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RESEARCH OF OPERATIONAL PROPERTIES OF MODIFIED SPECIALIZED CONCRETE FOR TRANSPORT CONSTRUCTIONS

It was established that the polymeric component of the organomineral modifying complex changes the nature of the super-molecular structures in the activated cement system - at optimal filling, globules decrease in size preventing the phase surface diffusion, which contributes to increase of the waterproofness of modified concrete. When introducing a modified cement system into the concrete mixture, the reduction of the open porosity to 3-5%, depending on the composition, has been achieved. Conducted tests for water resistance and frost resistance of the repair layer of concrete showed that the modified concrete corresponds to the mark on water resistance W14 and the brand on the frost resistance F300. The developed technology of physico-chemical activation of the cement system allows the use of conventional cement for obtaining durable concrete of special purpose, which allows to reduce the cost of such concrete by 27-34%.

Keywords: modified concrete, cement system, sulphate resistance, frost resistance, durability

1 Purpose

Investigation of the operational properties of modified concrete of special purpose with determination of the possibility of use of the ordinary Portland cement for construction of structures operating under aggressive sulphate environment.

2 Methods

The research of operational properties of modified concrete with use of the infrared spectroscopy, X-ray diffraction, microscopic, differential-thermal and chemical methods has been carried out.

3 Scientific novelty

It was established that the polymeric component of the organomineral modifying complex changes the nature of the super-molecular structures in the activated cement system - at optimal filling, globules decrease in size preventing the phase surface diffusion, which contributes to increase of the waterproofness of modified concrete; it was established that at temperatures of 20-40 °C the polymer particles of the organomineral modifying complex with their functional groups interact with the surface organic substances of fine silica, which increases the activity of calcium silicates and hydrosilicate new formations, contributing to increase of

the strength of the cement matrix by activating the curing process in a binding system.

4 Practical significance

When introducing a modified cement system into the concrete mixture, the reduction of the open porosity to 3-5%, depending on the composition, has been achieved. Conducted tests for water resistance and frost resistance of the repair layer of concrete revealed that the modified concrete corresponds to the mark on water resistance W14 and the brand on the frost resistance F 300. The developed technology of physico-chemical activation of the cement system allows the use of conventional cement for obtaining durable concrete of special purpose, which allows to reduce the cost of such concrete by 27-34%.

5 Introduction

The durability of concrete and reinforced concrete depends on a large number of factors, the main of which are the conditions of operation, the type and composition of concrete, as well as the degree of aggressiveness of groundwater, the impact of which is under construction structures.

As it is known [1-2], the main reason for destruction of the bulk concrete in the contact zone with groundwater is the corrosion of the cement matrix of concrete. The reason for this is formation of calcium hydrosulphoaluminate,

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the interaction of lime with magnesium salts, as well as direct leakage of lime from concrete. The most destructive effect on concrete is exhibited by the sulphate corrosion, regardless of the composition and structure of concrete, the type of structures, the nature and magnitude of operating load and conditions of service. For current presentations of salts that are part of the aggressive medium, sulphates of various nature and concentration are the most dangerous for the cement stone. Destruction of the cement matrix of concrete in sulphate media is accompanied by formation of the three-sulphate crystals of calcium hydrosulphoaluminate. Crystallization of the calcium hydrosulphoaluminates causes destruction of the cement matrix due to a significant increase in the volume of the solid phase. According to Lee [3], this fact itself is enough to explain destruction of the cement stone.

Formation and destruction of calcium hydrosulphoaluminate is an important chemical process. The study of the mineralogical composition of the cement stone samples stored in a sulphate medium showed that a significant amount of SO_4^{2-} ions bind to cement stone, [4-6]. The more of the three-calcium aluminate (C_3A) is in the cement, the more of SO_4^{2-} ions binding, that is, absorption is sulphoaluminate.

In connection with the main destructive factors of the sulphate corrosion, methods for increasing the durability of concrete under the sulphate aggression have been developed. These include use of the sulphate-resistant cement, Portland cement containing (C_3A) content not more than 5% and a number of special cements; increase in the content of gypsum in the cement with a faster binding of aluminates in the plastic state; increase in the density of concrete; introduction of admixtures in concrete; use of the carbonate fillers [7-8].

