

Хімічні процеси гідратації портландцементу забезпечують формування міцності бетону при стиску. За певних умов підвищення швидкості гідратації цементу сприяє підвищенню міцності бетону при стиску. Особливо це стосується ніздрюватих бетонів, зокрема газобетонів. В роботі було вивчено вплив комплексної добавки, яка сприяє газоутворенню при отриманні газобетону. Означена добавка складається із суміші гідрофобної поверхнево-активної речовини – олеату кальцію, пергідролі і наномодифікатора – мінеральної добавки, яка містить сполуки заліза. Особливістю досліджень було вивчення одночасного впливу гідрофобних поверхнево-активних речовин, пергідролі та мінеральних речовин, що містять сполуки заліза на зміну міцності безавтоклавного газобетону. Дослідження виконано через недостатню міцність при стиску безавтоклавних газобетонів, при виготовленні яких застосовують у якості газоутворюючої добавки алюмінієву пудру або пергідролі. При застосуванні алюмінієвої пудри не витримується однорідність її розподілу в об'ємі бетону, окрім цього вартість алюмінієвої пудри достатньо висока. У процесі досліджень встановлено, що означена комплексна добавка змінює характер формування міцності газобетонів, а саме збільшує її величину. Доведено, що для управління процесами тужавіння цементу й формування міцності штучного каменя, який отримують в процесі гідратації цементу, при виготовленні газобетону на основі пергідролі, можна використовувати добавки-наномодифікатори, що містять сполуки заліза, тим самим підвищуючи абсолютну величину міцності при стиску таких бетонів у віці 28 діб. Найбільш ефективно застосовувати наномодифікатори, які містять суміш сполук заліза, що призводить до збільшення міцності газобетону до 50 %

Ключові слова: неавтоклавний газобетон, поверхнево-активні речовини, наномодифікатор, міцність газобетону, пергідролі, сполуки заліза

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THE AERATED CONCRETE BASED ON AN INTEGRATED FOAM CONCENTRATE CONTAINING IRON COMPOUNDS

A. Shishkina

PhD, Associate Professor
Department of Technology of Building Products, Materials and Structures**
E-mail: 5691180@gmail.com

O. Nastich

PhD, Associate Professor*
E-mail: nasticholeg1964@gmail.com

K. Romanenko

PhD, Associate Professor*
E-mail: renkr8@gmail.com

S. Oliinyk*

E-mail: oleynic.sveta@gmail.com

*Department of Applied Mechanics and General Engineering Disciplines
**Kryvyi Rih National University
Vitaly Matusevicha str., 11,
Kryvyi Rih, Ukraine, 50027

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1. Introduction

The construction structures of industrial buildings and facilities, specifically located near thermal units, are affected by the environment, which changes the physical-mechanical properties of materials that these structures are made from, and, consequently, influences their durability. This leads to the need to predict, when renovating buildings and facilities, appropriate measures to improve their service life by reducing the temperature effects from the environment.

One of the effective materials for protection against thermal environmental influences is the light and porous concretes that have low thermal conductivity. However, such concretes do not demonstrate sufficient strength at compression.

Therefore, the issue of obtaining porous concretes, which have a sufficiently high strength, while using low-cost foam

concentrates, is of significant scientific and practical interest, and resolving it is a relevant task.

2. Literature review and problem statement

Concrete, according to [1], represents the poly-structural system “matrix – filler – their interface”, in which cement stone is the matrix. At the same time, cement stone is a hydration product of the dispersive system “dispersed phase – dispersion medium” in which the dispersed phase is the binder’s particles and the dispersion medium is water or aqueous solutions of chemical substances. The structure of the cement stone, according to [2], is determined by the shape and content of hydrated compounds. As well as by those grains that did not react, by the volume and size of pores, including technological cracks [1],

formed at hydration of starting particles of cement, as well as by the mutual arrangement of all elements within the structure.

