Досліджено вплив наномодифікаторів на міцність дрібнозернистого бетону. Встановлено вплив найбільш широко розповсюджених нанонаповнювачів, а саме мікрокремнезему, каоліну, вапна та гіпсу на змінення міцності цементного каменю та дрібнозернистого бетону. Виконано порівняння впливу означених нанонаповнювачів на міцність дрібнозернистого бетону. Показано, що найбільш ефективними нанонаповнювачами є речовини, що містять сполуки кальцію

Ключові слова: дрібнозернистий бетон, міцели, поверхнево-активні речовини, нанонаповнювач, наномодифікатор, міцність

Исследовано влияние наномодификаторов на прочность мелкозернистого бетона. Установлено влияние наиболее широко распространенных нанонаполнителей, а именно микрокремнезема, каолина, извести и гипса на изменение прочности цементного камня и мелкозернистого бетона. Выполнено сравнение влияния указанных нанонаполнителей на прочность мелкозернистого бетона. Показано, что наиболее эффективным нанонаполнителем являются вещества, содержащие соединения кальция

Ключевые слова: мелкозернистый бетон, мицеллы, поверхностно-активные вещества, нанонаполнитель, наномодификатор, прочность

UDC 666.948: 666.972.112
DOI: 10.15587/1729-4061.2018.127261

RESEARCH INTO EFFECT OF COMPLEX NANOMODIFIERS ON THE STRENGTH OF FINE-GRAINED CONCRETE

A. Shishkina
PhD, Associate Professor*
E-mail: alexshishkina15@gmail.com
A. Shishkin
Doctor of Technical Sciences, Professor*
E-mail: 5691180@gmail.com
*Department of Technology of building products, materials and structures
Kryvyi Rih National University
V. Matusevycha str., 11,
Kryvyi Rih, Ukraine, 50027

1. Introduction

Fine-grained concretes are expedient to use for manufacturing thin-walled, densely reinforced, and other structures whose fabrication implies a constraint for the size of a filler. Such concretes are a multicomponent composition system [1] and contain both a fine-grained filler and a finely-dispersed filler in its composition, as well as Portland cement [2–5] and high-performance superplasticizers acting as deflocculants. Optimal application makes it possible to control the rheological properties of concrete admixtures. In this case, it is also possible to modify the structure of the cement stone at the macro level. This allows providing concrete with properties that ensure high operational reliability of structures made both of light concrete [6] and by applying nanotechnologies [7], specifically utilizing technogenic raw materials [8].

One of the ways for modifying the structure of fine-grained concrete is the use of micelle catalysis when manufacturing both dense powdered and porous [10], as well as other types, of concrete [11].

Given the multifunctional effect of deflocculants, plasticizers and micelles of surfactants, we consider it important to study further improvement and development of the fine-grained concrete technology. Such a research should be aimed at the control over processes of the cement stone formation by using effective admixtures that modify the structure of concrete.

2. Literature review and problem statement

The urgent necessity of obtaining high-strength concretes based on ordinary cements necessitates the search for new technological approaches, using mineral modifying admixtures and an organic modifier [2–5]. At the same time, it was proposed to use the waste of metallurgical production as modifying admixtures [12, 13]. Papers [13, 14] and several other established that the use of active mineral additives produces a real opportunity to obtain concretes with the preset physical and mechanical characteristics at a considerable saving of Portland cement. However, the results of study into a simultaneous use of micelles of surfactants and mineral modifying admixtures are not given.

At present, microsilica [15, 16] and metakaolin [16] are widely used as modifying admixtures. However, they have certain disadvantages that inhibit the widespread use of these additives. These disadvantages of microsilica [15, 16] include a lack of the stability of its properties, since it is the wastes of production. The disadvantage of metakaolin [16] is its high cost due to rather high energy consumption for its production. In addition, known modifying admixtures were used simultaneously with superplasticizers [15] and hyperplasticizers [17], which act as defloculants. However, such studies were carried out without taking into consideration results of research in the field of micellar catalysis of reactions of synthesis of calcium hydrosilicates, which showed the possibility of using d-element compounds as modifying admixtures [18].

