6]. The building, for which the calculation was performed, operates in
Kharkiv; the enclosing structure is shown by the form of a wall of pressed cement and sand brick with
an area of 100 $\text{m}^2$ and a thickness of 0.5 $\text{ m}$. The outside part of the wall is covered with a thermal
insulation layer; the inside part is plastered with lime and sand mortar. When performing calculations,
it was taken into consideration that the heat flux $q$ from the outside wall to the surrounding space has
two components: the convective component $q_k$ with heat transfer from the wall surface to the outside air and the radiation component $q_r$ which is transmitted remotely by infrared radiation.

![Figure 3. Measuring the surface temperature using a thermal imager: a) on the surface of the plastic container (73°C); b) on the surface of the coating 1 mm thick (51°C); c) on a surface of a thermal insulation coating 2 mm thick (28°C) ](image)

**Table 1.** Physical and mechanical properties and performance of the hardened composition of the thin-layer thermal insulation coating

| Parameter                      | Test results | Requirements according to ДСТУ-П Б В.2.7-126: 2011 |
|--------------------------------|--------------|-------------------------------------------------|
| Average density, g/cm$^3$      | 0.42         | -                                               |
| Tensile strength at bending, MPa| 1.65         | 0.5                                             |
| Compressive strength, MPa     | 1.75         | 1.0                                             |
| Crack resistance               | No cracks    | No cracks in the layer with a thickness equal to the recommended maximum applied thickness in one go |
| Adhesion to the base, MPa     | 1.33         | 0.2                                             |
| Frost resistance F, cycles, at least | 25           | -                                               |
| Vapor permeability, not less than, mg/m²·h·Pa | 0.07         | 0.05                                            |

Since the thermal insulation coating consisting of hollow glass microspheres is an optical system, it leads to a change in the emissivity of the wall to reduce the radiation component of heat loss and reduce the amount of heat flux from the wall surface. As the coating changes the structure and magnitudes of heat loss from the wall surface, the heat transfer resistance of the wall changes. We define the change in heat transfer for the enclosing structure with and without coating at the indoor air temperature $T_i$. The emissivity of the thermal insulation coating has a lower emissivity $\varepsilon_t$ than the emissivity of the outer surface of the uncoated wall $\varepsilon_0$. From the classical definition of heat transfer resistance [7], we obtain the heat transfer resistance of an uncoated wall and the heat transfer resistance of a wall with a thermal insulation coating containing hollow microspheres.

The intrinsic thermal resistance of the thermal insulation (TI) coating with a thickness of 1 mm and thermal conductivity $\lambda = 0.067$ W/(m·°C) will be $R_t = 0.0150$ m²·°C/W. The effective emissivity of
brickwork is taken as \( \varepsilon = 0.95 \). The effective emissivity of the coating consisting of 90% of hollow glass and aluminosilicate microspheres by volume is taken as \( \varepsilon = 0.85 \). The thermal resistance of the wall without TI coating is \( R_t = 0.8118 \text{ m}^2\cdot\text{°C}/\text{W} \), and with TI coating is \( R_{ti} = 0.913 \text{ m}^2\cdot\text{°C}/\text{W} \).

The average annual heat consumption for the outside wall at the admitted heat transfer resistance is \( Q = 770860.6 \text{ W/year} \), and the average annual heat consumption for the entire surface of the wall with TI coating is \( Q = 625770 \text{ W/year} \). Heat savings by applying a TI coating containing glass hollow microspheres on a wall with an area of 100 m\(^2\) in the climatic conditions of Kharkiv allows reducing heat consumption by 18.82% per year or by 0.188% per 1 m\(^2\) per year.

To sum up, it should be noted as follows.

The developed thermal insulation material optimally combines the functions of effective heat protection and external finishing warm plastering. It is easy to apply on existing buildings, in particular when reconstructing and restoring historical objects with a lavish decoration as additional insulation. Plaster cannot be replaced when applying insulation on curved surfaces of facades, arches, architectural details, window slopes and sloping surfaces. The most effective application of this thermal insulation material is planned as a finishing plaster for indoor thermal insulation, in particular where intense infrared radiation (heating radiators) is present and for the installation of “warm floors”. For the developed composition of the mineral thin-layer thermal insulation coating, the cost of the mixture is almost 3 times lower than for the known composition of the thermal insulation coating on the polymer binder. The economic efficiency from the introduction of the developed composition for the arrangement of a thin-layer thermal insulation coating is about 70 UAH/m\(^2\).

The developed thin-layer thermal insulation coating does not require positive temperatures when applied (which are not below +50°C) or heated buildings for storage, has unlimited service life, unlike polymeric analogs (not exceeding 10 years). The thermal insulation compound may be applied both exteriorly and interiorly with no condensation being formed between the wall and the coating. Applying a thin-layer thermal insulation coating on a brick wall measuring 10 m by 10 m in the climatic conditions of Kharkiv allows reducing heat consumption by 0.188% per 1 m\(^2\) per year.

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