Currently, there are several known methods to control the porous structure of cement stone and concrete [3–5]. The first group of these methods includes control over sedimentation processes within the cement stone. A given method makes it possible to change both the total number of pores and their dimensions [3]. However, this method has certain limitations, since the number of pores in concrete is associated with the amount of a porous aggregate. That is, adjusting the structure of concrete simultaneously changes two parameters: the amount of a solid fraction (filler) and the number of cavities in concrete. That complicates and limits the ability to vary the density and strength of concrete. Under another method, cement slurry is added with surface-active substances (SAS), which absorb air and influence the formation of the structure and properties of cement stone in concrete [3]. The specified substances slow down sedimentation processes, reduce the number of large pores in concrete, formed as a result of water bleeding, disperse large pores into a large number of small ones. It should be noted that almost all hydrophobic-plasticizing admixtures, to a different degree, are susceptible to some air absorption. Such additives reduce the surface tension of water films on solids, thereby contributing to the formation of very small air pores – spheroids [3]. The role of the specified additives is not so much in the introduction of air into concrete but in the conversion of unevenly distributed large air pores in concrete to many small air bubbles with a diameter of 50–250 μm . The indicated method of cavity formation in concrete has its limitations as well. Specifically, the hydrophobic-plasticizing additives not only modify the porous space of concrete but also inhibit the hydration of cement. That leads to the need to limit the amount of the specified admixtures in concrete, that is, to limit the degree of modification of cavities in concrete. In a third case [4], concrete is introduced with the substances that, under the action of cement's components, starts to release gas whose bubbles form pores. The indicated method is the most effective one to form cellular concretes; however, it has its limitations. Thus, the formation of cavities employs the cement's components, whose amounts, under certain conditions, are not enough to ensure the normal hydration of cement, which reduces the quality of concrete.

The use of modern technologies in the production of concretes was investigated in a certain number of studies, among which are the results from research reported in papers [5, 6]. Work [5] gives the results from investigating dense concretes. Paper [6] outlines general principles of applying modern technologies for obtaining cellular concretes.

Article [7] considered the possibility of disposing of drilling sludge on the oil-based residues from shale gas pyrolysis in order to prepare non-autoclaved aerated concrete. However, the cited work applied aluminum powder, which did not eliminate the known deficiencies in concrete.

To reduce the cost of concretes, modern technologies of their manufacture [8] employ the nanomodifiers that improve the quality of concrete, both at a specific time [8] and during its service life [9]. However, the cited studies deal with dense concretes and cannot be applied to cellular concretes [10]. At the same time, papers [11, 12] determined that mineral complexes containing iron are efficient enough to be used as a concrete nanomodifier [11]. In this case, a sufficiently high effect is manifested in the application of the optimum ratio between the fractions of the specified complexes. However, these studies [11, 12] also refer to dense concretes, and their

results cannot be extended for cellular concretes, nor applied in the technology of their manufacture.

The phenomenon of gas distribution, defined in work [13], when using the compounds of transitional elements, specifically the oil-containing materials, in concretes as an additive, suggests the possibility of their application as a component of the gas-forming agent to obtain aerated concretes.

Based on the above, it should be noted that studying the properties of non-autoclaved aerated concrete is limited to studying such concretes when aluminum powder is used as a foam concentrate. Its application leads to the consumption of cement components for gas formation, to the absence of warranty to the complete use of a foam concentrate for gas production, to the high cost of concrete. Some of these deficiencies are absent in non-autoclaved concretes, whose production utilizes perhydrol to form pores. A small number of studies into the properties of such concretes, especially with the use of modern technologies, hinders the use of the specified concretes and necessitates further research.

3. The aim and objectives of the study

The aim of this study is to obtain cellular aerated concrete with increased durability by improving its composition through the application of an integrated foam concentrate, which consists of perhydrol and substances containing iron compounds.

To accomplish the aim, the following tasks have been set:

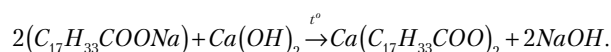
- to examine the effect of an integrated mineral-organic foam concentrate that represents the system “calcium oleate – sodium hydroxide – perhydrol – nanomodifier containing iron compounds”;
- to design optimal compositions for an integrated mineral-organic foam concentrate.

4. Materials and methods to study samples of non-autoclaved aerated concrete

The study was carried out using Portland cement M400 (made at PAT Heidelberg Cement Kryvyi Rih, Ukraine); the Dnieper river sand was used as a finely grained filler. Sodium oleate (Simagchem Corp., China) was used as a surface-active substance (MSAS). The oxide, iron carbonate, as well as waste from enrichment of iron ores at the mining and processing plants in Kryvyi Rih iron ore basin, were used as a nanomodifier containing iron; their particle size was 50...85 nm, which makes it possible to refer the specified substances to the nano particles.

The organic component of the integrated mineral-organic foam concentrate, calcium oleate, was prepared by thermal processing of the mixture at the assigned ratios of aqueous solution of sodium oleate to calcium hydroxide at a temperature of (375 ± 2) K.

