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FORMATION OF THE STRENGTH OF FINE-GRAINED CONCRETE BASED ON MODIFIED SLAG PORTLAND CEMENT

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The object of research is fine-grained concrete on slag Portland cement. Owing to the significant content of metallurgical industry waste in its composition, slag Portland cement belongs to ecologically acceptable products. However, the insufficient rate of formation of its structure and, as a result, the main quality indicator, which is compressive strength, limits the field of use of slag Portland cement. Therefore, in the studies, the goal was to increase the speed of formation of the strength of fine-grained concrete made on slag Portland cement. The studies of the influence of modification of slag Portland cement with water, activated by the use of the hydrophobic hydration mechanism, established the factors affecting the speed of formation and the value of compressive strength of fine-grained concrete made on slag Portland cement. It has been proven that these factors include the type and amount of applied water nanomodifiers, as well as the type and amount of fine concrete aggregate. The analysis of the study results confirmed that the introduction of water activated by the mechanism of hydrophobic hydration into concrete in ultra-small doses significantly increases the rate of formation of concrete strength. Given this, the strength of the resulting modified fine-grained concrete based on slag Portland cement at the age of 2 days exceeds the strength of the similar concrete without additives by 60 %, and at the age of 210 days – by 25 %. This allows us to assert the effectiveness of the identified mechanism of modification of slag Portland cement. Thus, there are reasons to assert the possibility of targeted regulation of the processes of forming a strong structure of fine-grained concrete based on slag Portland cement by using water activated by the mechanism of hydrophobic hydration

Keywords: fine-grained concrete, Portland slag cement, hydration, concrete modification, surfactants, water activation

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1. Introduction

Concrete is one of the most popular and widespread materials used in the construction of houses, residential and non-residential structures. It has sufficient strength at a relatively low cost. The basis of concrete is cement, the production of which consumes a significant amount of natural materials and energy. Of all types of cement, slag Portland cement is characterized by the lowest consumption of natural materials and the lowest energy consumption.

Slag Portland cement, containing up to 50 % of slag, is usually used under the same conditions as ordinary Portland cement. Cements containing the maximum content (up to 80 %) of slag are low-temperature and are used in massive hydraulic structures, for the manufacture of structures exposed to the action of aggressive waters.

But in slag Portland cement, the process of strength gain at the moment of the start of solidification of materials is significantly slower than in Portland cement. Slag Portland cement attains a strength close to that of cement after 6–12 months, depending on the temperature and humidity conditions of solidification. After some time, slag Portland cement shows significantly greater strength than Portland cement.

The grinding fraction of slag Portland cement affects its strength, activity, as well as the time of solidification of the finished mixture. Thus, the finer the grinding, the faster the solution hardens and gains strength, so the effect of grinding on the properties of cement is limited, mainly, to the improvement of its grain composition [1]. However, this technological technique causes an increase in the cost of cement.

Considering the effect of surface-active substances applied in ultra-low concentrations [2], research aimed at further improvement of concrete technology based on composite Portland cements containing granulated slag is relevant.

2. Literature review and problem statement

Paper [2] reports the results of studies into the influence of water modified by the use of hydrophilic hydration mechanisms on the speed of formation of the strength of fine-grained concrete on Portland cement. It is shown that the use of water modified in this way leads to a significant increase in the speed of formation of the strength of the specified concrete.

Since slag Portland cement has a lower rate of formation than Portland cement, the use of water modified by the use of hydrophilic or hydrophobic hydration mechanisms is more appropriate for it than for Portland cement. But such studies were not carried out.

This gives reason to assert that it is appropriate to conduct a study to investigate the influence of water modified by the mechanism of hydrophobic hydration on the speed of formation of the strength of fine-grained concrete on slag Portland cement.

The amount of water added to cement during the preparation of concrete is much greater than that required for its chemical binding in products of hardening of the binder. Excess water evaporates, leaving pores, which increases the porosity of the cement stone and increases its permeability to aggressive environments, thus reducing stability and durability. Therefore, increasing the density of cement stone may involve a method for reducing the amount of water that evaporates in cement stone and concrete.

