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КОМПОЗИЦИОННЫЕ МАТЕРИАЛЫ НА ОСНОВЕ ПОЛИСТРУКТУРНОЙ ИНТЕГРАЦИИ ГЕТЕРОГЕННЫХ СИСТЕМ

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Статья направлена обобщение теоретических представлений о зависимости эксплуатационных характеристик композиционных материалов от их состава и структуры. В ней, исходя из полиструктурной теории бетона, формулируются положения о влиянии компонентов на различные структурные уровни композита, экспериментально доказывается возможность качественного управления свойствами материалов и конечных объектов городской инфраструктуры на их основе. В статье приводится анализ особенностей технологических и конструктивных решений малых архитектурных форм, применяемых для создания условий повышения качества и комфорта городской среды и участвующих в мероприятиях по ее благоустройству. Рассмотрены существующие и перспективные варианты применения композиционных материалов при производстве объектов городской среды. Проведена деконструкция основных свойств композиционных материалов в разрезе уровней организации структуры композита. Предложены теоретические решения для интеграции разнородных материалов в единый композит на различных структурных уровнях. Представлены результаты экспериментов по подбору и оптимизации структуры композита, обеспечивающих эффективную совместную работу элементов гетерогенного материала, обеспечивающих рациональное управление свойствами конечного объекта городской инфраструктуры, с учетом требований к условиям эксплуатации.

Ключевые слова: строительные материалы, композиты, композиционные материалы, полиструктурная интеграция, полиструктурная теория бетона, бетон, вариотропная структура

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COMPOSITE MATERIALS BASED ON POLYSTRUCTURAL INTEGRATION OF HETEROGENEOUS SYSTEMS

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The article aims to generalize the theoretical concepts of the dependence of the performance characteristics of composite materials on their composition and structure. The authors formulate the provisions on the influence of components on various structural levels of the composite In terms of the concrete polystructural theory. Also the article provides the possibility of high-quality control of the properties of materials and final objects of urban infrastructure based on them. The article analyzes the features of technological and design solutions for small architectural forms used to provide the conditions for improving the quality and comfort of the urban environment and participating in measures to improve the urban environment. Also we consider existing and promising options for using composite materials in the production of of the urban environment objects. And carry out the main properties of composite materials deconstruction in terms of the levels of organization of the composite structure. We proposed the theoretical solutions for the integration of dissimilar materials into a single composite at various structural levels. The article presents the results of experiments on the selection and optimization of the structure of the composite. These provide the effective heterogeneous elements activity, which ensure the rational control the urban infrastructure final object properties, taking into account the operating conditions requirements.

Key words: building materials, composites, composite materials, polystructural integration, polystructural theory of concrete, concrete, variotropic structure

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INTRODUCTION

The State Programme of the Russian Federation "Providing Affordable and Comfortable Housing and Communal Services to Citizens of the Russian Federation", approved by Resolution No. 1710 of the Government of the Russian Federation of 30 December 2017 [1] not only aims to provide affordable and comfortable housing and communal services to citizens of the Russian Federation. Also there is the Sub-Program 2 "Creating Conditions for Providing Quality Housing and Communal Services to Russian Citizens" requires forming comfortable urban environments. It aims to radical increase of the urban environment comfort, the quality index of the urban environment, reduce the number of cities with an unfavourable environment, provide the conditions for a systematic improvement of the quality and comfort of the urban environment through the implementation of a set of priority improvement measures, including the implementation of integrated beautification projects. In this context, the creation of urban environments and infrastructures that increase the comfort of human habitation and at the same time are designed to maintain their performance over the long term with minimum maintenance costs is of utmost importance.

This regard, the development of urban environments and infrastructure increases the human habitation comfort and at the same time designs to maintain their performance with minimal costs. The development of such materials is very important.

