Insufficient determination of the effect of surface-active substances introduced in extremely low concentrations on the formation of the stability of the properties of fine-grained concrete based on composite Portland cements determined the feasibility of conducting research in this area. The studies investigated the influence of the modification of composite cement with water activated by the use of the hydrophilic hydration mechanism. It has been proven that these factors include the type and amount of applied water nano modifiers. The analysis of the study results confirmed that the introduction of water activated by the mechanism of hydrophilic hydration into concrete in extremely small doses significantly increases the rate of formation of concrete strength and reduces the coefficient of its variation. Owing to this, the strength of the resulting modified fine-grained concrete based on composite cement at the age of 3 days exceeds the strength of the similar concrete without additives by 300 %, and at the age of 27 days – by 25 %. At the same time, the coefficient of variation of strength has a minimum value at the optimal amount of nano additive – water modifier. This allows us to assert the effectiveness of the revealed mechanism of modification of composite cement. Thus, there are reasons to assert the possibility of targeted regulation of the processes of formation of a strong homogeneous structure of fine-grained concrete based on composite cement by using water activated by the mechanism of hydrophilic hydration

Keywords: fine-grained concrete, composite cement, concrete modification, surfactants, water activation

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ENSURING UNIFORMITY OF STRENGTH OF FINE-GRAINED CONCRETE BASED ON MODIFIED COMPOSITE CEMENT

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1. Introduction

The base of concrete is cement. Natural or industrial materials and a significant amount of energy are spent on the production of cement. Of all types of cement, composite Portland cement has the lowest costs in terms of processing natural materials and the lowest energy costs during production.

Composite Portland cement is typically used under the same conditions as Portland cement. But in composite Portland cement, the rate of structure formation, as evidenced by the rate of formation of its strength, is significantly slower than that in Portland cement. Therefore, composite Portland cement acquires a strength close to that of Portland cement after 5–6 months, depending on the temperature and humidity conditions during which it hardens.

The degree of grinding of the components of composite Portland cement affects its activity and final strength, as well as the time of its formation. So, the finer the grind, the faster the composite Portland cement hardens and gains strength. Therefore, at present, increasing the fineness of cement grinding is a technological technique that is most widely used in the production of cement [1]. However, this technological method causes an increase in the cost of cement.

Taking into account the effect of surface-active substances used in ultra-low concentrations [2, 3], it is a relevant task to investigate further improvement of concrete technology based on composite Portland cement.

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. However, the issue of the homogeneity of concrete, that is, the stability of its properties, was not considered.

Since composite Portland cement has a lower rate of formation of properties than Portland cement, it is obvious that the use of water modified by the use of hydrophilic or hydrophobic hydration mechanisms is more appropriate for it than for Portland cement [3]. In addition, studies into the stability of properties of fine-grained concrete were not performed for composite Portland cements.

This gives reason to assert that it is appropriate to conduct further research to study the influence of water modified by the mechanism of hydrophilic hydration on the speed of formation of strength of fine-grained concrete on composite Portland cement.

One of the significant indicators of concrete quality is its homogeneity. Therefore, the basic literature on concreting technology [4] determines that the acceptance of concrete by comparing its actual strength with the standardized one without taking into account the characteristics of uniformity of strength is not allowed.

According to [5], one of the ways to increase the homogeneity of lightweight concrete is to equalize the viscosity of the soluble part of concrete with the viscosity of the concrete mixture. However, no data on determining the coefficient of variation of concrete strength are given in the work.

Work [6] reports the results of research into highly functional self-compacting concrete reinforced with basalt fiber; a comparison of the strength of the obtained concrete with the strength class was performed, but without the specified coefficient of variation of strength, which is not permissible.

