

Original Article

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Research on the resistance of protective coatings for concrete to the effects of atmospheric moisture

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Abstract: The development of the construction industry has led to increased requirements for the operational properties of building materials in general and concrete in particular. Although concrete is designed primarily to withstand structural loads, it must also resist environmental influences to increase its durability. This article presents the results of the influence of the components of protective coatings on the hydro-physical properties of concrete. The edge wetting angle in concrete with a protective coating ranges from 95 to 101 degrees, which is about twice that of uncoated concrete. The mass of concrete under the influence of hygroscopic moisture increases, and after 30 days of exposure, it is 1.1–1.6 wt. % compared to 5.7–5.8 wt. % for control samples. The minimum increase (1.1–1.2 wt. %) is achieved when using coatings with the largest amount of heat-resistant varnish KO-08. The water absorption of the developed coating compositions decreases after 30 days of being in water from 5.2 to 1.6–2.2 wt. % for C20/25 concrete. Low temperatures negatively affect the hydrophysical properties of protective coatings, but only slightly. It has been found that water absorption increases by approximately 20 %.

Keywords: concrete, protective coating, edge wetting angle, water absorption, low temperature

1. Introduction

Concrete has become the most demanded material due to increased construction rates and high requirements for structures. It is a typical composite material obtained by hardening a carefully selected mixture of binder, aggregates, water, and additives. Nowadays, concrete is an irreplaceable and essential building material in most structures. However, surveys of

structural elements in industrial buildings [1] and bridges [2] demonstrate that several factors affect the durability of concrete or cause structural damage. One of these factors is a change in the internal humidity or temperature of the pores (carbonation, freeze-thaw cycles, wet-dry cycles, the influence of chloride salts, and sulphates), as well as the influence of various forms of loading [3–6].

The durability of concrete is mainly influenced by its pore structure. Considering the pore structure of concrete and its dependence on technological parameters, modern methods of protecting concrete from the destructive effects of physical and chemical factors are currently being developed. By altering the mineralogical composition of the binding material and the hardening conditions, it is possible to obtain different types of cement stone microstructure. The interfacial surface and the inner surface of neoplasms are collectively considered to be the surface that affects the processes of synthesis of properties and corrosion of the stone [6]. The use of engineering cementitious composites (ECC) – a developed class of dispersion-reinforced materials based on Portland cement – makes it possible to increase the load-bearing capacity, stability under various static and dynamic influences, and the durability of building structures due to the controlled cracking process. However, ECC uses a significant amount of cementitious materials, often up to 70%, which leads to significant shrinkage deformations, limiting dimensional stability and increasing the cost of the material [8, 9]. Supplementary cementitious materials, including ultra-dispersed mineral additives, are used to improve the quality of concrete [10, 11]. Methods that prevent the occurrence of corrosion by covering the surface with protective materials or creating artificial waterproofing are also effective [12–16].

The problem of increasing durability is considered in two aspects: studying the characteristics of the surrounding environment and determining the dominant factors whose actions are dangerous; and studying the mechanism and kinetics of corrosion processes to develop ways to increase the durability of artificial stone based on this knowledge. Units of measurement must be introduced to assess durability, defining it as a "measure" of a material's resistance to wear and physical and chemical changes under specific conditions of use. Such an interpretation makes it possible to substantiate methods of durability testing, using resistance to influences characteristic of the operating conditions of a given material or structure as a criterion [6, 11].

The presence of compounds containing atoms of elements other than carbon in the polymer chain, such as silicon and aluminium, can significantly enhance the weatherproof properties of materials. The end product of the destruction of polyorganosiloxanes is the polymer $(\text{SiO}_2)_n$, with the appropriate oxide content of the element, which imparts a certain strength to the material. The presence of an inorganic polymer in the composition of the material can serve as a framework for the formation of a protective coating when heated.

Synthesised polymers, whose main chain contains periodic inclusions of metal atoms alongside silicon and oxygen atoms, have properties that are significantly altered by the increased mineral content. These polyorganometallosiloxanes are characterised by high thermal stability [16], which surpasses that of organosilicon polymers.

Among the polyorganometallosiloxanes, there are polymers whose molecular chains are built from silicon, oxygen, and aluminium atoms. These polymers are used to produce plastics that can work effectively when heated to 573 K. During thermal decomposition, they retain the Si-O-Al bond. Heating above 523 K is characterised by the exchange of phenyl and alkyl groups between aluminium and silicon.