Those methods aim to prevent or slow down diffusion of the sulphate ions into concrete, reduce the content of calcium aluminates or their timely reaction with certain components of concrete. Sulphate interaction should become a component part of processes associated with the structure formation of the cement matrix of concrete. It is not as much to protect the structure from penetrating sulphate water into the concrete or to reduce the content of (C_3A) in the cement, as to get the cement matrix in the concrete, where hydrosulphoaluminate will be instead of hydrated aluminate. The authors of [9-10] came to the same conclusion about the positive influence on the sulphate resistance of cement when introducing gypsum.

6 Results

To determine the possibility for increasing durability of the exploited reinforced concrete structures, studies on the weather resistance of modified concrete have been carried out. Modified concrete samples are characterized by a slight deformation throughout the test period. When modifying the cement system, the mass gain of samples is insignificant compared to the normal concrete. Modified

concrete in specific conditions of operation is guaranteed a fairly high atmospheric resistance. This is also confirmed by the stable values of material strength during the test. The mathematical model of processes of the corrosion resistance of concrete was obtained, for which the method of the experiment factor planning was used. The essence of the method is the variation of all the factors that influence the process on a certain plan, representation of the mathematical model in the form of a linear polynomial and the study of the last method of mathematical statistics. The data processing allowed derivation of an equation that relates the sulphate stability of the concrete with parameters of the aggressive medium (the content of sulphate ions) and the characteristics of the concrete itself (the content of C_3A in the cement, the quantitative content of the active complex in the concrete and the $CaCO_3$ in the fine aggregate). Using the mathematical model of the concrete corrosion resistance gives an opportunity to calculate the coefficient of sulphate stability and predict the durability of the reinforced concrete structures that are exploited under conditions of sulfate aggression.

For an estimate of the water influence on the microstructure of the modified cement system, an infrared analysis of the samples was carried out before and after keeping them in water for 6 months. It was established that changes occur in the region of absorption bands of 1380 cm^{-1} and 1450 cm^{-1} . Introduction of the polymer component of the organomineral modifying complex (OMMC) into the cement system changes the nature of the super-molecular structures - at optimal filling globules decrease in size. An increase in diameter of the super-molecular structures can lead to development of micro porosity. The presence of micro cracks and defects leads to the fact that, along with activated diffusion, there is a phase surface diffusion, which leads to an increase in permeability [11-13].

The organomineral modifying complex consists of a plasticizer, an active mineral component and a chemical structure-optimizing agent. Amorphized silica with a specific surface area $1100\text{ m}^2/\text{kg}$ was chosen as the active mineral component. The peculiarity of the chemical optimizer of structure formation is its ability to stabilize the crystal formation of the cement matrix, being a structural and chemical analogue of the mass of the crystalline hydrates. Surfactant OMMC changes the relaxation processes, promotes creation of the less stressed and defective structures and prevents appearance of the phase diffusion. In addition, creation of a monolayer SAA on the surface of a mineral modifier in the form of a microfiber leads to emergence of the "surfactant-mineral microfiber" in contact with mobile (less rigid), easy to regenerate bonds, which positively affects adhesion of the polymeric component to the surface of a mineral modifier.

During the operation of special structures, their surface is exposed to stretching and compressing stress [7, 14]. To determine the possibility of increasing durability of used reinforced concrete structures, studies of atmospheric