One of the ways to reduce the amount of water that evaporates from concrete is the use of so-called new generation concretes, in particular on various types of binders with low water consumption [3, 4]. But the question of their durability remains unresolved due to the fact that the hydration of Portland cement does not occur to the full extent. Another type of concrete of the new generation is obtained with the use of nano additives of various types. For example, in work [5], "nanodiamonds" and powders of oxides of metals Ti, Al, Ca, Mg, silicon and metals W, Co were used as nanomodifiers of concrete in the research. But the research was conducted on Portland cement. In work [6] micro silica and crushed chalk were used as concrete nanomodifiers, but the research was conducted on Portland cement. Work [7] used a mixture of mineral dispersion systems of man-made origin, which have d-elements in their composition, but research was also carried out on Portland cement or complex modifiers of various types [8]. But the production of these concretes is hindered by the difficulty of uniform distribution of nano-additives in the volume of concrete. Therefore, such concretes have high strength at an early age, but high heterogeneity of properties. The above-mentioned disadvantages of new-generation concrete prevent its widespread use.

It is obvious that the more water during cement hardening is bound into stable, strong minerals, the less is the shrinkage of the cement stone and the higher its density and, therefore, its strength. This is consistent with the conclusion drawn in [3] that it is better to use those binders for concrete whose hardening is accompanied by a strong stable binding of the maximum amount of water with moderate contraction. This position is confirmed by the data given in [4] that when aluminates are converted into more complex forms, a significant decrease in the concentration of defects in the cement stone structure is observed.

Under certain conditions (introduction of calcium carbonates or calcium chlorides into the system of hardening Portland cement compositions), in the process of hydration of calcium aluminates, according to [9], calcium carbo- and chloroaluminates of the type of calcium monocarboaluminates and calcium monochloroaluminates can be formed. However, these minerals are not very stable and decompose at temperatures above 343 K.

But not only aggregates consisting only of carbonates have an effect on the properties of concrete. Thus, the iron ore rocks of the Kryvyi Rih deposit contain iron carbonate, which increases the strength of concrete when these rocks are used as a fine aggregate [9]. Work [10] also gives the results of concrete studies with different options for using the specified rocks. However, research is limited to the use of Portland cement.

Work [11] provides the results of studies of the "Portland cement-water-surfactant" system. It is shown that the rate of formation of certain new formations is determined by the mineralogical composition of Portland cement. In [12], it was also shown that the rate of formation of the concrete structure depends on the compatibility of plasticizers with Portland cements of different composition. The disadvantage of these works is the use of only one type of cement – Portland cement, as well as a significant content of plasticizers. As shown in [13], the use of surfactants in ultra-small doses to change the structure of water can be an option to overcome these shortcomings. This is the approach used in work [14], where it is shown that the strength of concrete increases when the structure of water is changed due to hydrophobic hydration, and in [15], it is due to hydrophilic hydration.

Despite the practical significance of the results reported in the above works, the kinetic regularities of the processes of forming the strength of concrete with the use of surfactants applied in ultra-small doses have not been sufficiently considered.

In addition, the concretes, the research results of which are given in the listed works, were obtained and studied using Portland cement, which has a high cost, which determines the high cost of its products. In addition, the production of Portland cement significantly affects the environment due to the significant use of natural resources and energy. The production of slag Portland cement, due to the significant content of metallurgical production waste in the composition of cement, has a much smaller impact on the environment.

Therefore, insufficient determination of the effect of surface-active substances introduced in extremely low concentrations on the speed of formation of the strength of fine-grained concrete based on slag Portland cement predetermines the expediency of research into this area.

3. The aim and objectives of the study

The purpose of this study is to determine the influence of water modified due to hydrophobic hydration on the rate of formation of the properties of fine-grained concrete based on slag Portland cement

To achieve the goal, the following tasks were set:

– to determine the influence of hydrophobically modified water on the change in the rate of formation of the compressive strength of fine-grained concrete based on slag Portland cement at different values of the water-cement ratio;

– to determine the effect of hydrophobically modified water on the change in tensile strength during bending of fine-grained concrete based on slag Portland cement.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of our study is fine-grained concrete on slag Portland cement.

The main hypothesis of the research assumes that the modification of the water structure by the mechanism of hydrophobic hydration will contribute to the increase in the speed of formation of the strength of fine-grained concrete on slag Portland cement.

The work assumes that the "Theory of ultra-small concentrations" is valid for the system "Portland cement slag-water-fine aggregate".

4. 2. Materials and equipment used in the experiment

Our research was carried out using cement ShPC III/A-400 PrJSC "Heidelbergcement Kryvyi Rih" (Ukraine), which contains 75 % of blast furnace granulated slag, and a modifier – sucrose hydrocarbon, which causes a modification of the water structure by the mechanism of hydrophobic hydration. Polyfractional Dnipro river sand was used as fine aggregate for the test in accordance with DSTU B V.2.7-189:2009 and DSTU B EN 196-1:2015.