In work [7], the homogeneity of mechanically activated concrete was investigated by the height of the sample, but the issues of homogeneity of their strength remained unresolved. Another type of concrete of the new generation is obtained with the use of nano additives of various types. For example, in work [8] powders of metal oxides and silicon were used as nano modifiers of concrete in the conducted research, but the results of studies into the homogeneity of the obtained concretes are not shown. The same applies to work [9], in which the results of research on concrete containing micro silica and crushed chalk are given. Such concretes have high strength at an early age but high heterogeneity of properties. Work [10] gives the results of research aimed at increasing the speed of formation of the structure of fine-grained concrete and its strength, but there are no data on the stability of strength. The above-mentioned disadvantages of new-generation concrete prevent their widespread use.

It is obvious that the more water during cement hardening will be bound into stable, strong minerals, the less the shrinkage of the cement stone will be and the higher its density and, therefore, its strength, and the smaller the coefficient of its variation.

Under certain conditions (introduction of calcium carbonates or calcium chlorides into the system of hardening Portland cement compositions), according to [11], calcium carbo- and chloroaluminates can be formed during the hydration process, which bind a large amount of water. The specified minerals can contribute to increasing the stability of concrete properties but experimental data on this issue are not given in the cited work.

Paper [12] reports the results of studies into 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. But the issue of homogeneity of concrete strength was not considered. In [13], 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 the cited works is the use of only one type of cement – Portland cement, as well as a significant content of plasticizers and the uncertainty of concrete homogeneity. 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], which shows an increase in the strength of concrete when the structure of water is changed due to hydrophobic hydration, and in work [15] due to hydrophilic hydration. But even in these works, the homogeneity of concrete strength is not fixed either.

Despite the practical significance of results reported in the above works, their authors insufficiently consider the kinetic regularities of the processes of forming the strength of concrete and ensuring its homogeneity.

In addition, the results of research, which are given in the cited works, refer to concrete obtained using Portland cement, which has a high cost. It should be taken into account that the production processes of obtaining Portland cement significantly affect the environment. The production of composite Portland cement, due to the significant content of components that do not require additional processing, exerts a much smaller impact on the environment.

Thus, the insufficient determination of the effect of surface-active substances introduced in extremely low concentrations on the formation of stability of the properties of fine-grained concrete based on composite Portland cements predetermines the feasibility of research in this area.

3. The aim and objectives of the study

The purpose of our study is to determine the possibility of ensuring the uniformity of strength of fine-grained concrete based on composite cement modified with structured water. This could make it possible to increase the rate of formation of the structure and strength of concrete with a simultaneous increase in the homogeneity of concrete, which would lead to a decrease in cement consumption.

To achieve the goal, the following tasks were set:

– to determine the influence of hydrophilic modified water on changes in the homogeneity of compressive strength of fine-grained concrete based on composite Portland cement at different values of the water-cement ratio;

– to determine the influence of hydrophilic modified water on the stability of strength of fine-grained concrete based on composite Portland cement during its hardening in media with different degrees of humidity.

4. The study materials and methods

4. 1. The object and hypothesis of the study

The object of research in our work was fine-grained concrete based on composite Portland cement. The study was performed using the methodological foundations of the system-structural approach in construction materials science: “composition – structure – properties”.

The hypothesis of the study is to increase the homogeneity in the size of concrete particles due to the destruction of flocs of cement particles, cement minerals that are on the surface of its particles, activation of the surface of the aggregate under the influence of protons, with which water is saturated in the process of its modification (structuring) according to the hydrophilic mechanism.

4. 2. Researched materials and equipment used in the experiment

The research was carried out using cement R 42,5 from PrJSC “Heidelbergcement Kryvyi Rih”, which contains 75 % blast furnace granulated slag; as a modifier that provides structuring of water by the mechanism of hydrophilic hydration, superplasticizer Sika Plast-520 (Federal Republic of Germany) was used. Polyfractional Dnipro river sand (Ukraine) in accordance with DSTU B EN 196-1:2015 was used as fine aggregate for testing. Chalk (Ukraine), ground to a specific surface area of 3500 cm^2/g, was used as the carbonate component of composite Portland cement.