Organosilicate coatings are products of physico-mechanical and thermal processes occurring in the "coating-silicate-oxide" systems. According to data, the formation of a strong spatial structure of organosilicate coatings occurs in several stages. At temperatures up to

973 K, reactions involving the interaction of components with hydroxyl groups in polycondensation reactions, primarily formed during the destruction of the polymeric and inorganic parts of the composition, are crucial at any stage of coating formation and heating. Moreover, the integrity of the coating structure depends not only on the chemical bonds that arise during the reaction of the destruction products but also on the structural similarity and crystal chemical composition of the six-membered rings of hydrosilicates and the products of the destruction of the polymer. Oxides play an important role in increasing the thermal stability of coatings. Depending on their chemical nature, they shift the onset of destruction of "polymer-silicate-oxide" systems to higher temperatures or extend the destruction interval. At temperatures above 973 K, the durability of coatings is determined by the properties of high-silica glass-ceramics, into which the organosilicate material transforms. The properties of coatings completely depend on the processes of structural rearrangement (amorphisation followed by the formation of new phases and their recrystallisation). At temperatures of 1473–1573 K, the material melts, and the coating turns into a glassy mass [15].

Organosilicate materials are products of the chemical interaction between high-molecular organic elemental compounds (polyorganosiloxanes, polyorganosilans) and specially processed finely dispersed silicates (chromium, titanium, zinc, zirconium, etc.). Organosilicate products combine the most valuable properties of polymers with the increased heat resistance and chemical resistance of thermal silicates and oxides [14].

At relatively low temperatures, mechanochemical interactions cause polyorganosiloxane to graft onto the surface of silicate particles, forming siloxane-silicate bonds. Condensation reactions complete at temperatures ranging from 573 to 973 K [16].

In the temperature range of 573 to 973 K, the gradual destruction and burning of the organic component of the polymer occur, removing light products. At 973 K and above, the system becomes an ordinary ceramic material.

Coatings with organosilicon bonds combine the properties of both inorganic and organic substances. These coatings include organosilicon polymers (polyorganosiloxanes) and organometallic polymer varnishes. The Si-O-Si bonds give polyorganosiloxanes heat resistance, while functional groups R provide a variety of properties. Materials with organosilicon bonds and silicate and oxide fillers are called organosilicate. The main advantages of organosilicate and organooxide coatings are elasticity, excellent electrical and thermal insulation properties, moisture resistance, hydrophobicity, good adhesion, simplicity and general availability of application technology, and long-term heat resistance at temperatures up to 773 K. At higher operating temperatures, the organic component is removed, with destruction starting at 573 K and ending at 1103–1123 K. The role of the binder gradually shifts to a silicon-oxygen framework that lacks organic radicals. However, the integrity of the structure is not violated, although the material becomes porous, turning into ceramics with open porosity of up to 35%. The number of pores decreases sharply in the presence of a vitreous component that fills the pores [16].

2. Materials and methods

Portland cement CEM II/A-S 42.5R from PJSC "Dyckerhoff Cement Ukraine" was used to produce C20/25 class concrete. The physical and mechanical parameters of the cement are as follows: specific surface area $S = 290 \text{ m}^2/\text{kg}$; residue on sieve No. 008 – 9.2 wt.%; start of hardening – 1 hour 40 minutes, end of hardening – 2 hours 50 minutes, and activity at 28 days – 54.8 MPa. Sand ($M_f = 1.28$) from the Yasynetske field was used as a fine aggregate, with a bulk density of $1,390 \text{ kg/m}^3$, true density of $2,590 \text{ kg/m}^3$, and hollowness of 45.1%. The coarse aggregate was granite crushed stone from the Tomashgorod

deposit, fraction 5–20 mm, with a mechanical strength grade of 120 MPa and frost resistance of 300. A polycarboxylate superplasticizer was used as a plasticizing additive, introduced as an aqueous solution with a concentration of 0.7 wt.% of the cement mass. The research was conducted on concrete cubes measuring 10x10x10 cm.

The combination of silicon fillers with organic bonds is most effective during mechano-chemical dispersion. Many authors have studied the processes of dispersion of oxides and silicates in organosilicon varnishes during grinding in ball mills. Of particular interest is the effect of mechano-chemical processing on compositions based on organosilicon varnishes filled with aluminium and zinc oxides. Considering the special hardness of aluminium oxide crystals, it was added to the composition after preliminary dry grinding for 50 hours. The compositions for protective coatings are given in Table 1. Heat-resistant varnish (KO-08) is a homogeneous solution of toluene and polymethylphenylsiloxane resin. Sodium silicofluoride is introduced to increase the integrity of coatings.

Table 1. Component content of protective coatings, wt. %

No of protective coating	Content of the component, wt. %			
	KO-08	Al ₂ O ₃	ZnO	Na ₂ SiF ₆
1	50	30	20	-
2	55	30	15	-
3	60	30	10	-
4	50	20	20	10
5	55	20	17.5	7.5
6	60	25	10	5

Compositions for protective coatings were prepared by simultaneously grinding the components in ball mills to achieve a maximum dispersed particle size of no more than 50 µm. The tested concrete samples are shown in Fig. 1.

