Fine grained concretes on fly ash cement basis with increased properties

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Abstract. The article is devoted to the study of dispersed reinforced fine-grained concrete, based on modified fly ash-cement binders, containing at least 55% by weight of fly ash. The use of the developed binder will allow the utilization of waste from the fuel and energy industry in the composition of fine-grained concrete, on the one hand, and on the other hand, it will reduce emissions of carbon dioxide into the atmosphere by reducing the consumption of OPC clinker in the composition of binders.

In the course of the research, the positive effect of the complex modification of the fly ash-cement composition with sulfate and carbonate additives was proven, and the phase composition of new formations of artificial stone was studied. It was found that during the simultaneous modification of the fly ash-cement composition, the synthesis of strength is ensured due to the formation of hydration products in the early stages of hardening of ettringite and its analogues with a carbonate and iron component.

The operational and technological properties of the developed binders and concrete based on them were studied. In the process of studying the atmospheric resistance of the developed compositions based on modified binders, a stable increase in strength by 13...15% was established after 350 cycles of alternating wetting and drying of fine-grained concrete samples, which indicates the continuation of the processes of structure formation in artificial stone and allows predicting high operational properties of developed materials.

It was found that the developed fine-grained concretes based on modified ash-containing binders are distinguished by a denser and more homogeneous structure of artificial stone, as

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evidenced by a decrease in the abrasion indicators of concretes based on modified systems by 50% and by 54.8% for dispersion-reinforced concrete compared to additive-free compositions, respectively.

The durability of the developed concrete compositions was studied by studying their kinetics of strength gain, wear, frost, atmospheric and corrosion resistance. It was established that the introduction of a sulfate-carbonate additive to the composition of fly ash-cement systems contributes to a more uniform set of strength of concrete at all stages of hardening. The increase in strength of modified concrete samples is: at the age of 7 days – 105.88%, at the age of 28 days – 141.17% and at the age of 90 days – 117.53%, the value of compressive strength is 8.05, respectively MPa, 24.6 MPa and 33.5 MPa.

Keywords: fine- grained concrete, fly-ash, plasticizing additives, durability, modified fly ash-cement binders.

INTRODUCTION

Recently, multi-component fine-grained

concrete has been actively introduced into construction. Previously, their use was restrained by some features of the structure and properties. For example, the use of unfractionated sand as an aggregate led to a significant increase in voids and a deterioration in the physical and mechanical properties of the resulting concrete. During the production of a mixture of specified mobility and homogeneous structure, the consumption of water and cement increased by 15...25%, compared to concrete on coarse aggregates. This, in turn, led to an increase in shrinkage. In modern conditions, new technical and technological possibilities have appeared, which made it possible to minimize the increase in the consumption of water and cement in fine-grained mixtures and significantly reduce the shrinkage of the material, even obtaining shrinkage-free concrete [1-4].

The advantages of the fine-grained structure include: the possibility of creating a finely dispersed, homogeneous, high-quality structure without large grains, high thixotropy and the ability to transform the concrete mixture, high manufacturability - the possibility of forming structures and products by casting, extrusion, pressing, stamping, spraying etc., the possibility of wide application of dry mixtures with a guarantee of high quality [5-7].

The development of modern society requires the use of new effective building materials, the production of which requires minimal consumption of natural and energy resources, in particular, fine-grained concrete. The cost of fine-grained concrete is primarily determined by the type of cement and its amount in the material. Reducing the cost of fine-grained concrete and structures based on it is possible due to the use of multi-component cements. In the world, the volume of production and use of these cements, which contain waste from the fuel and energy complex represented by TPP ashes, is constantly increasing [8-11]. However, an increase in the amount of ash in the composition of binders leads to a decrease in the strength, frost resistance, abrasion resistance and other indicators of the quality of binders and concrete based on them, therefore the use of such waste is limited to 10...55 wt.% [12]. It is possible to increase the ash content in the composition of binders and improve their physical and mechanical properties by filling the matrix of the binder system with mineral additives of different nature and fractional composition [13-16]. At the same time, not only are the strength and deformation characteristics improved, but there is also the possibility of directional formation of the micro- and macrostructure of cement stone, as well as the raw material base of the construction complex is significantly expanded due to the use of materials available in Ukraine. It is also known that a component of ensuring and improving the properties of fine-grained concrete is the use of chemical modifying additives (in particular, plasticizers), the selectivity of which action in relation to cements with mineral additives determines the relevance of coverage in this work on the possibilities of optimizing the composition of modified fly ash-cement compositions and fine-grained concrete according to strength criteria, frost, atmospheric and corrosion resistance [17-20].