The scientific importance of the implemented approaches in the development of compositions and production technology of composites with improved performance properties consist in:

- complex use of methods of structural modification of composite systems by introduction of dispersed functional additives and polymeric component, providing directed formation of variotropic structure;
- methods for the bulk and surface transformation of polymer and fibre elements using promising types of physical and chemical action and peripheral layer generation to modify the reactivity of components in, thus converting components that are inert in their analogues into chemically active ones;
- methods for controlling the micro- and macroporosity parameters of the composite material by introducing a system of fatty acid esters and organomodified silicones, which ensures the composite's density properties can be adjusted within a wide range while maintaining its high strength properties;
- the technology for managing the adhesive interactions between the composite components and the mineral-polymer matrix, increasing the inclusion of the filler surface in the system by 50% more, compared to analogues;
- the control system of processes of three-dimensional self-organization of objects during formation and hardening, consisting in consistent provision of optimal conditions for the course of reactions in the formation of microstructure, and directed mechanical influences, providing the formation of meso- and macrostructure of the composite.

The purpose of the study is to select and optimise the composite structure using the method of polystructural integration of heterogeneous materials for the manufacture of urban environment objects.

In order to achieve the goal, the following tasks were set and resolved in the work:

1) To analyse the design solutions of small architectural forms in order to be able to use composite materials for their production.

2) To develop material compositions for the polystructural integration of heterogeneous components into a single composite.

3) To study prototypes of the resulting composite materials.

4) To optimise the structure of composite materials and develop technology for the polystructural integration of heterogeneous composite materials for the manufacture of small architectural forms used in urban environments.

The presented scientific and engineering issues provide the production of heterogeneous composite material for the production of urban environment objects – small architectural forms, allowing to reduce operating costs by 40–60% and to increase the service life of such objects up to 25–30 years, while maintaining high technological efficiency of their production. The achievement of these goals allows us to develop and optimise the industrial technologies for the production of small architectural forms and other urban environment objects with high and stable properties, develop technical documentation, certify the product and act at the world market.

ANALYSIS OF DESIGN FEATURES OF SMALL ARCHITECTURAL FORMS

In the Russian legal and normative system the components of the architectural environment are the elements of complex improvement, differentiated into the following types: landscaping; coverings; fencing; and small architectural forms. Small architectural forms (SAF) include: elements of monumental-decorative design, mobile and vertical landscaping design devices, water devices, urban furniture, utility and technical equipment of the city, as well as sports, lighting equipment, means of outdoor advertising and information. When designing and choosing small architectural forms, it is recommended to use catalogues of certified products. The small architectural forms should be designed individually for areas of historic buildings, the central core of the city and urban multifunctional centres [2]. Individual design objects have more free interpretation of the typology. For example, a seating area is not only a bench, but also a tiered platform, an amphitheatre and a module system [3, 4].

The design of a SAF structure, in terms of its aesthetic expression, is based on the technique of proportionality (from the Latin "Proportio" - "ratio, proportionality of the parts") is a method of establishing the relationship between the parts of a form. The process of relating proportions of design is the first step to design the architecturally expressive highly artistic objects and small architectural forms. The right proportions produce new people's perception [5, 6]. Small proportions with a ratio between 1.0 and 1.618 are perceived by people as not causing aggression and tension. SAF with small proportions is perceived more harmoniously at close range due to its relatively small size.

In addition to artistic expression in the design of the SAF, the variability of their structure should be taken into account This structure implies irregular properties across the cross-section of the product. It is the result of the specific requirements for the functional purpose, expression, and the using specific conditions of the SAF.

The surface of the SAF requires increased resistance to weathering, mechanical stress and UV radiation. At the same time, the SAF should retain its artistic expression and have pleasing organoleptic properties. There are micro- and macrolevels of SAF structure.

The macro level provides the cross-section properties change, which is structurally expressed by the integration of load-bearing layers made of a stronger material and decorative and protective or insulating layers that give the material its special properties.

Other way of integrating heterogeneous materials to produce a variatropic structure of the final product is to transit to the meso- and micro-level, i.e. to combine heterogeneous elements in a quasi-monolithic material, which together give the composite new, unique properties.

By these features we have developed a method that combines options for integrating heterogeneous materials into a single composite on both macro-, meso- and micro-levels. But it depends on the type and purpose of the SAF. The technology combines macro- and mesostructure control by a rational combination of heterogeneous components to solve the problems of mass-size formation at the macro level, including the use of fixed components that work first as formwork forming elements and then as product components to reduce its average density, heat capacity and thermal conductivity. The rational combination of the particle size distribution of heterogeneous inert components and chemically active components at the meso level provides a three-dimensional co-programming of the system. At a micro level, the technology provides the formation of strength and hydrophobic properties of the composite and the product as a whole, through targeted control of hydration reactions of chemically active components and the introduction into the mineral body of the artificial stone of a polymerised three-dimensional reinforcing lattice formed by polymerising the copolymer.