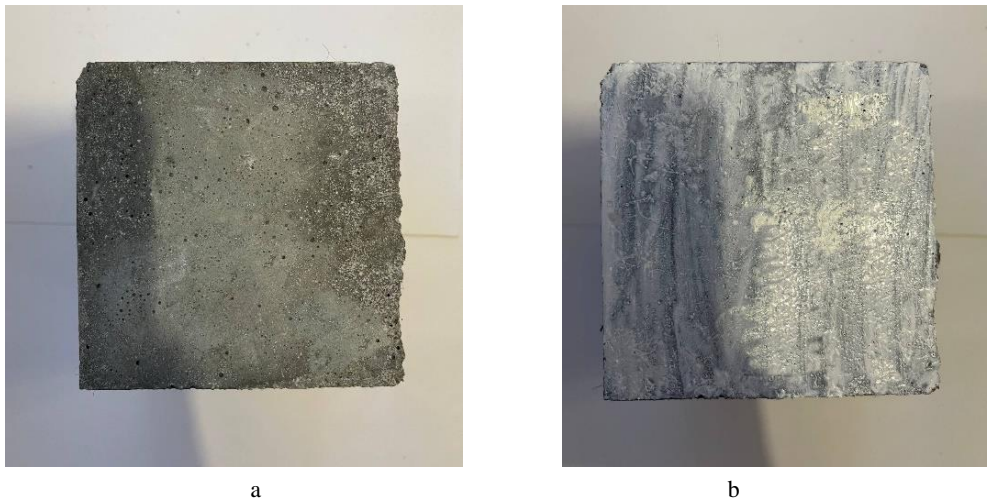


Fig. 1. Concrete samples without coating (a); with coating (b)

As can be seen from the figure, the protective coating imparts a light colour.

3. Results

It is known that the durability and operational reliability of building materials and structures are primarily determined by the operating temperature regime and the resistance of the protective coating to adverse atmospheric factors.

In real operating conditions, materials and products are exposed to the simultaneous action of numerous atmospheric factors. Additionally, the accumulation of various factors significantly increases their corrosion activity. Therefore, it is prudent to quantitatively assess the resistance of the developed protective coating compositions to atmospheric factors.

The proposed compositions of protective coatings were applied to previously treated surfaces with a thickness of 0.4–0.6 mm. The coating was hardened at room temperature for a day to achieve a maximum degree of microhardness (at least 200 MPa).

During operation, face brick covered with protective coatings undergoes aging, accompanied by irreversible chemical and physical processes under the influence of external and internal factors. Signs of coating deterioration include cracking, peeling, loss of mass and colour, etc. Concurrently, the mechanical, physico-chemical, and anti-corrosion properties also change, potentially leading to the loss of protective functions.

Tests of the developed protective coating compositions against factors of an aggressive external environment were conducted in laboratory conditions under the most stringent conditions. To ensure the protection of materials with low weather resistance, coatings must exhibit high and stable indicators of hygroscopicity, water resistance, corrosion resistance, and durability.

The hygroscopicity of the treated concrete was determined by the increase in the mass of the samples that were in a desiccator with distilled water for 30 days.

Research established that at a temperature of 293 K, the presence of moisture reduces the marginal wetting angle of coatings by 2–4 degrees for concrete class C20/25 (Fig. 2). This reduction does not significantly affect their water-repellent properties.

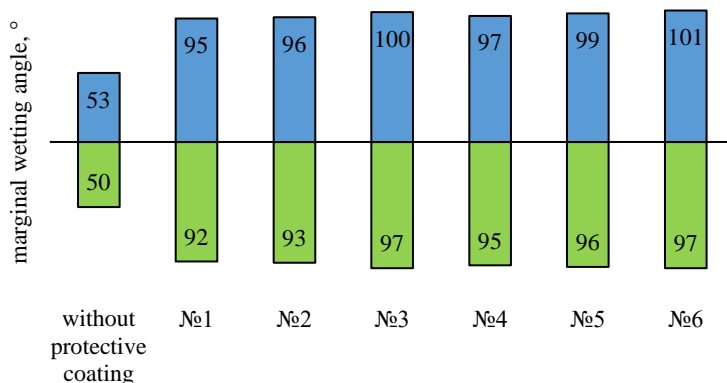


Fig. 2. Marginal wetting angle of concrete before the tests (a) and after the tests (b), 30 days

The mass of concrete under the action of hygroscopic moisture increases to 1.1 to 1.6 wt.% after 30 days of exposure, compared to 5.7–5.8 wt.% for control samples. The minimum increase (1.1–1.2 wt.%) is achieved when using coatings of compositions No. 3 and 6 (Fig. 3).