PURPOSE AND RAW MATERIALS

The purpose of the work is the development of compositions of fine-grained concrete based on modified fly ash-cement compositions, which contain the maximum amount of ash and do not differ in their technological characteristics from materials obtained on the basis of pure OPC and can be manufactured according to the technology of dry construction mixes.

To achieve the set goal, it is necessary to solve the following problems:

- to develop and optimize the compositions of binders modified with sulfate-carbonate additives;
- to develop and optimize the compositions of fine-grained concrete obtained on the basis of modified fly ash-cement compositions;
- to investigate the physical-mechanical and special properties of fine-grained concrete obtained by the technology of dry building mixes based on modified sand-cement compositions.

For the production of fly ash-cement binder, we used: OPC-I M500 of Volyntsement OJSC, fly ash from the Ladyzhynska TPP, gypsum anhydrite obtained by burning gypsum stone from the Artemiv deposit and chalk from the Bilhorod deposit. To improve ease of application, increase the plasticity of the mixture, reduce water consumption, as well as improve strength indicators, sulfate-containing superplasticizer C-3 was added to the binder in the amount of 0.75% by mass. For the preparation of fine-grained concrete on the basis of the developed binder, fractionated Dniper sand and granite dropouts of the Rokytnyan deposit were used. Plasticizers based on polycarboxylates (brands "Melflux" and "Sika") and based on sulfate-containing naphtha-linformaldehyde polycondensates (brand C-3) were used as plasticizing additives.

RESULTS AND EXPLANATIONS

At the first stage of the work, the expediency of modifying fly ash-cement compositions with sulfate and carbonate additives was studied according to the criteria of cement stone strength at a consumption of OPC in the range of 20-40 wt.%.

It has been confirmed that during the hydration of fly ash-cement binding systems activated by the addition of burnt gypsum stone, the greatest effect related to the increase in strength at all stages of hardening is achieved when the additive is used in the amount of 10% by weight. Modification of fly ash-cement compositions with a sulfate additive causes an increase in the strength of artificial stone at the age of: 2 days by 14.24; 25.0 and 35.47%; 7 days at 83.18; 43.6 and 40.6%; 28 days for 75.5; 41.6 and 31.5%, respectively, when used in the binder composition of cement 20; 30 and 40% by weight. Activation of fly ash-cement binding systems with a carbonate additive contributes to the maximum increase in strength when using chalk in the amount of 6% by weight with the consumption of 20-30% by weight of OPC.

Modification of fly ash-cement compositions with a carbonate component causes an increase in the strength of artificial stone at the age of: 2 days by 18.6...20%; 7 days by 105.12...45.3%; 28 days by 86.6...29.99%, respectively. With a consumption of OPC of 40% by mass, the optimal amount of carbonate additive is 9% by mass and causes an increase in the strength of artificial stone at the age of: 2 days by 33.3%; 7 days by 56.63%; 28 days for 43.5%.

The positive effect of the complex modification of the fly ash-cement composition with sulfate and carbonate additives has been proven, and the phase composition of new formations of artificial stone has been studied. It was found that during the simultaneous modification of the fly ash-cement composition, the synthesis of strength is ensured due to the formation of hydration products in the early stages of hardening of ettringite and its analogues with a carbonate and iron component. The increase in strength after 28 days of hardening is provided by the synthesis of the hydration products of low-base calcium hydrosilicates and solid solutions based on ettringite. In the products of the hardening of artificial stone at the late stages of hydration, new formations such as scoutite, epistilbite and compounds of variable composition, similar to hydrogarnets, are also present.

