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REGULATION OF POROSITY OF FINE-GRAINED CONCRETES WITH A MIXTURE OF CARBONATES AND SURFACTANTS

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Abstract. *The purpose of the work is the theoretical justification of the mechanism of water structuring using the effect of hydrophilic hydration on the example of using a polycarboxylate superplasticizer as a nanomodifier. To achieve the goal, the following tasks were set: to conduct experimental studies of the mechanism of influence of colloidal hydrophilic surfactants on the structure of water. The paper presents the results of theoretical studies of the influence of colloidal hydrophilic surfactants on the structure of water and the mechanism of Portland cement hydration. It is shown that the introduction of these surface-active substances into water in very low concentrations leads to the effect of hydrophilic hydration, that is, changes in the interaction between water molecules. Hydrophilic hydration in water contributes to the formation of the porous structure of concrete. It was established that hydrophilic hydration is characterized by the fact that part of the dissolved substance inhibits the translational movement of water molecules and is associated with the fact that part of the solution space, corresponding to the own volume of the dissolved substance particles, is oversaturated with water molecules. Hydrophilic and hydrophobic hydration have different mechanisms. Large hydrophilic ions cause ordering of the water structure. Having a more ordered structure than pure water, solutions of these substances require less work for dissolution, as a result of which the solubility of the latter increases. The conducted experiments make it possible to draw an unequivocal conclusion that polar groups are not capable of hindering hydrophilic hydration. The introduction of molecules of hydrophilic surfactants in the form of dimers into water leads to the structuring of water, that is, the formation of a continuous fractal network of water molecules.*

Key words: *fine-grained concrete, Portland cement, hydration, modification, surfactant, water activation*

Introduction.

Concrete production is one of the most important components of the construction industry, which significantly affects the development and functioning of other components. High-quality concrete is one of the main factors in the industrial development of society and its material growth. According to preliminary estimates, the need for concrete for the restoration of damaged civilian and industrial facilities will more than double. Concrete is one of the most important building materials that is widely used in modern construction. However, over time, its nutritional properties may deteriorate, which leads to a decrease in the quality of construction work. Therefore, it is important to know the possible ways that can lead to the prolongation of the preservation of the established consumable properties of cement

Problem statement and its connection with the most important scientific and practical tasks. According to H. Taylor's definition, composite Portland cements are a hydraulic binder consisting of grinding products of Portland cement clinker, additives that regulate the technological properties of cement dough and one or more mineral additives. The most important of them are blast furnace granular slag, removal ashes, natural pozzolans, trepel, opoka, microsilica. As mineral additives in Portland cements, waste from many industries can be used, or dump rocks formed in quarries during the opening of the main cement raw materials. In the domestic literature, such Portland cements were called multicomponent or mixed.

Artificial stone, which is formed during the hardening process of cement, is a capillary-porous body. That is, its volume is permeated with a network of pores of different sizes. Through these pores, components of an aggressive environment penetrate deep into the cement (concrete) stone, which lead to its destruction. Therefore, the solution to the issue of regulating the porosity of concrete, in particular fine-grained concrete, is quite relevant

Analysis of recent research and publications.

A large number of studies are devoted to the study of the properties of composite Portland cements and their influence on the quality of the resulting concretes [1-7].

It is believed that filler additives are also involved in chemical processes occurring during the hydration and hardening of cements, but their interaction with cement hydration products is very slow, so their effect on cement properties is limited, mainly, by improving its grain composition [8]. These additives include natural ones. calcium and magnesium silicates (wollastonite, diopside, rankinite, dunite), as well as calcium and magnesium carbonates (limestone, dolomite, dolomitized limestones, chalk).

Making cement from several main components makes it possible to optimize the properties of cement by exploiting the strengths of individual components and inhibiting their shortcomings. In addition, it gives the manufacturer a high level of flexibility in the choice of material, the content of individual components, as well as in the choice of cement grinding technology and parameters of the mixing process of components. Thus, in the work [7], the influence of microstructure on the physical properties of concrete made by replacing part of the fine aggregate with mineral powder was studied. The caution shown by cement producers when mastering the production of composite Portland cements is primarily explained by the poor study of the combined effect of several simultaneously introduced mineral additives on the properties of cements.