The final SAF characteristics dependence on the properties of the composite at the micro, meso and macro level is shown in Table 1. Analysis of Table 1 shows that only a systematic approach to managing the structure of the composite at all levels, provides improved product using.

***Table 1*. Dependence of the main properties of composite materials in terms of the levels of organization structure**

Composite structure level	Composite properties forming at the level	Properties of SAF
Micro level	Density	The bearing capacity of the product. Maintainability of the properties for a long time.
	Heat conductivity	Organoleptic comfort
	Hydrophobicity	The ability to resist penetration of moisture, solutions and aggressive media into the composite body, and as a consequence the stability of the product properties, increased frost resistance and water resistance.
Meso level	Friction resistance	The ability to resist mechanical abrasion during use as a long-lasting maintenance of the product's appearance without the need for additional painting.
	Linear deformations	The ability to keep linear and volumetric characteristics under changing temperature and humidity conditions as a long-lasting maintenance of the use of the product
	Crack resistance	The ability to support the crack growth and increased resistance to mechanical impact and shearing, both on the surface and in the volume.
Macro level	Density	Provides the product's mass dimensions within a rational range for the intended product use.
	Heat capacity	It decreases in heat capacity, and as a consequence provides comfortable organoleptic using.
	Durability	Thus, it provides guaranteed service life in urban environments by combining the components into a single system.

We identified the constructive principles for the integration of heterogeneous materials at the macro level, which have resulted in a variatropic structure of the final product. Further we implemented the ideas of managing the structure at all levels.

EXPERIMENTAL PART

The disadvantages of such traditional materials as metal, concrete, wood or plastic are the limited application possibilities and the relatively low resistance of much of the material to external aggressive influences. These classic materials do not integrate well with each other, which lead to a rapid loss of their functions, including decorative and aesthetics features of the product. To provide these features the urban environment objects should be made of the composites.

Composite materials are artificial, stone-like mixtures obtained by combining two or more heterogeneous elements. Their characteristic features are high physical and mechanical properties. They are not a sum of the properties of each individual component. The advantages of these materials are: high strength over a wide temperature range, chemical resistance, weathering and light fastness, resistance to wear and tear and durability as a rule.

The basic principles of mineral base modified by polymer additives composites production with a complex of improved physical-mechanical and operational properties are presented in works of Yu.M. Bazhenov [7], S.V. Fedosov, V.T. Erofeev, [8], V.I. Kalashnikov [9-11], etc. The main idea is the formation of mineral binders on a microlevel of low-base calcium hydrosilicates crystals by hardening. They compacted in a gel of hydrated initial binder components and new formations – the results of hydration of clinker minerals. This material has high physical and mechanical parameters, theoretically reaching values of 8–12 GPa, but due to the high defect structure resulting from its stochastic formation, the real strength of the composite is 90–120 MPa. It is difficult to use it directly because of its low cracking resistance, high thermal capacity and thermal conductivity, and relatively low resistance to aggressive environments.

To compensate for the disadvantages, the composite structure has traditionally been improved by the introduction of processing aids of various nature and purpose. Mineral sealing additives - fillers, both inert and chemically active are used to control the microstructure. Inert fillers become the centres of crystallisation and form the initial skeleton of the composite on a micro level. Chemically active fillers interact with the hydration products and bind products that can lead to undesirable processes, including corrosion. Other chemical-active components, such as rheological additives, are used to control the time, process and concentration of the mortar during the hydration.

We use the inert coarser fillers and fine aggregate of different nature at the meso level. We can obtain the less defective structure with controlled average density by air regulating and by controlling the fractional composition and the ratio of the different filler and aggregate fractions of the binder. This level provides the composite's specified density, water and vapour diffusion, water absorption, friction as well as thermal characteristics.

We add the coarse aggregate, reinforcing cage and embedded elements into the composite to form the properties for the specific product and conditions at the macro level. The final characteristics of both the material and the product made from it are controlling the shape, dimensions and content of the macro components forms.

But mineral-binder composite is a capillary-porous body capable of sorbing solutions and gases from the environment and degrading under their influence. Its surface remains insufficiently tactile and has a low artistic expression. Thus, we proposed and implemented measures to compensate these disadvantages.