The kinetics of increasing the strength of the modified fly ash-cement composition of the optimal composition and comparison compositions are shown in Fig. 1

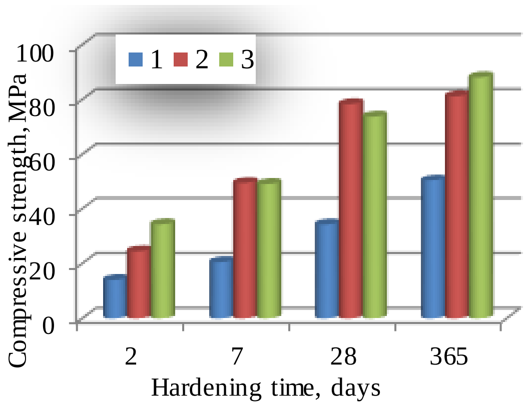

Figure 1. Strength gain of artificial stone based on fly ash-cement compositions, containing 30 wt.% of OPC and 70 wt% of fly ash (1), modified composition with OPc content 30 wt.% п, 56 wt.% of fly ash, 8 wt.% of sulfate admixture and 6 wt.% of carbonate admixture (2) and control composition on the pure OPC without admixture basis (3)

The analysis of graphic dependences of changes in the strength of the modified fly ash-cement mixture shows that the complex introduction of sulfate and calcium carbonate into the studied system allows obtaining compositions that are characterized by a high rate of structure formation in the early stages of hydration and practically do not differ in terms of strength from the compositions. At the first stage of the work, the feasibility of modifying fly ash-cement mixtures was studied of compositions with sulfate and carbonate additives according to the criteria of strength of cement stone with consumption of OPC within 20...40 wt.%.

It has been confirmed that during the hydration of fly ash-cement binding systems activated by the addition of burnt gypsum stone, the greatest effect related to the increase in strength at all stages of hardening is achieved when the additive is used in the amount of 10% by weight. Modification of fly ash-cement compositions with a sulfate additive causes an increase in the strength of artificial stone at the age of: 2 days by 14.24; 25.0 and 35.47%; 7 days at 83.18; 43.6 and 40.6%; 28 days for 75.5; 41.6 and 31.5%, respectively, when used in the binder composition of cement 20; 30 and 40 wt.%. Activation of fly ash-cement binder systems with a carbonate additive contributes to the maximum increase in strength when using chalk in the amount of 6 wt.% with the consumption of 20...30 wt.% of OPC. Modification of fly ash-cement compositions with a carbonate component causes an increase in the strength of artificial stone at the age of: 2 days by 18.6...20%; 7 days by 105.12...45.3%; 28 days by 86.6...29.99%, respectively. With a consumption of OPC of 40 wt.%, the optimal amount of carbonate additive is 9 wt.% and causes an increase in the strength of artificial stone at the age of: 2 days by 33.3%; 7 days by 56.63%; 28 days for 43.5%.

The positive effect of the complex modification of the fly ash-cement composition with sulfate and carbonate additives has been proven, and the phase composition of new formations of artificial stone has been studied. It was found that during the simultaneous modification of the fly ash-cement composition, the synthesis of strength is ensured due to the formation of hydration products in the early stages of hardening of ettringite and its analogues with a carbonate and iron component. The increase in strength after 28 days of hardening is provided by the synthesis of the hydration products of low-base calcium hydrosilicates and solid solutions based on ettringite. In the products of the hardening of artificial stone at the late stages of hydration, new formations such as scoutite, epistilbite and compounds of variable composition, similar to hydrogarnets, are also present.

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The presence of hydrosulfoaluminate-type neoplasms in the composition of hydration products and the presence of active mineral additives in its composition, on the one hand, and on the other hand, the contact of cement stone with the environment can cause the appearance of dangerous compounds (such as thaumasite) in hardening systems, the synthesis of which will lead to stress in concrete structure and its destruction.

At the second stage of the work, the stability of solid solutions based on ettringite and the possibility of thaumasite formation during hydration of modified fly ash-cement compositions were investigated. For this purpose, the influence of highly dispersed siliceous additives on the phase composition of hydration products of modified fly ash-cement compositions during their hardening in different temperature conditions (from +3ºC to +20ºC) was studied. The obtained results indicate the absence of thaumasite in the composition of hydration products, and the phase composition of neoplasms is represented by solid solutions. The kinetics of increasing the strength of artificial stone samples based on modified fly ash-cement compositions with the addition of microsilica are shown in Fig. 2.