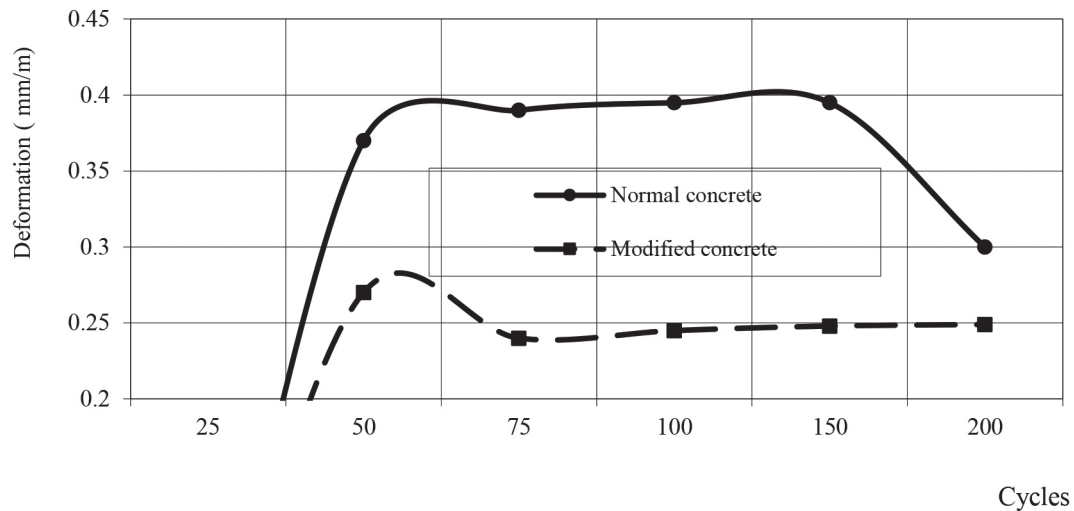


Figure 1 Change of linear deformations of concrete at alternating water saturation and drying (Portland cement PCI-400-P-H)

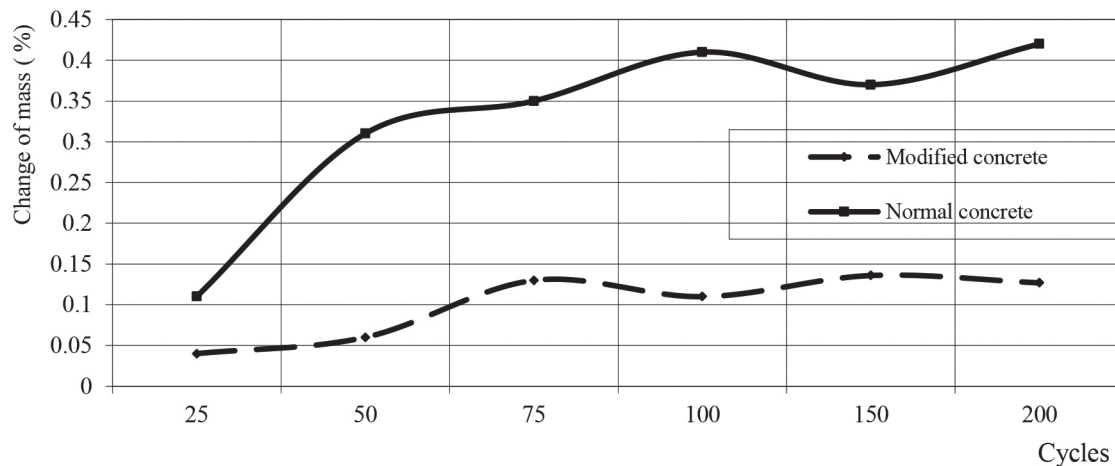


Figure 2 Change of mass of concrete samples at alternating water saturation and drying (Portland cement PCI-400PH)

stability of the modified concrete samples have been carried out using the following procedure.

Samples of the fine-aggregate concrete of size $4 \times 4 \times 16$ cm with $W/C = 0.5$ were made. After 28 days of hardening, three samples of each batch were dried at a temperature of 80 °C to constant weight, after that they were tested for bending and their halves were compressed. In the end, faces of other samples of all batches strictly centered rappers based on epoxy were fixed. The samples were then placed in a thermostat and dried at 80 °C for 15 h. Subsequently, after 1 hour of natural cooling the samples were weighed and with the help of engineers' dial gauge with a price of 0.0001 mm their initial length was measured. After that, the samples were immersed in fresh water for 7 hours at a temperature of 20 °C, they were taken out from water, wiped with a damp cloth, weighed and their length was measured. Samples were tested up to 200 cycles of water saturation and drying. After each 50 cycles testing, the three samples were taken, dried to a constant mass and tested for bending and their halves were compressed. The expending values in mm/m were determined in comparison to the length of samples of the same cycle after their drying.