The components of the concrete mixture were measured in portions according to the mass determined by the experiment plan and mixed for 4 minutes. The additive was injected with an aqueous solution based on the weight of water according to the experimental plan. Experimental samples with side dimensions of 40×40×160 mm were made by the method of vibration molding, part of which, after hardening in air for 3 days, continued to harden in air, and the other part – in water.

4. 3. Procedure for determining the indicators of samѳple properties

An indirect assessment of the effect of modified water on the kinetics of cement hardening was carried out at a water-cement ratio (W/C) of 0.5, 0.55, and 0.60 based on the results of determining the hardening terms on the Vika device (Ukraine), recording the depth of immersion of the needle into the cement dough over time. Determination of the effect of modified water 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 basic indicators of the properties of concrete samples determined in the experiment were compressive strength limits and its coefficient of variation. 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 applied for testing

Indicator	Regulatory document
Normal slurry thickness	DSTU B.V. 2.7-185:2009
Setting time	DSTU B.V. 2.7-185:2009
Water separation	DSTU B.V. 2.7-186:2009
Compressive/flexural strength	DSTU B.V. 2.7-187:2009, DSTU B EN 196-1:2015
Coefficient of variation of concrete strength	DSTU B.V. 2.7-214:2009, DSTU B 2.7-224:2009

The compressive strength of concrete of one composition (which corresponded to a certain amount of water modifier) was determined by the formula:

$$f_{c,cube}=\frac{\sum_{j=1}^{n} f_{ci}}{n},$$

$$f_{c,i}=(\alpha \cdot F/A),$$

where F is the destructive load, N;

A is the working cross-sectional area of the sample, mm^2;

α is a scaling factor for bringing the strength of concrete to the strength of concrete in samples of the basic size and shape;

n is the number of unit values of concrete strength (in experiments according to DSTU – n=6).

The mean square deviation of concrete strength in batch s_m, MPa:

$$s_m=W_m/\alpha_1,$$

where W_m is the range of concrete strength unit values, which is defined as the difference between the maximum and minimum unit strength values;

α_1 is a coefficient that depends on the number of unit values.

The coefficient of variation of concrete strength V_c, in percent, was calculated according to the formula:

$$V_c=\frac{s_m}{f_{c,cube}}\cdot 100.$$

The rate of formation of compressive strength of fine-grained concrete was determined by the formula:

$$V_f=f_{c,cube}/t, \text{ MPa/day},$$

where $f_{c,cube}$ – compressive strength of concrete of one composition at age t.

5. Results of investigating concrete sample properties

5. 1. Determining the effect of hydrophilic modified water on changes in the homogeneity of the compressive strength of fine-grained concrete based on composite Portland cement

The results of determining the compressive strength of cement concrete samples made on the basis of water, modified by the mechanism of hydrophilic hydration, in the early stages of hardening are shown in Fig. 1.

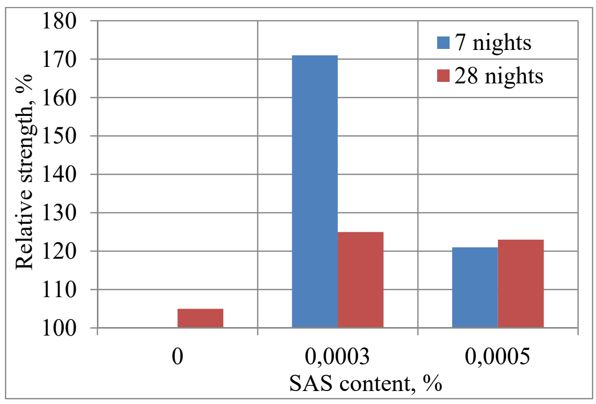

Fig. 1. Influence of the modifier on the relative compressive strength of concrete at the age of 2 days with a content of 20 % calcium carbonate in the cement

At the same time, the coefficient of variation of concrete strength follows a different dependence on the amount of modifier in water (Fig. 2–4).