The result was the aqueous colloidal solution of calcium oleate containing sodium hydroxide



As shown by chemical analysis, the obtained colloidal solution contains up to 5 % of sodium hydroxide depending on the ratio between the starting components.

The resulting solution was added in the amounts, defined by the experiment design, to the system “Portland cement – water”.

Experimental samples of concrete were prepared from concrete mixtures, whose components were dosed in the specified amounts, according to the experiment design, stirred at a laboratory mixer for 3 minutes. The resulting mixture was placed in a metallic mold – a cube that has a side size of 7 cm. The molded concrete samples were hardened over 28 days at an ambient humidity of $70 \pm 10 \%$ and an ambient temperature of $293 \pm 2 \text{ K}$.

Such independent factors were varied in the experiment:

X_1 – content of a mineral admixture-modifier in concrete;

X_2 – content of MSAS in concrete;

X_3 – kind of a mineral admixture-modifier in concrete.

The response functions (y_i) accepted in the study were the coefficient of concrete mixture loosening and the concrete strength at compression.

The averaged estimation of the effect of the modifiers on concrete strength was derived according to the results from determining the compressive strength of aerated concrete, taking into consideration the latest procedures for experimental and statistical estimation of properties for the activated and non-activated finely-grained mixtures and concretes. The composition of concrete was considered to be constant in all experiments at the ratio “cement/ fine filler” of 1/1. We determined the magnitude for tensile strength of the samples at compression in accordance with standard procedures. The samples strength was tested at the universal machine UMM-100 (Russia).

5. Results from studying the indicators of properties for the samples of concrete

The first stage of research implied determining the effect of a gas-forming agent on the properties of the concrete mixture – the degree of an increase in volume.

The influence of the type of a gas-forming agent on the degree of increase in the volume of the system “binder – gas-forming agent – water” was studied by the method of a single-factor experiment.

The result of our study is the established influence of the type and content of a gas-forming agent on the degree of an increase in the volume of the system “Portland cement – foam concentrate” (Fig. 1). We have found the influence of ratio between the ferriferous and oxidative components of the foam concentrate on the degree of increase in the system’s volume (Fig. 2) and the influence of ratio between starting components at obtaining calcium oleate on the degree of increase in the system’s volume (Fig. 3). The second stage of our study implied determining the influence of a gas-forming agent on the

properties of concrete – strength at compression, which is one of the main quality indicators and defines the scope of application of concretes on its basis.

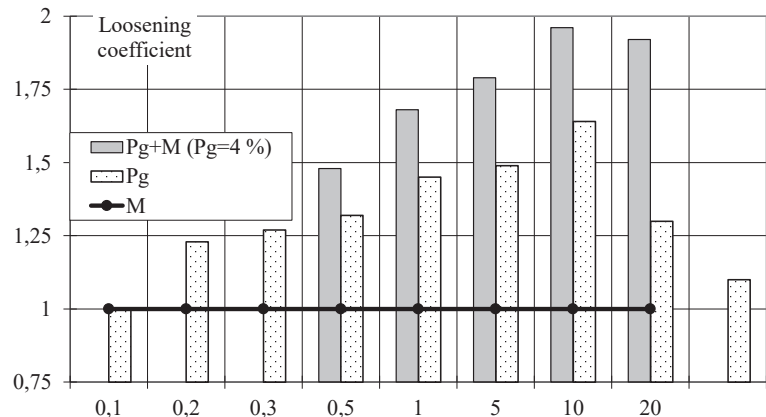


Fig. 1. Effect of the type and content of a gas-forming agent on the degree of increase in the volume of the system “Portland cement – foam concentrate”: Pg – perhydrol, M – iron oxide

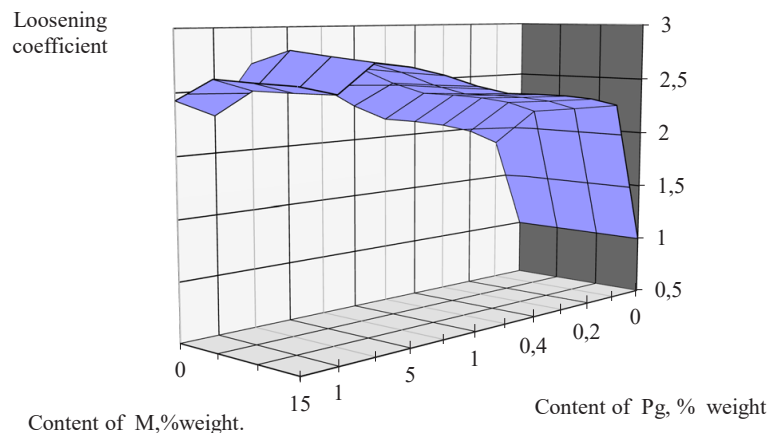


Fig. 2. Influence of ratio between the ferriferous and oxidative porosity components of foam concentrate on the degree of increase in the volume of the system “Portland cement – foam concentrate”: Pg – perhydrol, M – iron containing nanomodifier (iron oxide)