Therefore, there are reasons to believe that there is a lack of certainty about the influence of known modifying admixtures, along with micelles of surfactants, on the characteristics of nanostructures formed during hydration of Portland cements. In particular, the main characteristic of the formation of a concrete structure is the compressive strength, which determines the need for undertaking research in this direction.

3. The aim and objectives of the study

The aim of present work is to determine the influence of modifying admixtures, specifically kaolin, gypsum, lime and microsilica, modified by micelles of a colloidal surface-active substance, on the magnitude of strength of fine-grained concrete and the rate of its formation.

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

– to determine optimal magnitudes of the consumption of modifying admixtures, modified by micelles of a colloidal surface-active substance, to obtain fine-grained concrete of maximum strength;

– to compare effectiveness of the effect of modifying admixtures, modified by micelles of a colloidal surface-active substance, on the strength of fine-grained concrete.

4. Materials and methods to study the effect of complex nanomodifiers on the strength of fine-grained concrete

The research was conducted using the Portland cement CEM I 42.5 according to EN 197-1 (manufactured by PAT «Heidelberg Cement Kryviy Rih», Ukraine); the Dnieper river sand was used as a fine filler; its granulometric characteristics are given in Table 1. Sodium oleate (Simagchem Corp., China) was used as a micelle-forming surface-active substance (MSAS). Microsilica (trade mark Elkem Microsilica Grade 940-U, the content of SiO_2 is 94.6 %), the gypsum for construction G-4 (PAT «Gipsovik», Kamyanets-Podilsky, Ukraine), slaked lime, and kaolin from Polonivsky deposit (Khmelnytska oblast, Ukraine), were used as the modifying admixtures.

The magnitude of specific surface of Portland cement, gypsum, lime, and microsilica is given in Table 2.

Table 1

Granulometric characteristic of filler

Filler physical appearance	Real density, kg/m^3	Bulk density, kg/m^3	Partial residue on screens, %				
			2.5	1.25	0.63	0.315	0.16
The Dnieper river sand	2,600	1,490	–	12.1	26.9	32.6	28.4

Table 2

Characteristic of mineral components of the examined system

Substance	Specific surface, m^2/kg
Cement	325
Microsilica	14,000
Gypsum	298
Lime	352

Modification of the modifying admixtures was performed by the treatment with an aqueous micellar solution of MSAS whose MSAS concentration was 0.1 %.

Experimental samples of concrete were prepared from concrete mixtures, the components of which were dosed in the required quantities according to the plan of our experiment and agitated in a laboratory mixer for 3 minutes. The resulting mixture was placed in a metal cube-shaped mold with the size of sides 7 cm. The concrete samples thus formed were hardened during 28 days at ambient humidity 70±10 % and an ambient temperature of 293±2 K. Compressive strength of the concrete, which did not contain micelles from a colloidal surface-active substance and modifying admixtures, was 16.2 MPa.

The following independent factors varied in the experiment:

X_1 – content of the mineral modifying admixture in concrete;

X_2 – content of MSAS in concrete;

X_3 – type of the mineral modifying admixture in concrete.

An indirect evaluation of the effect of modifiers on the strength of concrete was carried out based on the results of determining the strength at compression of fine-grained concrete. The composition of concrete was taken to be constant in all experiments with the ratio «cement/fine filler» = 1/2, at a constant water-solid ratio equal to 0.5. Determining the magnitude of strength limit at the compression of samples was carried out in accordance with standard procedures. Strength control of the samples was tested at the universal device UMM-100.

The conditions for the homogeneity of experiment were verified while determining in parallel the strength of concrete with each composition.

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

Results of determining the mechanical strength when compressing the samples of fine-grained concrete at a certain stage of hardening (28 days) are shown in Fig. 1–4.

It should be noted that in the presence of micelles of a colloidal surface-active substance, the modifying admixtures used ensure an increase in the strength of fine-grained concrete. For each modifying admixture, there is a certain amount in the concrete composition, which enables it to reach maximum strength.