4. 3. Procedure of determining the indicators of sample properties

The work was performed using the system-structural approach of building materials science "composition-structure-properties". Methods of planning and processing the results of experiments are adopted as the methodological basis of the research. Experimental studies were carried out on laboratory samples, manufactured and tested on certified equipment according to the current regulatory documents of Ukraine using standard test methods.

An indirect assessment of the influence of modifiers on the kinetics of cement hardening at a water-cement ratio (W/C) of 0.5, 0.55, and 0.60 was carried out based on the results of determining the hardening terms on the Vick device (Ukraine). At the same time, the depth of immersion of the needle of the device into the cement dough was recorded over time. Determination of the influence of modification of the structure of water, the degree of which changed with the amount of dissolved modifier, on the hardening of cement stone in the early stages was carried out on cement samples with W/C of 0.5, 0.55, and 0.60. The main indicators of the properties of concrete samples determined in the experiment were compressive and bending strength limits. Determination of the specified indicators was carried out according to the methodology of the relevant State Standards of Ukraine (Table 1).

Table 1

State standards used for testing

Indicator	Document
Normal slurry thickness	DSTU B. V. 2.7-185:2009
Hardening terms	DSTU B. V. 2.7-185:2009
Water release	DSTU B. V. 2.7-186:2009
Compressive/bending strength	DSTU B. V. 2.7-187:2009 DSTU B. EN 196-1:2015

To change the degree of water modification, the modifier was dissolved in water until the concentration specified by the experimental plan was reached (0.0002 %; 0.0004 %; 0.0006 %; and others according to the specific experimental plan of the mass of cement). The resulting solution was used instead of water when making concrete. Normal water was used in the control samples. The concrete components were moistened to the humidity determined by the experiment plan and mixed for 4 minutes. Experimental samples with side dimensions of 40×40×160 mm were made by the method of vibration molding, part of which, after hardening in the air for 3 days, continued to harden in the air, and the other part – in water.

For simplification and clarity of result processing, strength indicators were converted into relative units (%).

5. Results of studies of concrete sample properties

5. 1. Determination of the rate of formation of the compressive strength of fine-grained concrete based on slag Portland cement

The results of determining the compressive strength of cement concrete samples in the early stages of hardening (2 days) with W/C=0.5–0.6 are shown in Fig. 1.

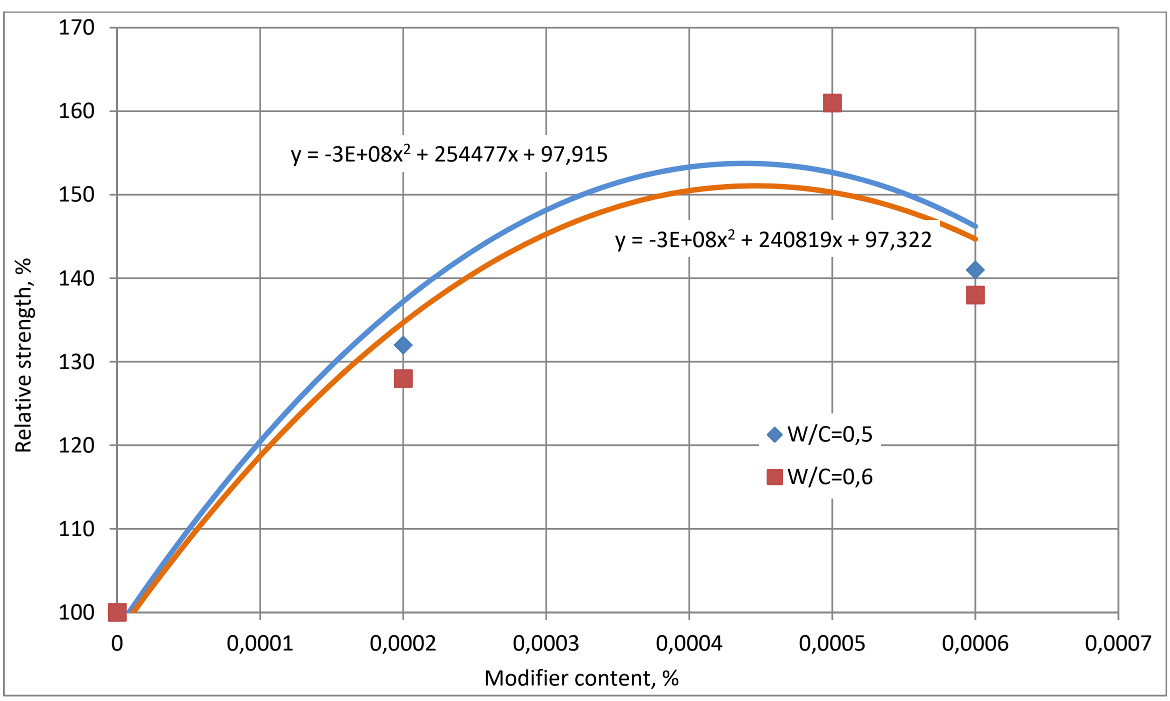

Fig. 1. Influence of the modifier used to modify the structure of water on the relative compressive strength of concrete at the age of 2 days

As demonstrated by the results of the experiments (Fig. 1), the influence of water modified by the mechanism of hydrophobic hydration on the compressive strength of concrete at the age of 2 days depends on the concentration of the modifier.