It should be noted that the effectiveness of the modifier practically does not depend on the water content in the system. The greatest effectiveness of the modifier is manifested at average (relative to the experimental plan) values of its consumption.

According to the experimental data shown in Fig. 3, the effectiveness of the modifier changes over time. That is, the effect of the modifier on the strength of concrete does not depend on water content. At the same time, the presence of the modifier leads to an increase in the strength of concrete at the age of 28 days by no more than 30 % with a modifier content of 0.0003 % of the cement mass.

At the same time, over time (7 and 28 days are used as control points of time change in the studies), the value of the coefficient of variation of concrete strength changes slightly (Fig. 2–4).

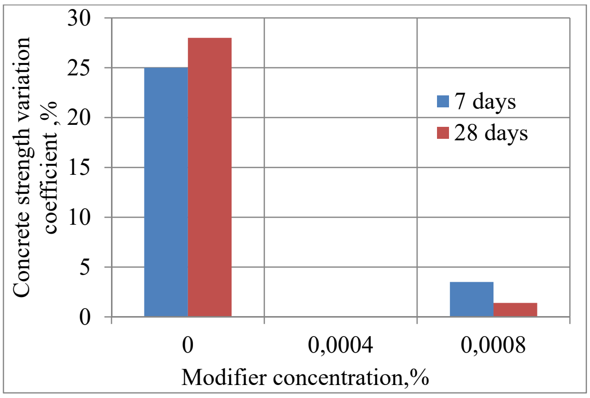

Fig. 2. The coefficient of concrete strength variation at W/C=0.5

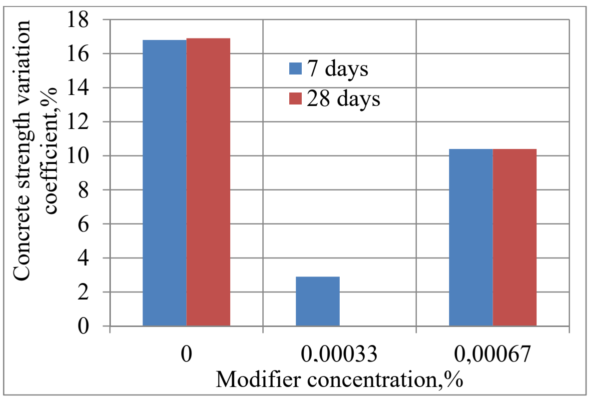

Fig. 3. The coefficient of concrete strength variation at W/C=0.55

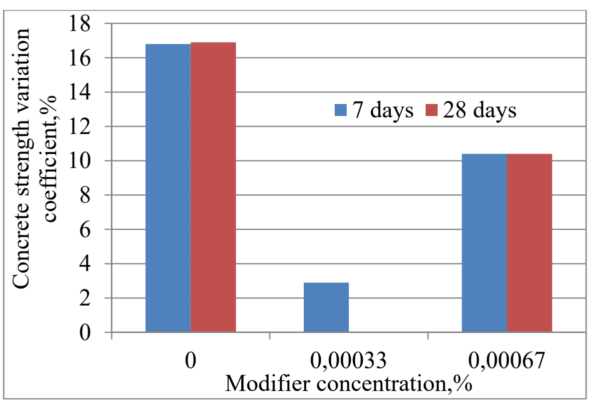

Fig. 4. The coefficient of concrete strength variation at W/C=0.6

Our results show that the applied water modifier effectively increases the compressive strength of concrete based on composite Portland cement at an early age. This confirms the expediency of using hydrophilic modified water to change the speed of formation of the strength of fine-grained concrete based on composite Portland cement.

Analysis of the dependence of coefficient of variation of the compressive strength of concrete based on composite Portland cement on the concentration of the modifier in water (Fig. 5) reveals that there is clearly a multi optimal relationship between them. In addition, there is a zone of the smallest value of the coefficient of variation of concrete strength.