We used White Portland cement 2-400-D0-GOST-965-89 and 1-500-D0-GOST 965-89 as the main binder. Its characteristics were regard to GOST 310.1 - GOST 310.4. The fineness of the cement was 4500–5000 cm^2/g, normal density 23–26%, setting time – the beginning not earlier than 40 minutes and the end not later than 10 hours, activity 49.0–52.5 MPa.

We use sealing and hydrophobic additives, such as microcalcite KM80 GOST R 56775-2015 and zinc stearate TU 6-09-17-316-96 to provide low water and vapour permeability and low water absorption.

To control rheological properties, we used hardening accelerator - calcium nitrate, setting retarder - nitrilotrimethylphosphonic acid (NTPh) TU 2439-347-05763441-2001, hyperplasticizer PC-40 TU 5745-005-13453677-2008. All additives meet GOST 24211-2008.

We used the various fractions quartz sand for the glass industry GOST 22551-2019 as a fine aggregate.

Mixture parameters are determined by GOST 10181-2014, strength of samples by GOST 18105-2018 and GOST 10180-2012, abrasion by GOST 13087-2018, density by GOST 12730.1-2020, porosity by GOST 12730.4-2010, water absorption by GOST 12730.3-2020, heat capacity by GOST 23250-78, thermal conductivity by GOST 7076-99, linear expansion by GOST 30459-2008. The selection of compositions was by GOST 27006-2019.

The structure of the developed composite material should contain such a concentration of fillers, which is rationally and physically justified. Also, they should correspond to the amount of the binder, which predetermines the speed of chemical reactions. This allows to see the regularities for the mutual arrangement of binder, filler and fine aggregate particles. This provides the following conditions:

- we achieve a conditional optimum filler concentration and an optimum system packaging at the final stage of structure formation.

- we reduce the nucleation energy of the crystals due to the presence of the filler crystallisation centres.

- we reduce the surface tension at the crystal-liquid interface through the use of various processing aids. The nucleation rate of the new phase is increased.

- the resulting composite contains oversized particles - a fine aggregate designed to compensate for the internal stresses generated by high filler concentration.

- mechanical action on the filler phase provides maximum contact strength between the particles.

- the use of surface-active additives provides the change of the cement rheology, including polycarboxylate-type hyperplasticisers.

- the filler, provides maximum adhesion between the binder and the aggregate and consequently maximum strength and minimum hollowness, by displacing the binder into the contact zone at the macro level.

Table 2 presents the summary of the technological solutions adopted for shaping the composite properties.

***Table 2*. Technological decisions by selecting the composition**

Composite structure level	Composite properties at the level	Technological decision by selecting the composition
Micro level	Density	The use of high-strength hydraulic binder White Portland cement CEM 1B provides a composite strength of up to 60 MPa.
	Heat conductivity	We reduce the thermal conductivity by using a finely ground filler. It forms a three-dimensional bulk grid of low thermal conductivity at the micro level, displacing the highly conductive water and forming the insulating interlayers between the composite components.
	Hydrophobicity	The use of a sealing additive - microcalcite KM 80 and a hydrophobic additive - zinc stearate, provides a reduction of water absorption below 2.5%
Meso level	Friction resistance	The use of high-quality White Portland cement CEM 1B together with polycarboxylate hyperplasticiser PC-40 provides a hard dense product surface
	Linear deformations	Application of discrete, grain-optimised aggregate
	Crack resistance	Use of micro-calcite as a filler, together with redispersible powder and hyperplasticiser
Macro level	Density	Use of large dimensioned fixed elements for the formation of macrostructure, playing the role of forming element, permanent formwork and coarse aggregate at different stages of the technology
	Heat capacity	Application of large-sized non-removable elements with low heat capacity for the formation of macrostructures
	Durability	Integration of individual heterogeneous elements into a single composite

The composite mixture has colloidal-sized particles and larger particles, due to a discrete filler grain composition of 0.1 mm or less. The electrolyte is a calcium nitrate hardening accelerator. The polycarboxylate hyperplasticiser PC-40 regulates the rheological properties of the mixture and influences the crystallisation process of low-base calcium hydrosilicates.