The greatest effectiveness of the modifier at this age is manifested at average (relative to the experimental plan) values of its consumption (0.0004–0.0005 %). The coefficient of variation of concrete strength at this age ranges from 2 % to 7 % and does not depend on the concentration of the modifier. It should be noted that the degree of modification of the water structure does not make a difference in the application efficiency depending on the water content (W/C) in the system.

According to experimental data, the results of which are shown in Fig. 2, the effectiveness of influence of water structure modification on concrete strength changes over time. That is, the effect of modifying the water structure on the compressive strength of concrete (at the age of 28 days) practically does not depend on the water content but it leads to an increase in the strength of concrete by only 30 % when using water, the structure of which is modified at a modifier concentration of 0.0006 % of the cement mass.

The coefficient of variation of concrete strength at this age (28 days) is from 2 % to 7 % and does not depend on the concentration of the modifier. It should be noted that even at this age, the degree of modification of the water structure has practically no difference in the efficiency of application depending on the water content (W/C) in the system.

The generalized change in the effect of the modifier on the strength of concrete over time is shown in Fig. 3.

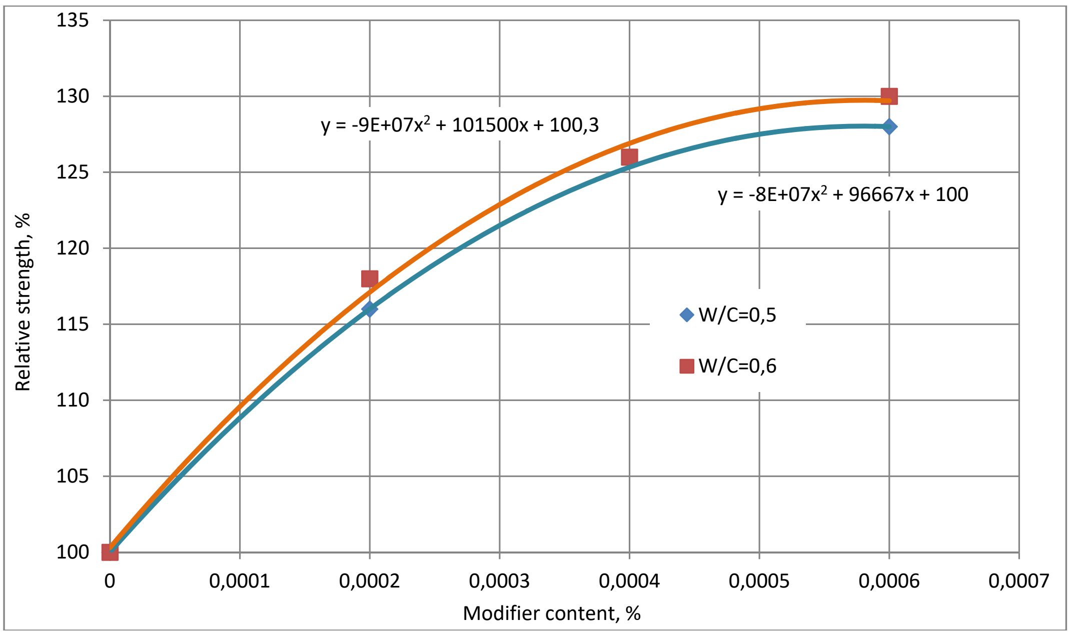

Fig. 2. Influence of the modifier used to modify the structure of water on the relative compressive strength of concrete at the age of 28 days