The results of research on the influence of alternating water saturation and drying of concrete samples are shown in Figures 1 and 2. Experiments revealed that linear changes in samples depend on the composition of concrete. Modified concrete samples are characterized by the low deformability throughout the test period (see Figure 1). Similar character of the weather resistance of modified concrete was also observed with respect to change in the mass of the test samples. It should be noted that when modifying the cement the weight gain of the samples is insignificant in comparison to the normal concrete (see Figure 2). The mass increase of samples of the normal concrete is accompanied by an increase of irreversible deformations, apparently due to water absorption in the presence of open porosity.

The mass loss of samples with alternating water saturation and drying is observed for all the samples; however, for the modified concrete this process is not extreme. Obviously, this can be explained by the more dense structure of the modified cement matrix of concrete.

As it follows from the results of experiments (see Figures 1, 2), a fairly high atmospheric resistance is

Table 1 The strength of modified concrete after alternating water saturation and drying (Portland cement PC-I-400P-H)

Type of concrete	Strength (MPa) after alternating water saturation and drying (cycles)							
	50		100		150		200	
	Compression	Bending	Compression	Bending	Compression	Bending	Compression	Bending
Normal	32.4	4.6	27.6	4.1	-	-	-	-
Modified	67.3	8.7	67.4	8.4	66.1	7.6	64.6	7.1

guaranteed for the modified concrete in specific conditions of operation. This is also confirmed by the stable values of material strength during the test. For the normal concrete there is a decrease in strength both during compression and bending. Standard samples began to collapse after 127 cycles of alternating water saturation and drying, while samples of modified concrete were in satisfactory state up to almost 200 cycles, after which the tests were stopped. Results of determining the strength of concrete throughout the duration of experiments alternating water saturation and drying are given in Table 1.

When the water content of the concrete is lower than the boundary, determined in each case by the peculiarities of the materials and the state of the cement matrix, the material becomes permeable. On the other hand, the waterproofness of concrete with permanent composition decreases with increasing its water content. In this case there is no explanation for the reasons for reducing the waterproofness of the concrete. According to [8], with an increase in W/C from 0.45 to 0.8, the permeability of concrete increases by 100 times. The authors of [2, 7] found that when using the Portland cement, the coefficient of filtration of the cement stone increases by 10-20 times with an increase in W/C from 0.4 to 0.8. It is also argued that the main reason for reducing the waterproofness of concrete is the increase of its initial water content. A number of experts explain this by influence of reducing the cement content [7, 9, 15].

Considering the significant influence on formation of the structure of waterproof concrete by contraction processes, as well as considering solidifying concrete as a single system, it is most likely to assume that the primary effect on the waterproofness of concrete is the value of the cement paste W/C . It is known that with increase of the W/C the quality of the cement paste decreases, destructive processes intensify in it, as a result of which a powerful system of pores and capillary channels is created in the material [6].

When modifying the cement system, the reduction of the open porosity of concrete to 3-5%, depending on the composition is acquired. Conducted tests on the waterproofness of concrete established that the modified concrete corresponds to the waterproof mark W 14.

In the aggregate of results of studies on the waterproofness of concrete, it can be concluded that influence of the modified concrete composition on fluctuations of the water resistance is expressed not so sharply, as for normal concrete.

Taking into account the operation of the elements of concrete and reinforced concrete structures in conditions of variable water level, they are subjected to alternate freezing and thawing under conditions of capillary suction. Therefore, concrete, designed for building and restoration of special structures, should have the high frost resistance.

Modern ideas about causes and mechanism of destruction of the concrete under the influence of moisture and frost come to the following, [16-17]: concrete is considered as a capillary-porous body, the structure of which is defined both by its components and technological parameters - conditions of preparation, placing, compaction, hardening and storage. The distribution of moisture and its total amount in concrete depends on both the nature of its structure and the environmental conditions.