The question of the active participation of carbonate additives in the chemical processes occurring during the hydration of composite Portland cements is still debatable. Usually, these additives are classified as fillers. With their possible interaction with the hydration products of clinker minerals, the above hydrate phases cannot be formed, until only the possibility of interaction of CaCO3 with calcium hydroaluminates with the formation of calcium hydrocarboaluminate of the composition $3CaO\cdot$ is reliably established. $Al_2O_3\cdot CaCO_3\cdot 12H_2O$ [8]. According to the authors, hydrocarboaluminate crystallizes in the form of hexagonal plates, which rapidly increase in size and turn into crystalline growths that form dense accumulations on the surface of cement and calcium carbonate particles, providing increased bonding strength.

In the paper [9] the effect of the addition of limestone on the mechanisms of calcium leaching in cement-based materials is investigated, in the work [9] – the durability of concrete with the addition of limestone powder is investigated, in the work [10] – the hydration of C_3A in the presence of Ca $(OH)_2$, $CaSO_4{\cdot}2H_2O$ and $CaCO_3$ is investigated.

Only in the work [11] the physicochemical properties of aqueous suspensions of microfillers with superplasticizers were investigated. Where carbonates were used as microfillers, but the formation of porosity of cement stone was not studied.

Taking into account the results of the work [12], it was investigated to ensure the uniformity of the strength of fine-grained concrete based on modified composite cement, which contained carbonates and a superplasticizer [11], but the formation of porosity of cement stone was also not investigated.

The purpose and objectives of the work: to determine the effect of the carbonate component and the superplasticizer on the porosity of cement stone (fine-grained concrete). To achieve this goal, it was necessary to solve the following tasks: to determine the influence of the carbonate component on the porosity of fine-grained concrete; to determine the effect of the superplasticizer on the porosity of fine-grained concrete.

Materials and methods of research.

The methodology of the study was based on theoretical and empirical methods based on experiment, comparison, generalization, system approach, mathematical modeling, planning and processing of experimental results. The work was carried out using the system-structural approach of construction materials science "composition - structure - properties". Experimental studies were carried out on laboratory samples manufactured and tested on certified equipment in accordance with the current regulatory documents of Ukraine using standard test methods.

The study was carried out using cement SEM II/B-S 400 of Kryvyi Rih Cement PJSC, containing 35% of blast furnace granular slag, and modifiers – hyperplasticizer of organic origin Sika Plast-520, chalk. As a fine aggregate for testing fine-grained concrete, polyfraction river Dnieper sand was used. The ratio of fine aggregate to cement (by weight) was 3:1.

The components of the concrete mixture were moistened to the humidity determined by the experiment plan and the mass was mixed for 4 minutes. The superplasticizer was injected with an aqueous solution at the rate of Sika Plast-520 - per mass of cement. Experimental samples with a side size of 40x40x160 mm were made by vibration molding, some of which, after hardening in air for 3 days, continued to harden in air, and the other part in water.

An indirect assessment of the effect of modifiers on the kinetics of cement hardening at a water-cement ratio (V/C) of 0.5, 0.55 and 0.60 was carried out based on the results of determining the curing time on the Vika device. Determination of the effect of modifiers on the hardening of cement stone in the early stages was carried out on cement samples with V/C 0.5, 0.55 and 0.60. The main indicators of the properties of concrete samples determined in the experiment were chosen: compressive and bending strength. Determination of these indicators was carried out according to the methodology of the relevant State Standards of Ukraine/

To simplify and clarify the processing of results, the strength and porosity of concrete were converted into relative units (%).

Research results.

The results of determining the porosity of cement concrete samples at the early stages of hardening with V/C = 0.50–0.60 are presented in Fig. 1 and Fig. 2.