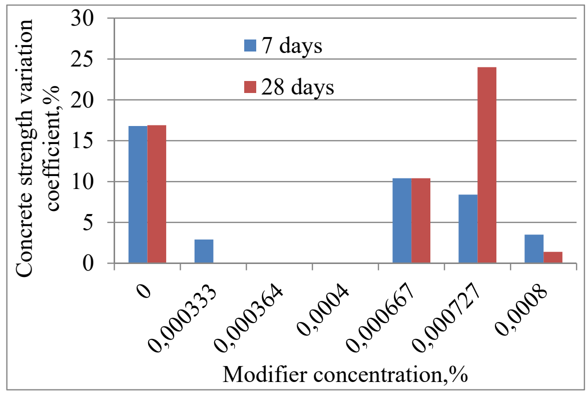

Fig. 5. The coefficient of concrete strength variation

Analysis of the dependence of relative compressive strength of concrete based on composite Portland cement on the concentration of the modifier in water (Fig. 6–8) reveals that there is also a multi optimal relationship between them.

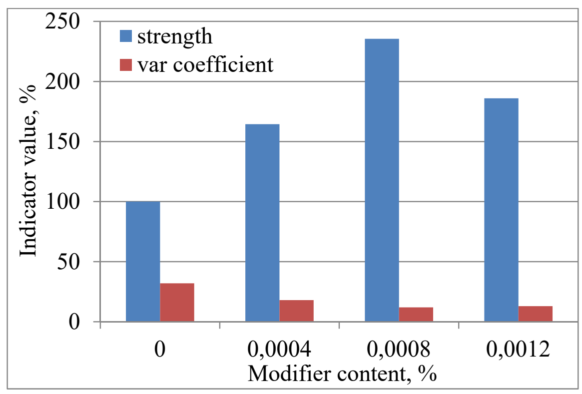

Fig. 6. Relative strength of concrete at W/C=0.5

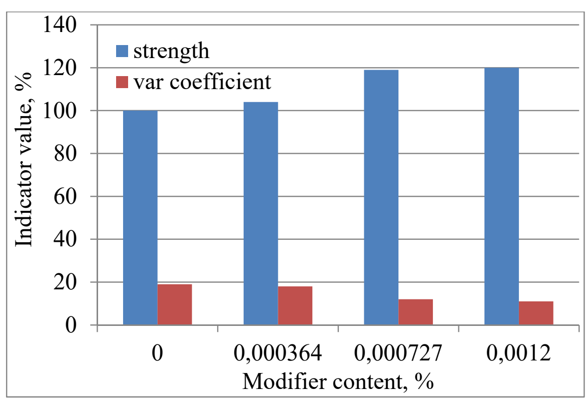

Fig. 7. Relative strength of concrete at W/C=0.55

This fully confirms the basic propositions of the theory of ultra-small concentrations, which was the basis of our research.

In a given case, the zone of the smallest coefficient of variation of concrete strength coincides with the zone of the highest concrete strength, which is observed when the cement contains 20 % of carbonate rock.

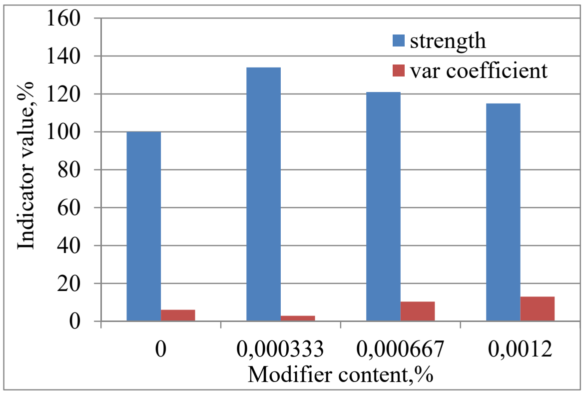

Fig. 8. Relative strength of concrete at W/C=0.6

This fully confirms the basic propositions of the theory of ultra-small concentrations, which was the basis of our research.