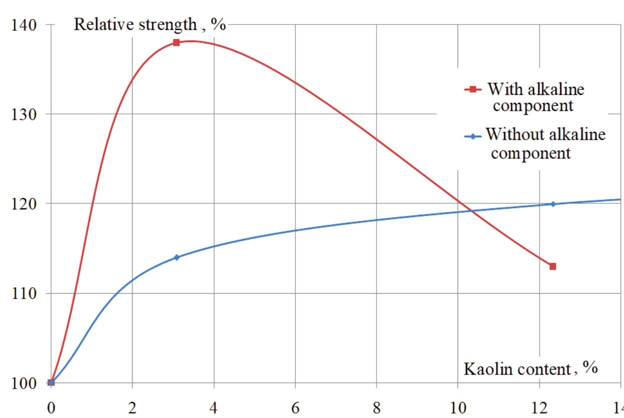

Fig. 1. Effect of modified kaolin on the strength of fine-grained concrete (MSAS content – 0.0004 %)

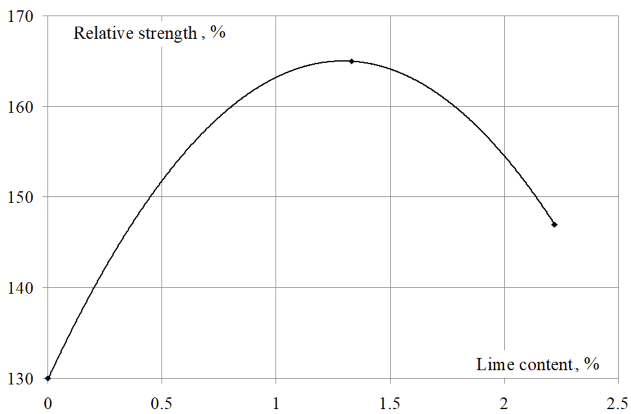

Fig. 2. Effect of modified lime on the strength of fine-grained concrete (MSAS content – 0.0004 %)