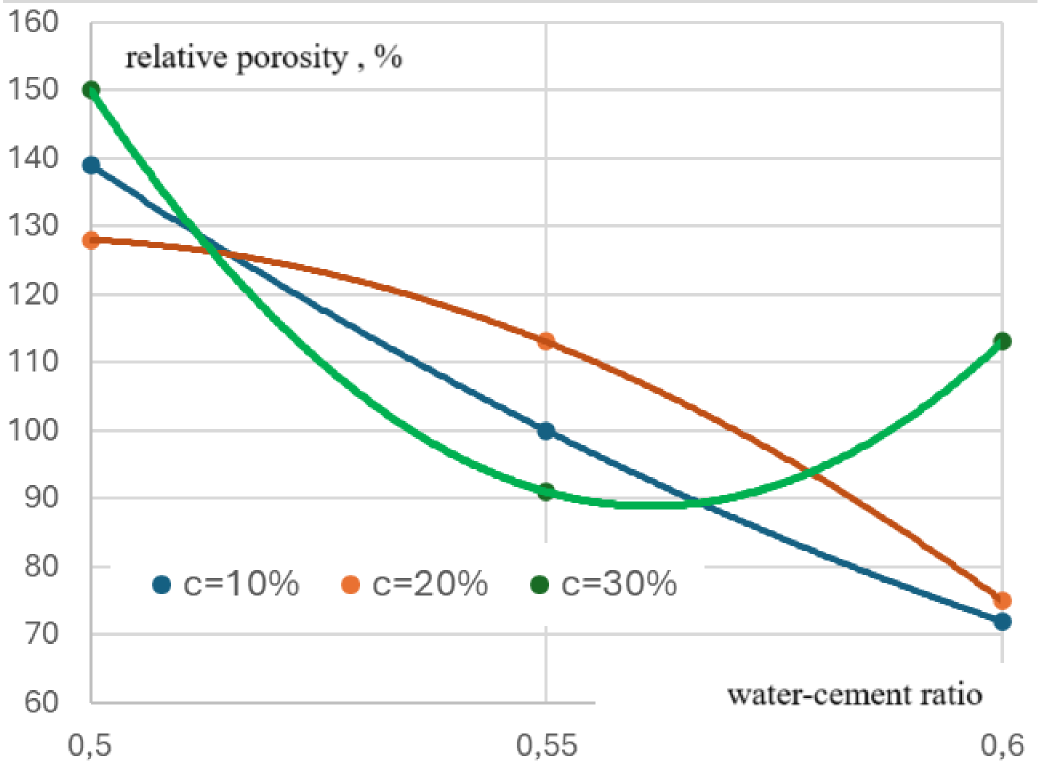

Figure 1. The effect of the water-cement ratio on the porosity of concrete (c – calcium carbonate content)