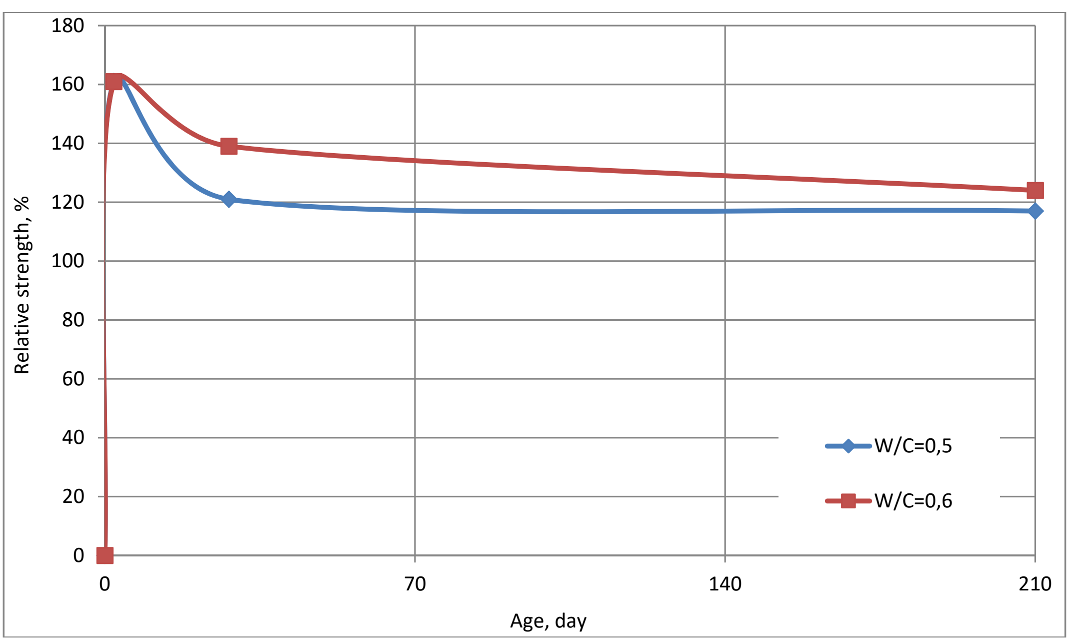

Fig. 3. Change in concrete compressive strength over time (modifier content 0.0006 % of cement mass)

Our results show that water with a structure modified by the mechanism of hydrophobic hydration effectively increases the compressive strength of concrete based on Portland slag cement at an early age. This confirms the expediency of using water with a structure modified by the mechanism of hydrophobic hydration to change the speed of formation of the strength of fine-grained concrete based on slag Portland cement.

Analysis of the dependence of the relative compressive strength of concrete based on slag Portland cement at an early age on the concentration of the aqueous solution of the modifier (Fig. 4) reveals that there is a clearly multi-extreme dependence between them.

The results of our experiment confirm the occurrence of the "Effect of ultra-low concentrations" in the hardening concrete system, which is evidenced by the presence of several extremes (Fig. 4). That is, the above fully confirms the main provisions of the "Effect of ultra-small concentrations".

5. 2. Determination of the rate of formation of tensile strength of fine-grained concrete based on slag Portland cement

The results of experiments on determining the tensile strength of fine-grained concrete in bending, shown in Fig. 5, demonstrate that the water-cement ratio changes the nature of the influence of the degree of modification of the water structure (characterized by the content of the modifier) on the value of the relative tensile strength of concrete during bending. With such a generally accepted approach to planning an experiment, it is practically impossible to generalize the obtained experimental data. At the same time, the analysis of the influence of the concentration of the aqueous solution of the modifier on concrete tensile strength during bending (Fig. 6) reveals that there is a clearly observed multi-extreme dependence between them. This also fully confirms the main principles of the "Effect of ultra-small concentrations", which was the basis of the research, the results of which are reported in the current work.