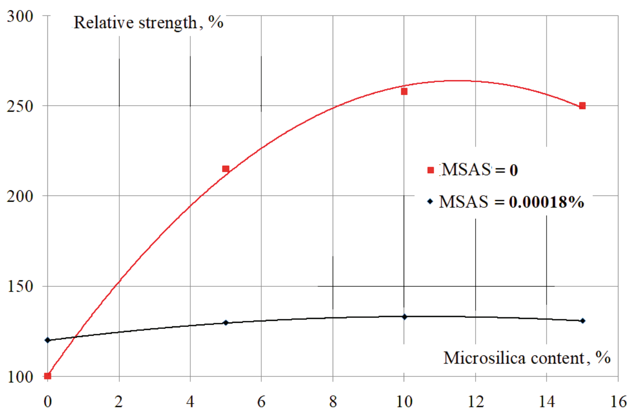

Fig. 3. Effect of modified microsilica on the strength of fine-grained concrete

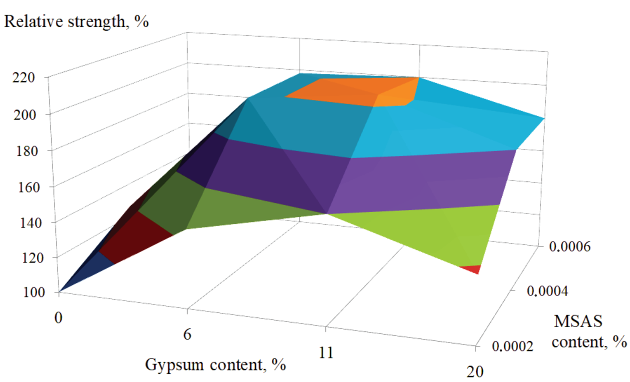

Fig. 4. Effect of modified gypsum on the strength of fine-grained concrete

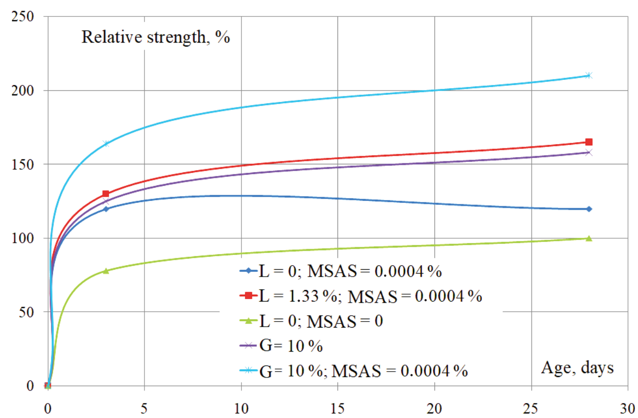

Fig. 5. Change in the strength of fine-grained concrete, which has lime (*L*) and gypsum (*G*) as a modifying admixture, over time

Using gypsum as a modifying admixture as an example, it was found that there is a certain content of MSAS and the modifying admixture (Fig. 4), which ensure that concrete achieves maximum compressive strength.

Based on experimental data on determining the rate of strength formation at the compression of fine-grained concrete (Fig. 5), one can see that an increase in the rate of strength formation occurs due to the presence of colloidal surface-active substances in the micelle system.

We have determined a change in the strength of fine-grained concrete over time when employing the system «lime – MSAS» as a nanomodifier (Fig. 5).

The results of research show that the type of a mineral modifying admixture affects the magnitude of strength of fine-grained concrete and could be used to analyze the influence of nanomodifiers depending on the type of a mineral modifying admixture.

6. Discussion of results of studying the effect of complex nanomodifiers on the strength of fine-grained concrete

When determining the effectiveness of using nanomodifiers to increase the strength of fine-grained concrete, as follows from the obtained results (Fig. 1–5), the phenomenon of synergism is logical. This, obviously, is due to the dispersing action of the applied nanomodifiers relative to cement particles and a change in the conditions of their interaction with a mineral modifying admixture, which occurs inside the micelle of MSAS. In this case, adsorption layers form at the surface of clinker minerals, which, however, do not slow down the processes of diffusion of the ions of hydroxides and the formation of crystalline hydrates, but only transfer this process inside the micelles.

Such a mechanism of influence of MSAS micelles is obviously a factor that regulates the process of formation of the products of hydration of clinker minerals, which leads to an increase in the formation rate and the resulting magnitude of strength of fine-grained concrete.

However, at the same time, this mechanism negatively affects the process of interaction between clinker minerals and microsilica (Fig. 3). This results in a reduction in the effect of the introduction of microsilica into a hardening cement system and cannot be recommended for use.

Comparison of the strength of fine-grained concretes containing various mineral modifying admixtures (Fig. 6) allows us to conclude that the most effective nanomodifier is the system «gypsum – MSAS».

As regards the use of kaolin as a mineral modifying admixture, it should be noted that in the experiments we did not use meta-kaolin – a product of kaolin processing, but the natural kaolin. In this case, applying the system «kaolin – MSAS» as a nanomodifier leads to a slight (up to 25 %) increase in the strength of fine-grained concrete. A rather significant increase in the strength of fine-grained concrete occurs when applying a nanomodifier as the system «kaolin –

a substance that produces an alkaline reaction – MSAS». In this case, an increase in the strength of fine-grained concrete amounts to 40 %.

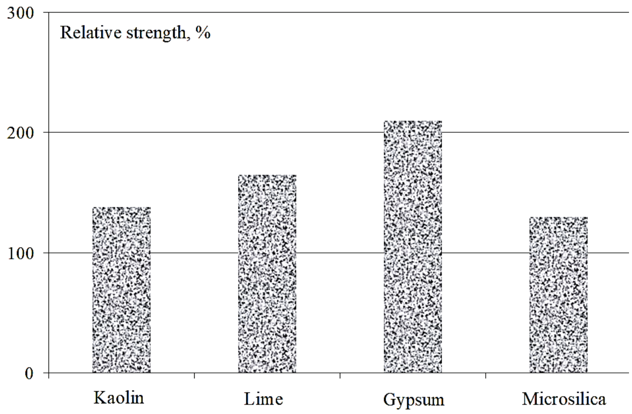

Fig. 6. Effect of the type of a modifying admixture on the strength of fine-grained concrete (MSAS content – 0.0004 %)

This corresponds to the results of studies [18–20], which proved that in order to activate natural kaolin it is necessary to treat it with alkali metal compounds (under conditions of experiment, it is sodium carbonate, as recommended in papers [19, 20]).