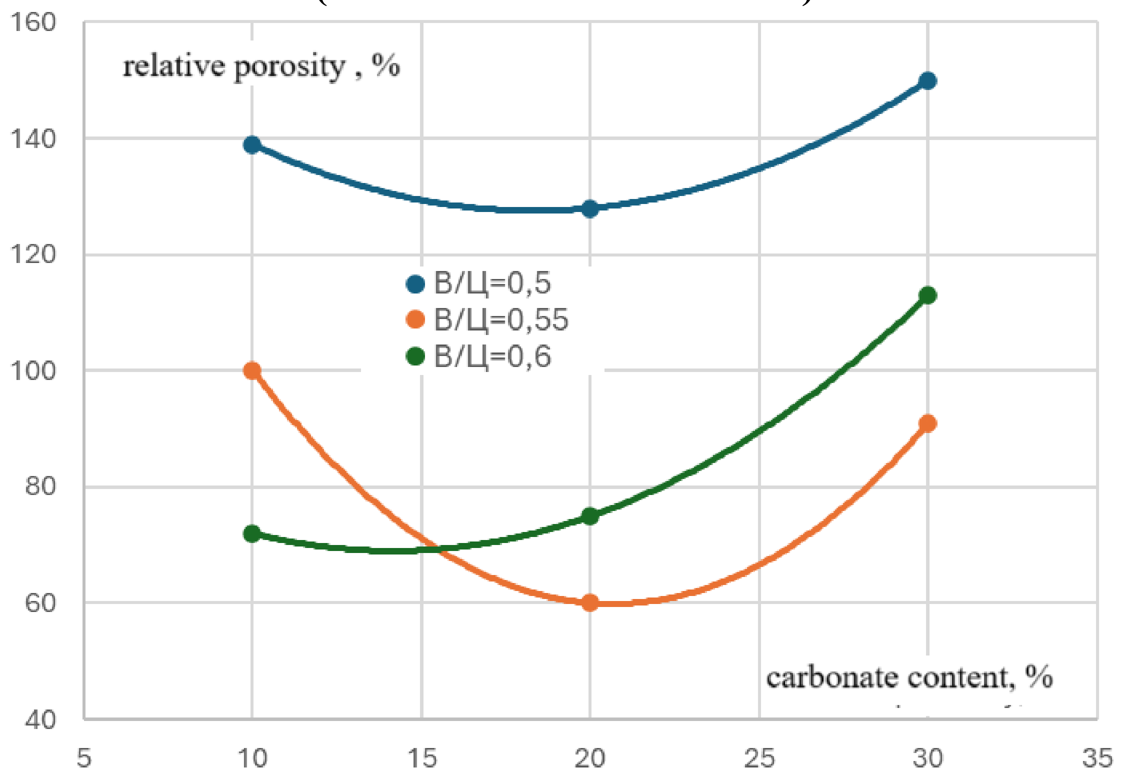

Figure 2. The effect of the water-cement ratio on the porosity of concrete (V/C – water-cement ratio)

It should be noted that, as the results of experiments show, the degree of influence of calcium carbonate on the porosity of concrete depends on the value of the water-cement ratio. Within the framework of the experiment (with a water-cement ratio of 0.5 to 0.6), the dependence of the magnitude of the porosity of concrete on the concentration of the modifier (carbonate) has a form close to a parabola. At the same time, there is a minimum value of porosity at a concentration of the modifier (carbonate) of about 20%. However, in most cases, the porosity remains greater than the porosity of concrete without carbonate.

The indicated optimal value of carbonate content coincides with the results of determining the effect of the carbonate modifier on the strength of concrete [11], which also has the form of a parabola, which has a maximum value of concrete strength at a modifier concentration of 20%.

The introduction of a surfactant into the "Portland cement – carbonate" system, which ensures the flow of hydration of the hydrophilic type [12], leads to a significant decrease in the porosity of concrete (Fig. 3).