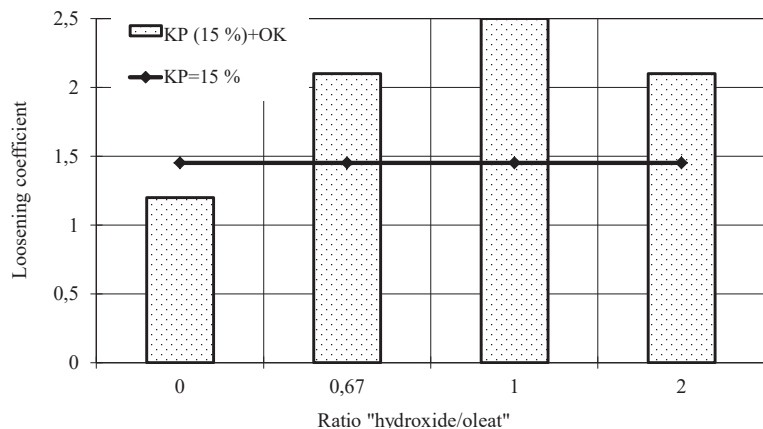


Fig. 3. Influence of ratio between starting components in the preparation of calcium oleate on the degree of increase in the volume of the system “Portland cement – foam concentrate”: KP – integrated foam concentrate (15 % M + 0.15 % Pg); Pg – perhydrol; OK – products from reaction between sodium oleate and calcium hydroxide; M – iron oxide

In this group of experiments, we studied the strength of the cellular concrete, obtained as a result of hardening of the dispersed system “Portland cement – water – integrated foam concentrate” depending on the water-cement ratio and the content of the integrated foam concentrate (Fig. 4). Change in the strength of concrete over time is one of the main indicators in the formation of its structure. The next group of experiments implied determining a change in the strength of cellular concrete over time (Fig. 5).

To determine the optimum composition (type) of the nanomodifier containing iron compounds, we studied the strength of aerated concrete with the application of an iron-containing substance, which had a different ratio of carbonate to iron oxide (Fig. 6).

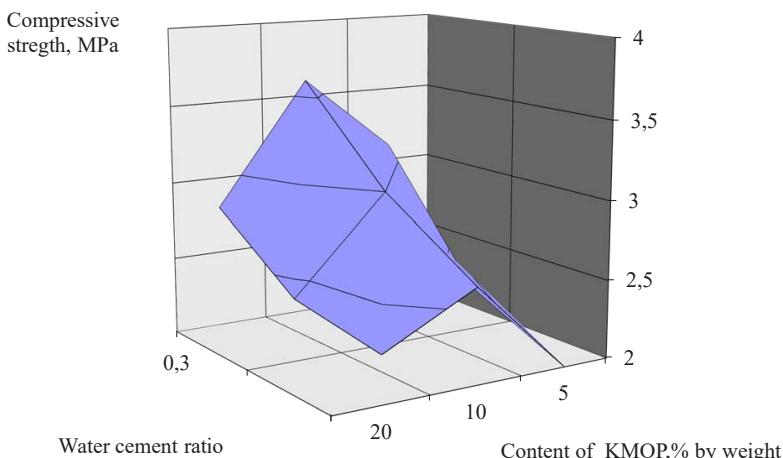


Fig. 4. Compressive strength of concrete (KMOP – integrated mineral-organic foam concentrate: (99.35 % M+0.15 % Pg+0.5 % OK); Pg – perhydrol; OK – products from reaction between sodium oleate and calcium hydroxide; M – iron oxide)