In a given case, the zone of the smallest coefficient of variation of concrete strength coincides with the zone of the highest concrete strength, which is observed when the cement contains 20 % of carbonate rock.

5. 2. Determining the influence of medium humidity on the formation of the homogeneity of the structure of fine-grained concrete

During the experiments, the compressive strength of fine-grained concrete and its coefficient of variation were determined.

The results of the experiments shown in Fig. 9–11 demonstrate that the water environment where concrete hardening took place changes the nature of the influence of the modifier content on the value of the coefficient of variation of concrete strength.

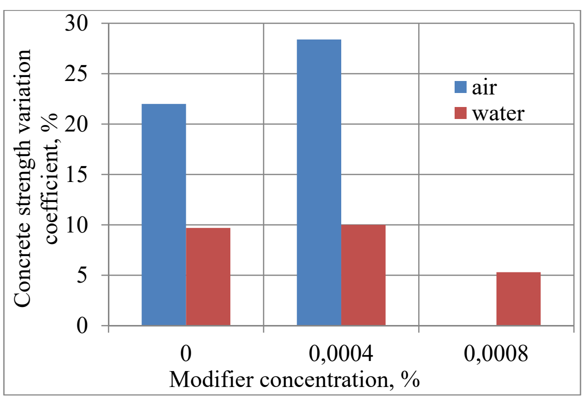

Fig. 9. The coefficient of concrete strength variation depending on the conditions of its hardening (W/C=0.5)

The greatest degree of influence of modified water on the value of the coefficient of variation of strength is manifested at the largest (relative to the experimental plan) values of modifier consumption.

In a given case, the zone of the smallest coefficient of variation of concrete strength coincides with the zone of the highest concrete strength, which is observed when the cement contains 20 % of carbonate rock.

As can be seen from Fig. 6–8, using a modifier whose action is based on the hydrophilic modification of water is not clearly reflected in the coefficient of variation of concrete strength.

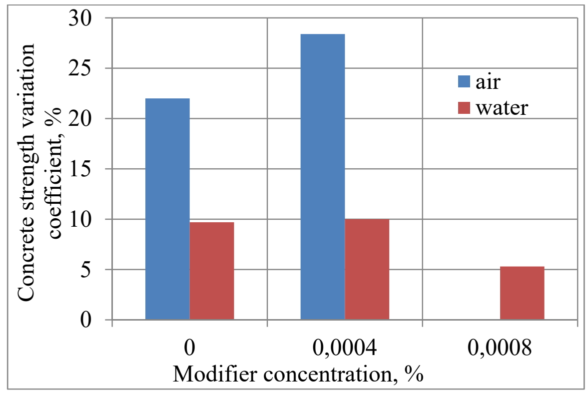

Fig. 10. The coefficient of concrete strength variation depending on the conditions of its hardening (W/C=0.55)

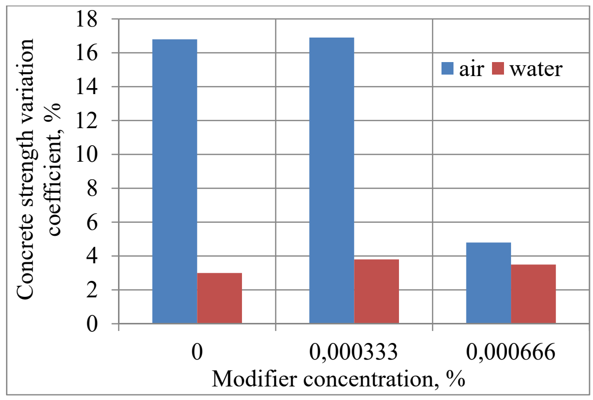

Fig. 11. The coefficient of concrete strength variation depending on the conditions of its hardening (W/C=0.6)

According to the experimental data shown in Fig. 6–8, the effectiveness of modified water varies with the amount of modifier applied to modify the water. The use of modified water at low modifier costs leads to a decrease in tensile strength during bending.