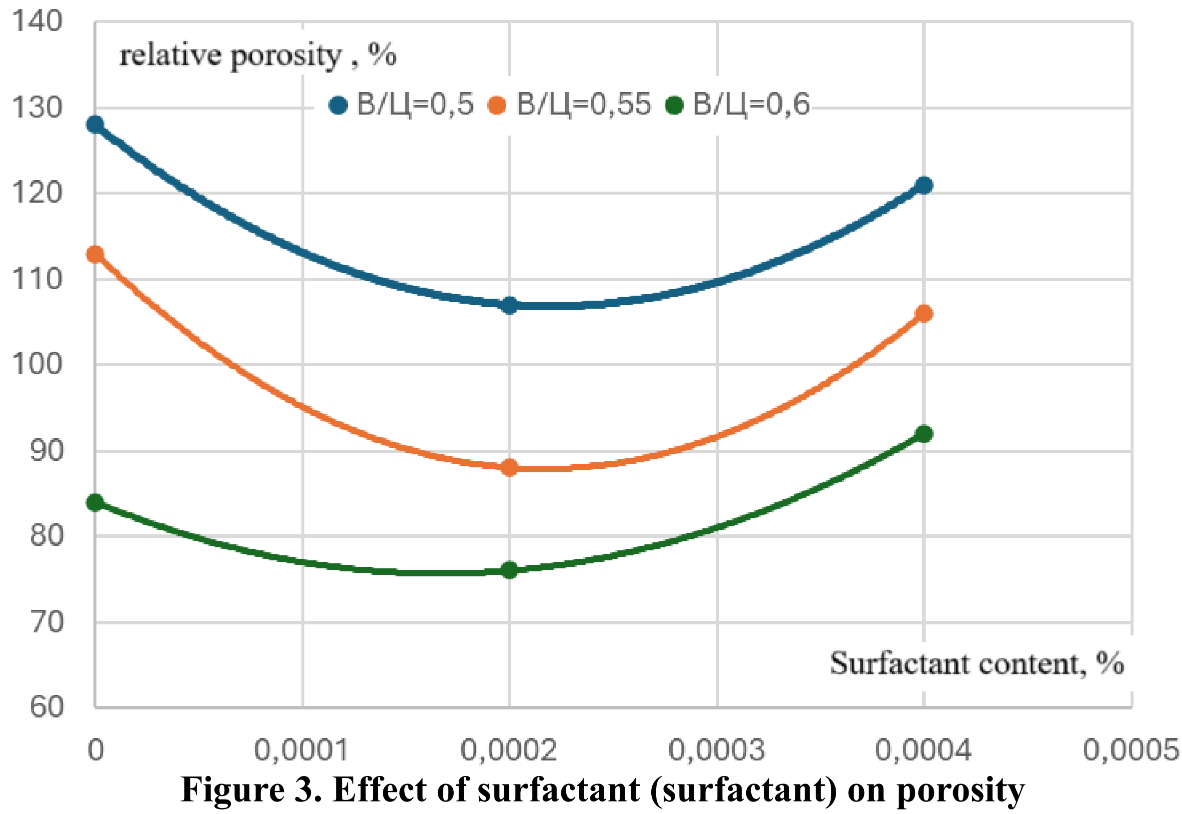

Figure 3. Effect of surfactant (surfactant) on porosity fine-grained concrete, which contains 20% calcium carbonates

Based on the results obtained, the theoretical model of the initial phase of the interaction of cement with structured water can be presented as follows. In the process of cement hydration, one problem arises – the lack of water for hydration at values of W/C, which does not exceed a certain value of $[W/C]_m$ (under experimental conditions $[W/C]_m$ – less than 0.55). the formation of evenly distributed pores in the cement stone, into which the resulting Portlandite and ettringite migrate. As a result, the structure of cement stone is formed with a high content of high-strength, low-basic calcium hydrosilicates. This leads to an increase in the strength of the cement stone by almost 2 times [11]. The difference between the "cement particle – structured water" system is that when its reactants collide, water molecules (respectively, protons) are actively absorbed by the hyperamorphized layer of the cement particle. Protons penetrating the amorphized layer of the cement particle have abnormally high mobility and high penetration and bind strongly to electronegative oxygen atoms and form hydroxylions. The appearance of active Ca^{2+}, $(SiO4)^{4-}$, H_3O^+, OH^- and others, their fleeting interaction is the reason for the increase in the strength of concrete at $W/C > [W/C]_m$, despite the increase in its porosity. Since protons from water molecules on the surface migrate into the original cement crystal, calcium atoms move in the opposite direction and, to a lesser extent, silicon outside into solution through hydration products.

The inability to remove all the questions that have arisen within the framework of this study determines the direction of further research. They, in particular, should be focused on identifying the composition of neoplasms in the process of hydration of the "Portland cement – water modified in the process of hydrophilic hydration" system.

Conclusion.

Water activation by the use of the hydrophilic hydration mechanism significantly affects the change in the nature of the processes of hardening and structure formation of fine-grained concrete. The peculiarities of the formation of the structure of fine-grained concrete, which is obtained on the basis of water activated by the use of the hydrophilic hydration mechanism, are the ambiguous effect of the amount of water modifier on the porosity of concrete. Separately, it should be noted that the experiments carried out confirmed the main provisions of the theory of ultra-low concentration, which has not yet

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