Under the influence of negative temperature on a capillary-porous material containing moisture, there are its own temperature deformations, which are imposed by deformation of ice, formed from the water frozen in the pores. The magnitude and sign of the resulting deformation, which determine the state of the system, are variable quantities and depend on the conditions of the external environment and the nature of the concrete structure.

Alongside with studies of the frost resistance, the X-ray diffraction and differential-thermal analysis of the cement matrix of concrete have been carried out. As follows from defectograms, the composition of new formations in the cement stone of normal concrete is somewhat different from the same composition of modified concrete. In conventional concrete, the three-sulfate form of calcium hydrosulphoaluminate ($d = 9.73; 5.61; 3.85 \cdot 10^{-10} m$), C_3AH_6 ($d = 4.45; 2.30; 1.572 \cdot 10^{-10} m$) ($CaOH$)₂ ($d = 4.91; 2.61; 1.79 \cdot 10^{-10} m$), hydrosilicates of calcium are of increased basic capacity ($d = 4.91; 2.61; 1.79 \cdot 10^{-10} m$). As part of the new formations of modified concrete the formation of four-calcium hydroaluminate ($d = 7.8; 3.85; 2.43; 1.67 \cdot 10^{-10} m$) was marked, as well as recrystallization into a mono-sulphate form of calcium hydrosulphoaluminate ($d = 8.92; 4.96; 3.99; 2.25 \cdot 10^{-10} m$), which obviously contributes to increasing the frost resistance of the modified concrete.

The data of the differential-thermal analysis confirm the results obtained during the radiographic studies. The endo-effect with a maximum of 132 °C on a thermogram of the cement stone of normal concrete, subjected to a frost resistance test, corresponds to dehydration of the three-sulphate form of calcium hydrosulphoaluminate and calcium

hydrosilicates. Temperatures of 440 to 445 °C correspond to the decomposition of $(CaOH)_2$, while the effect for the modified cement matrix is less noticeable. At temperatures 586, 698, 716 °C, the low-basic hydrosilicates of calcium type $CSH(B), C_2SH_2$ are dehydrated. The endo-effects at temperatures of 690 and 710 °C for conventional cement are also responsible for expansion of $CaCO_3$, although calcium carbonate is released in small amounts.

Thus, the composition of cement and the structure of additives determine the nature of the interaction with the aluminate and silicate components of cement. The ability to preferentially localize on the surface of the aluminate components has additives that do not react with Ca^{2+} , but contain functional groups that give complexes with Al^{3+} , as well as insoluble products of the interaction of polyelectrolytes with Ca^{2+} , if they contain free polar active groups, which are fixed on hydroxylate surface of hydroaluminates and calcium hydrosulphoaluminates.

Formation of hydrosulphoaluminates during the precipitation on the lime quickly fades due to the surface shielding by hydrated films. The generated coagulation structures do not compact much in the first stages of hydration. The high adsorption capacity of the polymeric component of the OMMC containing amido groups in relation to the products of hydration of Portland cement clinker, and especially to calcium hydroaluminates, results in the rapid formation of loose moisture coagulation structures in the modified cement system, which causes avalanche growth of initial strength.

The high-molecular SAA change the conditions for formation of the phase contacts in the emerging structure. When localized in the contact zone, aliphatic macromolecular SAA increase and aromatic reduce the bond strength of hydrate-hydrate and hydrate-carrier or hydrate-hydrate, which affects the integral strength of the structure [5].

Speaking about selective adsorption of the SAA on clinker minerals and hydrated phases, one cannot but note that many researchers, characterizing and assessing the effectiveness of the SAA, assign great importance to the value of the ξ -potential on the surface of solid-phase particles [18]. For cements of different mineralogical composition, the ξ -potential values are different and this should be reflected in plasticization of suspensions.

The study of processes of the corrosive destruction of concrete proceeding under the influence of aggressive groundwater containing sulphate ions allowed to consider and determine the nature and degree of destruction of the reinforced concrete structures, depending on various parameters of the aggressive medium, properties of the concrete itself and the conditions of its testing.