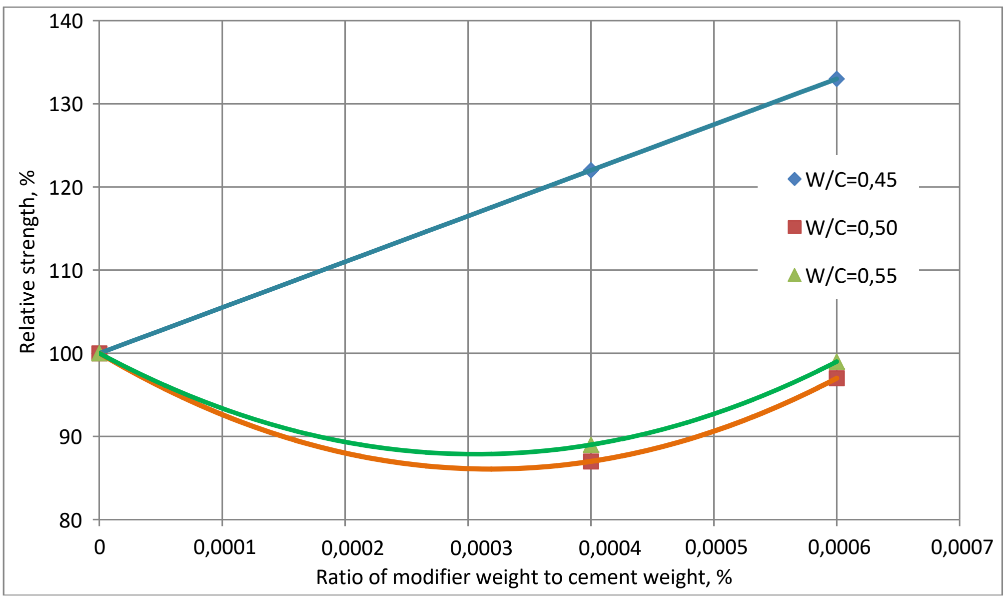

Fig. 4. Change in the compressive strength of concrete depending on the concentration of the aqueous solution of the modifier

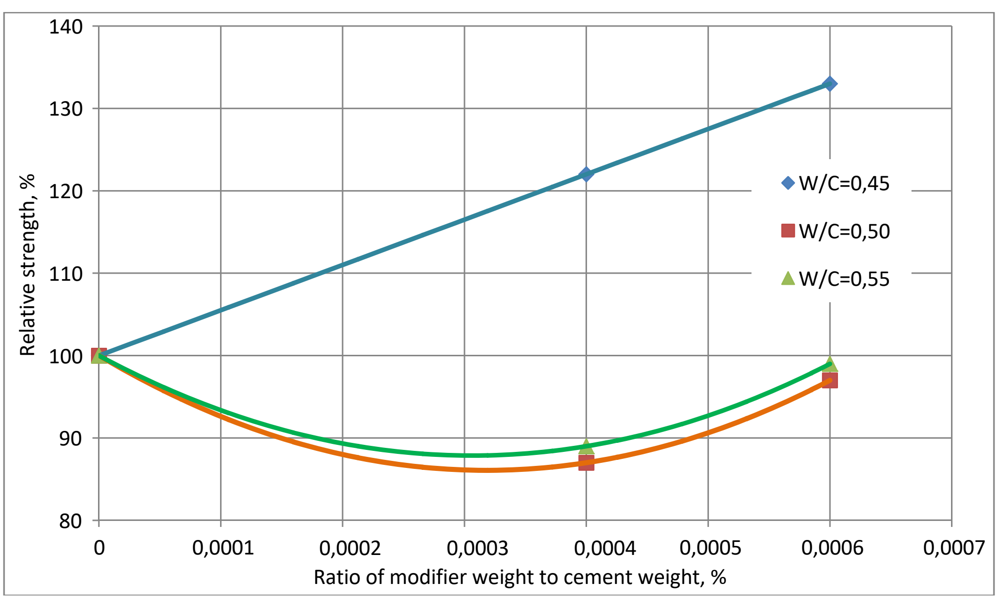

Fig. 5. Flexural tensile strength of concrete depending on the water-cement ratio and the amount of modifier used to modify the water structure

The results of determining the tensile strength during bending of cement concrete samples at the age standardized by state standards (28 days), with W/C=0.5, are shown in Fig. 7. The greatest degree of influence of modified water on the tensile strength during bending is manifested at the largest (relative to the experimental plan) values of modifier consumption.

Fig. 7 demonstrates that when using water with a structure modified by the mechanism of hydrophobic hydration, it is not unambiguously reflected on the strength of concrete under compression and tension during bending.

According to the experimental data shown in Fig. 7, the effectiveness of modified water varies depending on the amount of modifier applied to modify it. The use of modified water at low modifier consumption leads to a decrease in tensile strength during bending.

Thus, the optimal content of the modifier used to modify the structure of water in fine-grained concrete made on slag Portland cement is at least 0.0006 % of the mass of slag Portland cement.

Thus, the concentration of the aqueous solution of the modifier in fine-grained concrete, which is made on Portland cement slag, to achieve the maximum increase in compressive strength is about 0.0009 %. To achieve the maximum increase in tensile strength during bending, it is about 0.0013 %.