The methods for calculating the composition consist in establishing the volumes of inert and filler fractions, taking into account the coating of grains. But the amount of fine fraction is calculated by the displacement of the binder from the intergranular voids. Thus, the aggregate with the lowest porosity will be the most rational fractional composition.

The purpose of applying the mixture is to make SAF elements. They are not very thick. The maximum aggregate grain size should be less than 1/4 of the thikness of SAF element, the maximum aggregate grain size will be 5.0-2.5 mm. A composite similar to fine-grained concrete will be the result.

During the experiments it was found that the introduction of sufficiently fine sand of continuous fraction with fineness modulus 1.5-1.3 into the binder when the mass ratio of cement: sand exceeds 1: 1.5, leads to a sharp decrease of strength (Fig. 1).

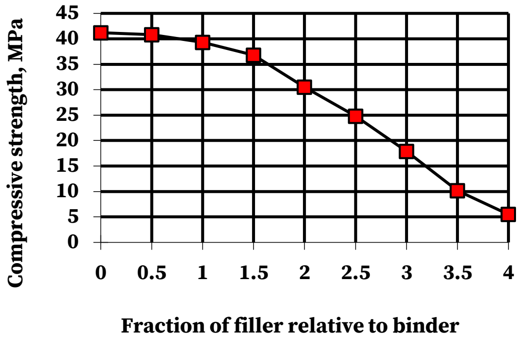

Fig. 1. The dependence of composite strength on the amount of filler

The shape of the fine filler grains plays a significant role in this process. Sand obtained by crushing or sieving is irregularly shaped grains, so the total porosity of the mixture reaches 25–28%. Indirectly, the value of the porosity can be determined by the bulk density – the higher the filler bulk density, the denser the mixture and therefore the lower the porosity. Thus, a denser mixture of fine filler fractions will require less cement to produce a composite. Fig. 2 shows the results of the experiment to identify the dependence of the bulk density on the amount of finer fraction.

Fig. 2 analysis shows the maximum bulk density lies within the range of fine fraction consumption of 20-40%, the finer fraction most effectively fills the inter-grain voids, so a mixture including both coarse and fine fractions has a higher density. Andersen [12], Fuller and S.R. Zamyatin [13] laid the theoretical background and basic laws of formation of properties for mixtures with continuous filler fraction compositions. P.I. Bozhenov 14] and L.I. Dvorkin [15] identified ratios between coarse and fine fractions for fractional mixtures.

The most effective is a discrete particle size distribution of the mixture. The real filler grains are not perfect, so the fraction-to-fraction transition factor proposed by L.I. Dvorkin [16] becomes ineffective. Thus, the most appropriate transition coefficient is the value suggested by P.I. Bozhenov - 0.255 [14]. The average sand fraction size of 2.5 to 5.0 corresponds to 3.75 mm, the next fraction should be 3.75·0.255=0.84 mm, which corresponds to a fraction of 1.25-0.63 mm. By the Fuller equation the amount of this fraction is 44–46%. The following fraction is required to increase packing density. Calculating the size of the new fraction by analogy, we obtain a fraction of 0.315-0.14 mm. The amount of component will be 24% of the weight of the medium fraction. The porosity will be 29%. Thus, the ratio of the fractions in the mixture would be: 9:4:1 by mass, for fractions 5.0–2.5, 1.25-0.63, 0.315-0.14.

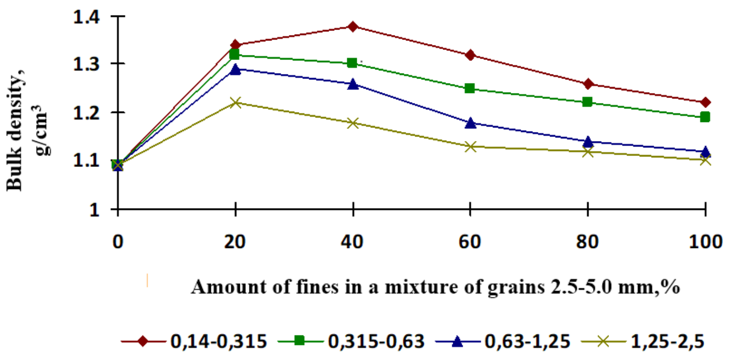

Fig. 2. Dependence of filler bulk density on the mixture particle size distribution

Effective production requires a high level of mobility to provide complete filling of the mould, before the surface self-levels and the entrapped air is released. Fig. 3 shows the flowability dependence of the mixture by the Suttard viscometer for the composition with optimised particle size distribution. The polycarboxylatehyperplasticiser has a higher efficiency than the traditional phenol-formaldehyde-based plasticiser at equal costs per mass of binder.