Thus, as with curing in water, there is an optimal concentration of modifier in water. As with air hardening, the zone of the smallest coefficient of variation of concrete strength coincides with the zone of the highest concrete strength, which is observed when the cement contains 20 % of carbonate rock.

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

Determination of the effectiveness of the modifier on the cement hardening process follows from our results (Fig. 2–4). It is normal to have a certain content of the modifier, which determines the smallest value of the coefficient of variation of concrete strength. This is primarily due to the dispersive effect of active protons, which arise as a result of hydrophilic hydration, which occurs during the interaction of modifier molecules with water. In addition, active protons contribute to the destruction of adsorption layers on the surface of clinker minerals and activate particles of the carbonate component and particles of granulated blast furnace slag.

According to [11], hydrophilic components of organic surface-active 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 clinker without an organic additive. Water structured due to hydrophilic hydration, intensifying the dissolution of clinker silicates, helps accelerate their hydration. In this case, the influx 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 slurry. The obtained data on the effect of the hydrophilic modifier on the hardening process of composite Portland 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 action of protons of the modified water. The specified phenomenon of dispersion of the particles of composite Portland cement increases the homogeneity of the cement stone, which results in a decrease in the coefficient of variation of concrete strength. In addition, there is an opportunity to exclude the technological operation of additional grinding of Portland cement clinker in order to increase hydraulic activity. Such conclusions are fair from a practical point of view, as they allow a reasoned approach to determining the effective amount of the modifier. In addition, there is an opportunity to reduce energy costs for the production of composite Portland cement and simultaneously increase its hydraulic activity and quality. From a theoretical point of view, our research results allow us to determine a certain mechanism of hydration processes of composite Portland cement in the presence of water activated due to hydrophilic hydration, which are advantages of the current research.

However, it is impossible not to note that the results of determining the coefficient of variation of the strength of fine-grained concrete indicate an ambiguous influence of water activated by hydrophilic hydration on changes in strength stability. This is manifested, first of all, in a much greater effect of activated water at an early age and a different nature of the effect on the coefficient of variation of strength during hardening of concrete in air or in water. Such uncertainty imposes certain restrictions on the use of our results.

The disadvantages of the results are the impossibility of removing the mentioned limitations within the framework of this study, which creates a potentially interesting direction for further research. In particular, it can focus on identifying the composition of new formations in the process of hydration of the "composite Portland cement – water modified in the process of hydrophilic hydration" system. Such studies could make it possible to investigate the microstructural transformations occurring at this time and to determine the input variables of the process that significantly affect the transformation.

7. Conclusions

1. Our studies have established that the activation of water using hydrophilic hydration significantly affects the change in the nature of hardening processes, phase and structure formation of fine-grained concrete in the early stages of hardening. This is manifested in a significant increase in its compressive strength at an early age with a simultaneous decrease in the coefficient of its variation, which is of practical importance for concretes based on composite Portland cement. Thus, with the introduction of a water modifier in the concentration range of 0.0002–0.0006 %, an increase in the strength of concrete is observed up to 300 % compared to the strength of concrete without additives.

2. Features of the formation of the structure of fine-grained concrete, which is obtained on the basis of water activated by the use of hydrophilic hydration, are the ambiguous influence of the amount of water modifier on the strength of concrete and the value of its coefficient of variation. There is a certain range of concentration of the modifier in water (0.0002–0.0006 %), which ensure high concrete strength at small values of its coefficient of variation. This indicates the possibility of targeted regulation of the processes of forming a strong structure of fine-grained concrete on composite Portland cement by using water activated by the application of hydrophilic hydration.

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.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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