Regarding the use of lime as a mineral modifying admixture, a rather high efficiency of its application should be noted (Fig. 5).

The optimal amount of lime, that is the amount that provides the maximum strength of concrete, is 1.3–1.4 % of the mass of cement.

The results of experiments show (Fig. 5) that when applying gypsum or lime as a modifying admixture, the processes of forming the strength of concrete at the initial period of its hardening (3 days) are accelerated.

Subsequently, the rate of formation of the strength of concrete, which contains a nanomodifier with the use of lime or gypsum, further exceeds the rate of formation of strength of the concrete, which contains only MSAS, and the concrete without additives. Given the above, it can be concluded that lime and gypsum increase the efficiency of micellar catalysis of the synthesis of hydrosilicates in the process of setting a cement slurry. This agrees with data, well known from studies [8, 9].

However, it is impossible to deny that the results of determining the strength of fine-grained concrete containing a nanomodifier in the form of the system «microsilica – MSAS» (Fig. 4) indicate an ambiguous effect of MSAS on changing the mechanical strength. This is manifested, first of all, by the fact that the effectiveness of application of a given nanomodifier is lower than the effectiveness of using microsilica without MSAS.

Such an uncertainty imposes certain limitations on the application of the results obtained regarding the choice of mineral modifying admixtures. This may indicate a potentially interesting direction for further research, which, in particular, might be aimed at identifying the types of mineral modifying admixtures as the components of a nanomodifier, which lead to a decrease in its effectiveness. Such a case requires examining the transformations of the microstructure of concrete that significantly affect the «negative» effect.

7. Conclusions

1. The study conducted has revealed patterns in the effect exerted on the compressive strength of fine-grained concrete by the nanomodifier representing the dispersed system «mineral modifying admixture – MSAS», depending on the type and amount of a mineral modifying admixture, as well as the amount of MSAS in concrete. Based on this, it can be argued that the dispersed system «mineral modifying admixture – MSAS» significantly affects the formation of structure of fine-grained concrete at all stages of its hardening. It manifests itself by a change in the rate of formation and the magnitude of compressive strength of fine-grained concrete.

2. Each type of a mineral modifying admixture has its own peculiarities in the formation of a structure of fine-grained concrete, which contains the dispersed system «mineral modifying admixture – MSAS», which imply the magnitude and rate of formation of compressive strength of fine-grained concrete. Due to the mechanism of micellar catalysis, the mechanical strength of concrete increases by 20...150 % compared to concrete, which does not contain the dispersed system «mineral modifying admixture – MSAS».

The study conducted allows us to argue about the effectiveness of using a nanomodifier, which contains kaolin, lime, gypsum as a mineral modifying admixture. Application of microsilica as a mineral modifying admixture requires further research. The results obtained indicate the possibility of targeted regulation of the processes that form a strong structure of fine-grained concretes by using a complex nanomodifier that contains colloidal surface-active substances, which are capable of forming micelles and a mineral modifying admixture.

References

1. Murthy A., Palani G., Iyer N. Impact Analysis of Concrete Structural Components // Impact Analysis of Concrete Structural Components. 2010. Vol. 60, Issue 3. P. 307–319. doi: 10.14429/dsj.60.358
2. Kaprielov S. S., Sheynfel'd A. V., Kardumyan G. S. Novye modificirovannye betony: monografiya. Moscow: Paradiz, 2010. 258 p.
3. Konsta-Gdoutos M. S., Metaxa Z. S., Shah S. P. Highly dispersed carbon nanotube reinforced cement based materials // Cement and Concrete Research. 2010. Vol. 40, Issue 7. P. 1052–1059. doi: 10.1016/j.cemconres.2010.02.015
4. Haifeng L., Jianguo N. Mechanical behavior of reinforced concrete subjected to impact loading // Mechanics of Materials. 2009. Vol. 41, Issue 12. P. 1298–1308. doi: 10.1016/j.mechmat.2009.05.008
5. Iqbal M. A., Rajput A., Bhargava P. Plain and Reinforced Concrete Targets Subjected to Projectile Impact // Procedia Engineering. 2017. Vol. 173. P. 138–144. doi: 10.1016/j.proeng.2016.12.050