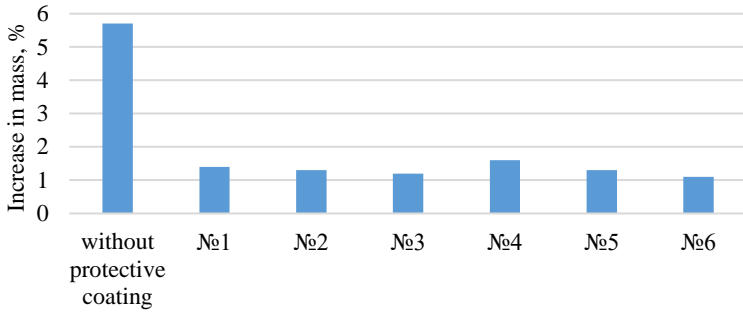


Fig. 3. Increase in the mass of concrete under the action of hygroscopic moisture

The stability of protective coatings to the action of water indicates the feasibility of choosing oxide fillers (Fig. 4). The water absorption of the developed coatings decreases after 30 days in water from 5.2 to 1.6–2.2 wt.% for C20/25 concrete.

It should be noted that the water absorption of protected samples depends on the type of filler, especially the content of zinc oxide. The introduction of zinc oxide, with the same content of aluminium oxide and Na₂SiF₆, increases water absorption by 0.2–0.4 wt.%.

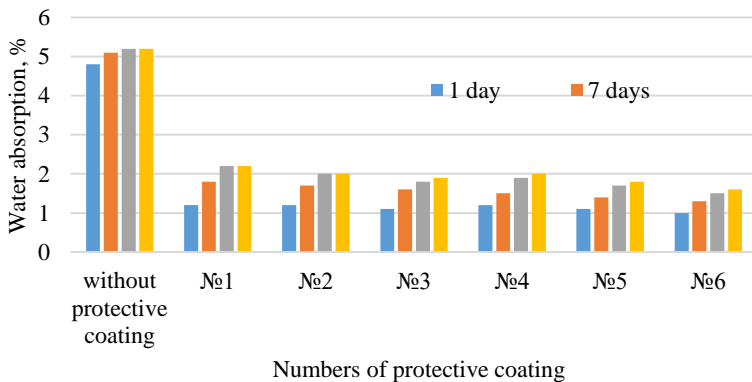


Fig. 4. Water absorption of concrete treated with protective coatings

Filled organosilicon coatings based on industrial products significantly change their properties during long-term exposure to sub-zero temperatures (exposure 240 h; T = 243 K; substrate – concrete). Water absorption at this temperature is 1.9–2.8%, which is 20–27% higher compared to the initial value. The maximum hydrophobicity is observed when using coatings of compositions 2, 4, and 6. Therefore, the resistance of protective coatings to the action of negative temperatures depends mainly on the content of the hydrophobizer (Fig. 5).

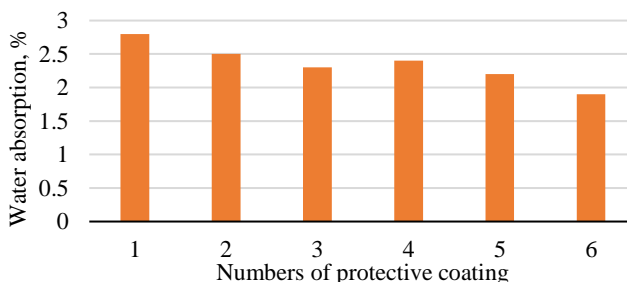


Fig. 5. Water absorption of concrete under the influence of low temperatures

Analyzing the results of studying the atmospheric resistance of coatings, it should be noted that the proposed method of mechanochemical dispersion of oxides and silicates in the environment of a hydrophobizer ensures the formation of a material with improved insulating and protective properties. The action of atmospheric factors does not cause significant destruction. The main oxidation processes occur only in the surface layer of the polymer without a significant decrease in the filler content.

4. Conclusions

An effective method of increasing resistance to atmospheric moisture is covering the surface with protective materials or creating artificial waterproofing.

The high insulating ability of protective coatings, which depends on the content of polymethylphenylsiloxane and Na_2SiF_6 , has been experimentally confirmed. The marginal wetting angle for all coatings is greater than 90 degrees, indicating a high hydrophobicity index, and the water absorption value of concrete is 1.6–2.3% by mass.

At low temperatures, the properties of organosilicon coatings deteriorate significantly. The water absorption of the samples increased by 20–27%, reaching 1.9–2.8%. The hydrophobizer content has the greatest effect on the hydrophysical properties.

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