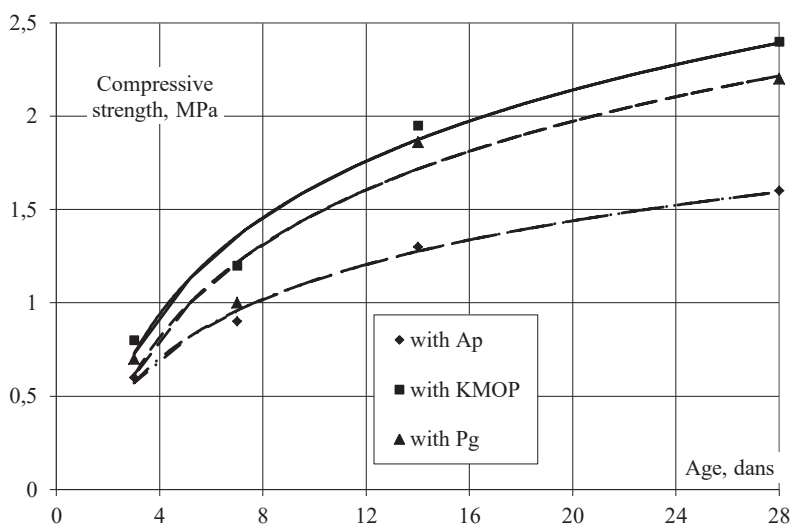


Fig. 5. Change in the strength of concrete over time (Ap – aluminum powder)

All the research results obtained were tested and statistically treated, to ensure reliability and credibility of our findings.

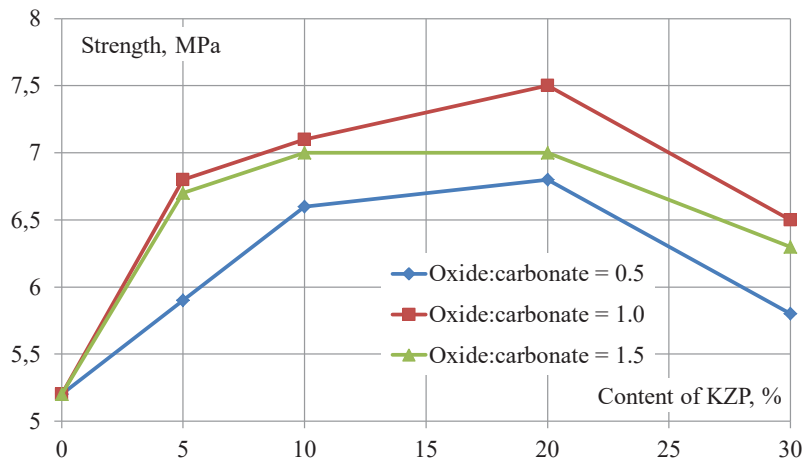


Fig. 6. Influence of the composition of an integrated iron-containing nanomodifier (KZP) on the strength of aerated concrete with a density of 700 kg/m³

The magnitude of variation factor in experiments for all experimental points did not exceed 4 %, which predetermines sufficiently high reliability of the obtained results.

6. Discussion of results from studying the properties of non-autoclaved aerated concrete based on perhydrol

Our study has shown that the simultaneous introduction of perhydrol and iron oxide to the system provides the degree of loosening the examined system that exceeds the degree of its loosening when using perhydrol only (Fig. 1).

Under experimental conditions, an increase in the content of perhydrol in the system by more than 5 %, and iron oxide by more than 20 %, of the weight of cement almost does not lead to the further increase in the system loosening (Fig. 2).

This can be explained by the fact that at the specified consumption of the foam concentrate’s components such an amount of gas is released, which the system cannot retain in its volume; the gas breaks through and the system’s volume increases no more.

Mathematical treatment of the results from experiments has established the form of a regression equation relating the loosening coefficient to certain factors:

$$K_B = 72,31 \times X + 0,12 \times Y - 3,36 \times X \times Y + 92,5 \times X^2 \times Y + 0,11 \times X \times Y - 952,35 \times X^2 - 0,006 \times Y^2 - 3,42 \times X^2 \times Y^2, \quad (1)$$

where X is the content of perhydrol, 0.1, % by the weight of a binder; Y is the content of iron oxide, % by the weight of a binder.

Our calculations based on (1) showed that the optimum magnitude for the ratio of the ferriferous component in a

foam concentrate to perhydrol, X_2 , is 40; in this case, the loosening coefficient equals 2.28.

Thus, the established increase in the gas release by the mixture “iron-containing mineral complex – perhydrol” makes it possible to replace the costly gas-forming agent, perhydrol, with iron-containing substances.