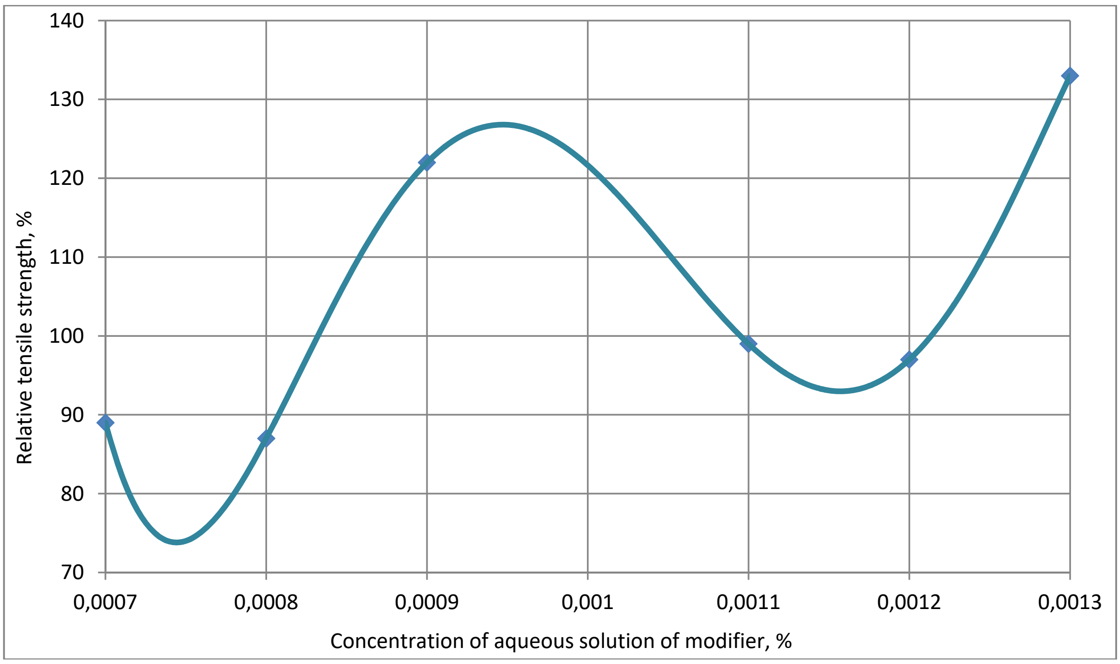

Fig. 6. Dependence of the flexural strength of concrete on the concentration of the aqueous solution of the modifier used to modify the water structure

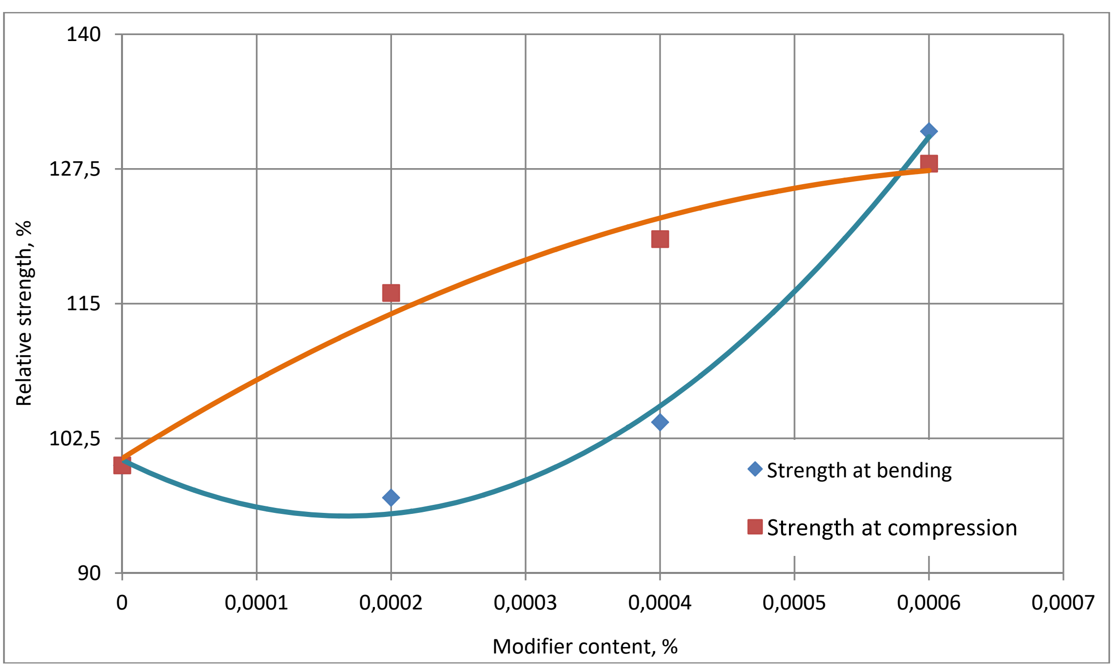

Fig. 7. Comparison of the influence of the modifier used to modify the structure of water on the value of compressive and tensile strength during bending (water-cement ratio in concrete 0.5)

6. Discussion of results of investigating the influence of modifier on the formation of strength of fine-grained concrete made on slag Portland cement

When determining the effectiveness of the influence of water, the structure of which is modified by the mechanism of hydrophobic hydration, on the cement hardening process, as follows from the obtained results shown in Fig. 1–3, it is natural to increase the speed of strength formation by fine-grained concrete. This is evidently due to the dispersive action of active protons, which arise in water as a result of hydrophobic hydration, which occurs during the interaction of molecules of the hydrocarbon radical of the modifier with water. In addition, active protons destroy adsorption layers on the surface of clinker minerals and blast furnace granulated slag particles, which slow down the processes of diffusion of hydroxyl ions and the formation of crystal hydrates.