6. Ekonomichnost' ispol'zovaniya i vliyanie nanorazmernyh chastic na svoystva legkih vysokoprochnyh betonov / Frolov A. V., Chumadova L. I., Cherkashin A. V., Akimov L. I. // Stroitel'stvo unikal'nyh zdaniy i sooruzheniy. 2014. Issue 4 (19). P. 51–61.
7. Ponomarev A. N. Vysokokachestvennye betony. Analiz vozmozhnostey i praktika ispol'zovaniya metodov nanotekhnologii // Inzhenerno-stroitel'nyy zhurnal. 2009. Issue 6. P. 25–33.
8. Powder concretes with technogenic materials / Tolstoy A., Lesovik V., Zagorodnyuk L., Kovaleva I. // Vestnik MGSU. 2015. Issue 11. P. 101–109. doi: 10.22227/1997-0935.2015.11.101-109
9. Shyshkina O. O., Shyshkin O. O. Study of the nanocatalysis effect on the strength formation of reactive powder concrete // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 1, Issue 6 (79). P. 55–60. doi: 10.15587/1729-4061.2016.58718
10. Shyshkina O. O. Study of the effect of micelle-forming surfactants on the strength of cellular reactive powder concrete // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 2, Issue 6 (80). P. 66–70. doi: 10.15587/1729-4061.2016.63706
11. Shishkin A., Shishkina A., Vatin N. Low-Shrinkage Alcohol Cement Concrete // Applied Mechanics and Materials. 2014. Vol. 633-634. P. 917–921. doi: 10.4028/www.scientific.net/amm.633-634.917
12. Ocenka ul'tradispersnyh othodov metallurgicheskih proizvodstv kak dobavok v beton / Batrakov V. G., Kaprielov S. S., Ivanov F. M., Sheynfel'd A. V. // Beton i zhelezobeton. 1990. Issue 12. P. 15–17.
13. Bazhenov Yu. M. Tekhnologiya betona. Moscow: AVS, 2003. 500 p.
14. Formirovanie struktury vysokoprochnyh betonov / Runova R. F., Rudenko I. I., Troyan V. V., Tovstonis V. V., Shcherbina S. P., Pashina L. D. // Budivelni materialy, vyroby ta sanitarna tekhnika. 2008. Issue 29. P. 91–97.
15. Barabash Y. V., Ksonshkevych L. M., Krantovska O. M. Vysokomitsni betony na mekhanoaktyvovanomu viazhuchomu // Zbirnyk naukovykh prats UkrDAZT. 2014. Issue 149. P. 130–136.
16. Characteristics of cement mortar with nano-SiO_2 particles / Jo B.-W., Kim C.-H., Tae G., Park J.-B. // Construction and Building Materials. 2007. Vol. 21, Issue 6. P. 1351–1355. doi: 10.1016/j.conbuildmat.2005.12.020
17. Morozov N. M., Borovskih I. V. Vliyanie metakaolina na svoystva cementnyh sistem // Izvestiya KGASU. 2015. Issue 3 (33). P. 127–132.
18. Shyshkin O. O. Study of the effect of compounds of transition elements on the micellar catalysis of strength formation of reactive powder concrete // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 2, Issue 6 (80). P. 60–65. doi: 10.15587/1729-4061.2016.63957
19. Ivashchenko Yu. G., Muhambetkaliev K. K., Timohin D. K. Effektivnye glinocementnye kompozicii, modificirovannye organicheskimi dobavkami // Vestnik SGTU. 2014. Issue 4 (77). P. 199–205.
20. Dudina S. N. Sorbciya iz rastvorov ionov Fe3+ i Ni2+ prirodnymi i aktivirovannymi glinami // Nauchnye vedomosti. 2010. Issue 9 (80). P. 131–136.