RESULTS AND DISCUSSIONS

The presented principles for determining the structureof the composite consist of selecting the ratio of the amount of binder to the volume of optimised filler. The maximum strength of the composite material provides its high mobility. By a grain coating thickness of 0.05-0.06 mm, the filler volume ratio will be 2. The results are shown in Table 3.

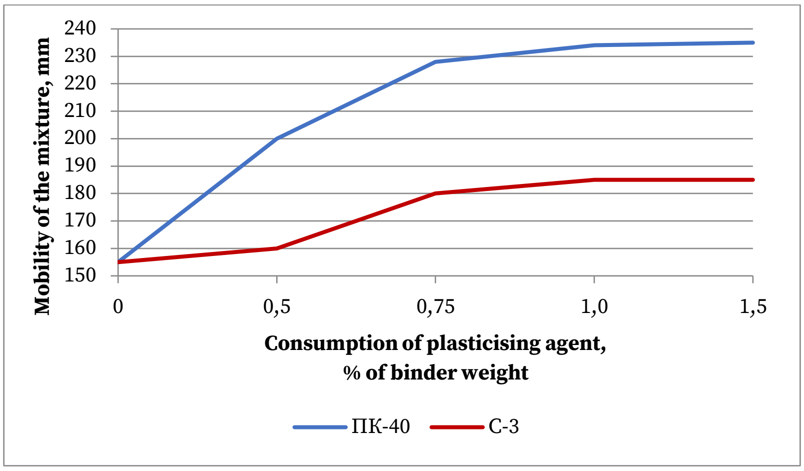

Fig. 3. The dependence of the mobility of the concrete mixture on the consumption of the plasticizing additive

***Table 3*. The dependence of the strength of the composite on the consumption of components and the activity of cement**

Cement, kg	Filler, kg	Optimised filler, kg	Density at CEM 1 42.5, MPa	Density at CEM 1 42.5, MPa
250	125	1725	12.0	15.2
300	150	1650	13.8	17.5
350	175	1575	15.8	19.9
400	200	1500	24.2	30.4
450	225	1425	30.5	35.6
500	250	1350	35.8	41.9
550	275	1275	38.2	46.8
600	300	1200	40.1	49.1

We can see a non-linear increase in strength with increasing cement consumption, with a slowing down of the growth during the complete matrix saturation phase on Table 3. A further increase in the binder consumption does not lead to an increase in strength, as the maximum possible strength for the cement grade has been reached. The strength parameters of the composite provide the requirements of SP 63.13330.2012 "Concrete and reinforced concrete structures" and correspond to the strength class B35-B40 for fine-grained concretes of natural solidification.

CONCLUSIONS

Thus, in our study we identified the basic structural parameters for obtaining a new type of composite material, combining the properties of polymer and mineral-based composites, characterised by high strength, low crack resistance, low heat capacity and thermal conductivity. The new material, unlike traditional materials, can have a variatropic structure. It will allow to form the properties of products for different directions. Also, this will provide the product with unique structural, thermal and aesthetic properties, high consumer qualities and will made it possible to use it in urban environment and infrastructure objects. Integration of mineral components will allow the material to resist effectively to external aggressive influences, having increased terms of nonrepair operation of products in 2-3 times in comparison with traditional. That will lead to considerable decrease in expenses for maintenance of a normative condition of products from the developed composite material.

This gives a composite with a density of 2.1 g/cm^3, a compressive strength of 46–49 N/mm^2, an abrasion resistance of 0.55 g/cm^2, a linear expansion coefficient of 0.52 mm/m, a heat capacity of 1.14 kJ/(kg ·°C) and a thermal conductivity of 0.65 W/(m ·°C). The achieved characteristics of the composite material are sufficient for products exposed to alternating wetting-drying, freezing-thawing, abrasion and mechanical stress. The resulting properties meet the requirements of structural concrete for products over 100 years of age.

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