For example, in order to obtain a loosening coefficient equal to 2, it is necessary to introduce to the system “Portland cement – gas-forming agent” either 4 % of perhydrol or 15 % of iron oxide and 0.5 % of perhydrol. In order to obtain a loosening coefficient equal to 1.7, it is necessary to introduce either 2 % of perhydrol or 15 % of the iron-containing component and only 0.15 % of perhydrol.

An increase in the degree of porosity of these systems in comparison with the systems “Portland Cement – perhydrol – iron-containing nanomodifier – water” and “slag Portland cement – perhydrol – iron-containing nanomodifier – water” can be explained by the capability of SAS of this type to microfoaming. In this case, the resulting microfoam retains the released gas by limiting its evolution from the system, which increases the volume of the latter.

In addition, a hydrophobic SAS, by creating a waterproofing layer at the surface of cement, provides a more complete participation of water molecules in the gas formation. The present sodium hydroxide accelerates the processes of hydration of the examined systems. Thus, the system “perhydrol – iron-containing nanomodifier – hydrophobic SAS – sodium hydroxide” is an effective foam concentrate for the cement slurry obtained from hydraulic binders.

In terms of the magnitude of a loosening coefficient for the system “Portland cement – water – calcium oleate – sodium hydroxide – perhydrol – iron-containing nanomodifier”, the optimum content of a hydrophobic SAS, X_3 , is 0.15 % by weight of cement. In this case, there is a maximum increase in the system’s volume.

In terms of the compressive strength of aerated concrete, the optimal content of the integrated mineral-organic foam concentrate in the system depends on the magnitude of the water-cement ratio in it.

Under conditions of experiment, the curing rate of the cellular concrete with the introduced integrated mineral-organic foam concentrate exceeds the curing rate of the cellular concrete, to which we introduced aluminum powder or perhydrol only.

We have derived a regression equation relating the strength of aerated concrete on the content of an integrated foam concentrate, K , and a water-cement ratio, Z

$$R_w = -22.77 + 21.6 \times Z - 0.6 \times Z^2 - K(30.3 - 1 \times Z + 0.68 \times Z^2) - K^2(4.34 - 2.4 \times Z + 0.3 \times Z^2) \quad , \text{ MPa} \quad (2)$$

where $K=0.1 \cdot P$, %; $Z=(W/C) \cdot 10$; P is the content of KMOP, W/C – water-cement ratio.

The optimum ratio between the oxide and carbonate of iron is 1.0, and the optimum ratio between perhydrol and a nanomodifier is 1:40.

Compressive strength of the aerated concrete, obtained using an integrated foam concentrate, when applying Fe_2O_3 as a nanomodifier in the amount of 5...8 % of the amount of the dispersed phase of the system, exceeds the strength of admixture-free concretes. The same is observed when applying 10...20 % of iron carbonate.

The most effective iron-mixing nanomodifier is the mineral complexes, which contain a mixture of oxide and carbonate of iron. The use of this type of a nanomodifier leads to an increase in concrete strength by 50 % relative to the strength of concrete without an integrated foam concentrate. Such mineral complexes include iron-containing rocks – iron ores and wastes from iron ores enrichment.

In practice, the resulting regression equations produce sufficiently reliable accuracy of calculations when designing aerated concrete with an average density of 600...700 kg/m^3 . In this case, a deviation between the estimated and actual magnitudes for average density and strength of aerated concrete does not exceed 7...8 %, which is enough for practical application.

In the future, it is necessary to clarify the resulting equations for aerated concretes with lower and greater average density than in those investigated.

7. Conclusions

1. Our study has established the patterns in the influence exerted on the degree of porosity and compressive strength of aerated concrete by an integrated foam concentrate, which represents the dispersed system “mineral iron-containing nanomodifier – perhydrol – calcium oleate”. The specified regularities have been defined depending on the type of a mineral iron-containing complex and its amount in concrete.

Owing to the action of the integrated foam concentrate, mechanical strength of concrete at compression increases by 20...50 % compared to concrete that does not contain an integrated foam concentrate.

2. The efficiency of using a nanomodifier containing a mixture of oxide and carbonate of iron has been proven. The optimum ratio between oxide and carbonate of iron is 1.0. The optimum ratio between perhydrol and a nanomodifier is 1:40. Effectiveness of using a nanomodifier that contains other iron compounds requires further investigation. Our results indicate a possibility of targeted control over the processes of forming a strong structure of aerated concretes by using an integrated foam concentrate, which contains perhydrol, colloidal surface-active substances, which are capable of forming micelles, and a mineral nanomodifier containing iron compounds.

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