The influence of the type of cement, the quantitative and qualitative content of the organomineral modifying complex and the concentration of sulphate ions in the environment on the stability of concrete were studied under conditions of one-sided and comprehensive influence of the aggressive medium on the samples. Based on the

experimental data array a statistical mathematical model of the investigated process was constructed.

To obtain a mathematical model of processes of the corrosion resistance of concrete, the method of factor planning of the experiment was used, the essence of which consists in variation of all the factors influencing the process according to a certain plan, the representation of the mathematical model in the form of a linear polynomial and the study the latter by the method of mathematical statistics.

The general form of the statistical mathematical model, in this case, is expressed by a linear polynomial

$$Y = b_0 + b_1x_1 + \dots + b_nx_n, \quad (1)$$

where:

b_0 is a constant term,

b_1 is a linear effects ($s = 1, 2, \dots, n$),

n is a number of factors.

Y The coefficient of sulphate stability is chosen as the outcome variable Y . According to the results of previous studies the following factors have the most significant effect on concrete corrosion:

x_1 is C_{3A} content in Portland cement,

x_2 is a content of sulphate ions in the aggressive environment,

x_3 is as content of particles of $CaCO_3$ in the sand,

x_4 is a quantitative content of the active complex.

Application area of these factors, taking into account the data of previous experiments, is determined by the following limits: $5 = x_1 = 8$; $2 = x_3 = 10$; $1 = x_2 = 20$; $10 = x_4 = 50$.

For convenience, the parameters that correspond to each value of the experimental data were chosen. The principle of correspondence between the experimental data and parameters is as follows: the increasing value of the experimental data must correspond to the greater value of the parameter. Moreover, if the experimental data are in a clearly defined group of specific data, then this source code corresponds to the group code. By increasing or decreasing the value of the parameter, it is possible to determine how the value of the experimental data increases or decreases and how it affects the sulphate stability coefficient K_c .

The data processing allowed to derive an equation that relates the sulphate stability of the concrete with the parameters of the aggressive medium (the content of sulphate ions) and the characteristics of the concrete itself (the content of C_3A in the cement, the quantitative content of the active complex in the concrete and the $CaCO_3$ in the fine aggregate):

$$Y = 0.9552 - 0.3438 \cdot 0.1x_1 + 0.6292 \cdot 0.1x_2 - 0.1709 \cdot 0.1x_3 + 0.71x_4 \quad (2)$$

The test for adequacy has shown the good convergence of model results. Deviation of the calculated value of from the experimental one, does not exceed $\Delta K_c = \pm 0.1$ in the

whole range of test conditions. Translated into physical scale, equation (2) takes the form:

$$K_C = 0.9552 - 0.3438C_3A + 0.6292CaCO_3 - 0.1709SO_4 + 0.71AK. \quad (3)$$

The active influence on the sulphate stability coefficient of concrete samples is made by the active complex (x_d); the following influence, by value, is the content of $CaCO_3$ in the fine aggregate. The minus sign indicates the reversal of the dependence of sulphate resistance on the content of C_3A in the cement.

Using the mathematical model of the concrete corrosion resistance gives an opportunity to calculate the coefficient of sulphate stability and predict the durability of reinforced concrete structures that are exploited under conditions of sulphate aggression.

7 Conclusions

A. When maturing samples of concrete in a sulphate medium for 360 days, the reduction of strength of the modified concrete is 3-6% (reduction of the strength of normal concrete is 12-23 %), the coefficient of sulphate resistance K_C is within 0.91-0.93. Stabilization of the strength of modified concrete with time indicates the prevailing of constructive processes over destructive.

B. The mathematical model of corrosion resistance processes is obtained. The processing of the data allowed to derive an equation that relates the sulphate stability of the concrete with the parameters of the aggressive medium (the content of sulphate ions) and the characteristics of the concrete (content of C_3A , cement, $CaCO_3$ in the fine aggregate, degree of modification of the cement system). The test for adequacy has shown the good convergence of the model results. Deviation of the calculated value of K_C from the experimental one, does not exceed $\Delta K_C = \pm 0.1$ in the whole range of test conditions.

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