According to [11], hydrophobic radicals of organic substances change the main properties of cement stone and its structures due to changes in the structure of water. This happens due to the slowing down of the growth of new growth crystal nuclei, and the formation of much more small crystals than during the hardening of cements without an organic additive. Water structured due to hydrophobic hydration, intensifying the dissolution of silicates, helps accelerate their hydration. In this case, the introduction of lime into the liquid phase is accelerated and supersaturation increases, during which the formation of hydrosulfoaluminate occurs.

A comparison of the hardening terms and the duration of the hardening periods of modified cement with different W/C indicates the acceleration of the hardening processes of the cement dough. The data on the influence of modification of the structure of water by the mechanism of hydrophobic hydration on the hardening process of Portland slag cement allow us to state the following: the main regulator of the process is not so much the formation of a significant number of nanostructures, but the deflocculating effect of modified water protons on the dispersed particles of Portland slag cement. This phenomenon makes it possible to exclude the technological operation of its additional grinding in order to increase the hydraulic activity. Such conclusions are expedient from a practical point of view because they make it possible to reasonably approach the determination of the necessary amount of modifier, reduce energy costs for the production of slag Portland cement, and simultaneously increase its hydraulic activity. From a theoretical point of view, the research results allow us to assert the determination of a certain mechanism of the hydration processes of Portland slag cement in the presence of water with a structure modified by the mechanism of hydrophobic hydration, which are certain advantages of this research.

However, it is impossible not to note that the results of determining the strength of fine-grained concrete (Fig. 4) indicate an ambiguous influence of water structured by hydrophobic hydration on changes in mechanical strength. This is manifested, first of all, in a much greater effect of water at an early age and a different nature of the effect on compressive strength and tensile strength during bending [4, 6].

As follows from our results shown in Fig. 5, 7, the effect of ultra-small concentrations of water modifier on the compressive and tensile strength of concrete during bending is not unambiguous. To achieve the maximum increase in the tensile strength of concrete during bending, a slightly higher concentration of the modifier (about 0.0013 %) should be used.

Such uncertainty imposes certain restrictions on the use of the results, which can be interpreted as a limitation of this study.

The impossibility of removing these limitations within the framework of this study creates a potentially interesting direction for further research. In particular, it may be aimed at identifying the composition of new products in the process of hydration of the system "Portland cement slag - water modified in the process of hydrophobic hydration". Such detection will allow us to investigate the microstructural transformations taking place at this time and to determine the input variables of the process that significantly affect the transformation.

Thus, it has been proven that the use of water structured due to hydrophobic hydration for the production of fine-grained concrete based on slag Portland cement provides an increase in its mechanical strength.

This testifies to the possibility of directed regulation of the processes of forming a strong structure of fine-grained concrete on slag Portland cement by using water structured by the application of hydrophobic hydration.

Separately, it should be noted that our experiments confirmed the main provisions of the "Effect of ultra-low concentration", which until now has not been used to regulate the properties of concrete.

7. Conclusions

1. Our research has established that changing the structure of water using hydrophobic hydration exerts a significant effect on changing the nature of hardening processes and structure formation of fine-grained concrete based on slag Portland cement in the early stages of hardening. This is manifested in a significant increase in its compressive strength at an early age (which reaches 160 % of the strength of concrete without additives), which is of practical importance for concretes based on Portland slag cement.

2. Features of the formation of the structure of fine-grained concrete, which is obtained on the basis of water structured by the application of hydrophobic hydration, are the ambiguous influence of the amount of water modifier on the tensile strength of concrete during bending. Small consumption of the modifier leads to a loss of tensile strength during bending. Therefore, the consumption of the modifier should be limited to 0.0006 % of the mass of slag Portland cement. In this case, the degree of increase in the speed of formation and strength values, both in compression and in tension in bending, are equal and have high values (respectively, 40 %/day and 160 % at the age of 4 days).

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study and the results reported in this paper.

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Data availability

All data are available in the main text of the manuscript.

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