The analysis of graphical dependences of the change in strength (Fig. 2) shows that a decrease in the hardening temperature has a negative effect on the early set of strength of the artificial stone obtained on the basis of the developed binder, however, when favorable conditions occur, all crystallization processes are accelerated and the samples are intensively recruited strength.

At the third stage of the work, the optimal composition of fine-grained concrete was selected, based on modified fly ash-cement binders, which corresponds to the composition of dry construction mixes (DSTU PB V.2.7-126:2006). The tests were carried out on sample beams measuring 4x4x16 cm. Samples were prepared from a mixture of the required consistency (the sediment of a standard cone of 8...9 cm). The composition of binders and fine-grained concrete is given in table. 1.

When a plasticizer based on polycarboxylates of the trade mark "Melflux" is introduced, the increase in strength at the early stages of hydration (3...7 days) is 3.5...52.4%, and at the design age it reaches only 8.8...70.2%. The use of plasticizing additives containing sulfate groups allows to increase the strength by 3.5...129% at the age of 3...7 days and by 20.1...128.8% after 28 days of hardening.

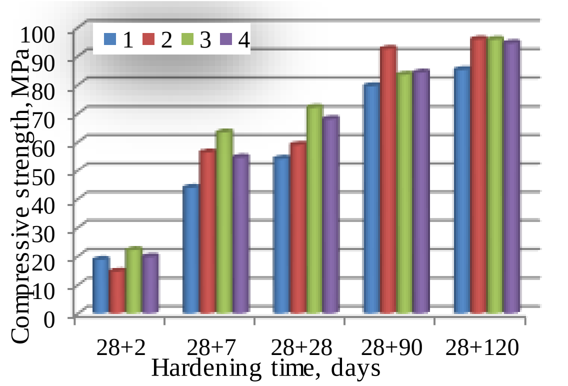

Figure 2. Strength gain of the specimens on the pure OPC basis (1) and fly ash-cement compositions, containing 30 wt.% of OPC, 6 wt.% of chalk and 8 wt.% of anhydrite (2) and with micro silica admixture in quantity 3 wt.% (3) and 5 wt.% (4) after 28 days of hardening at temperature +3…5 ºC and further storing at 20±2ºC during 2, 7, 28, 90 and 120 days.

Table 1 – Composition of binders and fine-grained concretes based on modified fly ash cement

No	Composition, wt.%									
	OPC	fly ash	burned gypsum	chalk	aggregate			admixture		
					quartz sand		granite dropouts 0.63-2.0	Melflux	C-3	Sika
					0-0.5	0.5-1.2				
1	20	11	-	-	28.4	25.6	15	-	-	-
2	10	19.2	1.2	0.6	28.4	25.6	15	-	-	-
3	10	19.2	1.2	0.6	28.4	25.6	15	0.1	-	-
4	10	19.2	1.2	0.6	28.4	25.6	15	0.5	-	-
5	10	19.2	1.2	0.6	28.4	25.6	15	-	0.4	-
6	10	19.2	1.2	0.6	28.4	25.6	15	-	0.8	-
7	10	19.2	1.2	0.6	28.4	25.6	15	-	-	0.1
8	10	19.2	1.2	0.6	28.4	25.6	15	-	-	0.5

The strength of the solution based on the fly ash-cement composition (composition No. 8 of Table 1), modified with the additive "Sika" in the amount of 0.5 wt.% at the design age is 24.6 MPa, while the strength of the base composition without plasticizing additives is 7.5 MPa. The obtained results testify to the positive influence of plasticizing additives on the increase in strength of the artificial stone obtained on the basis of the developed binders. The increase in strength of concretes modified with plasticizing additives can be explained by the formation of a denser structure of cement stone and accelerated synthesis of crystal hydrate neoplasms in compressed conditions, compared to systems without additives.

Therefore, composition No. 8 of the table can be considered optimal according to the criteria of adequate strength at the design age among the developed concretes. 1.

In order to improve the operational properties of the developed fine-grained concrete, the impact of polypropylene fiber on the kinetics of increasing the strength of artificial stone based on composite cement, modified with a polycarboxylate-type additive of the "Sika" brand, was studied. It was established that the maximum strength in compression (27.0 MPa) and bending (5.1 MPa) at the design age is achieved by dispersed reinforced fine-grained concrete modified with fiber in the amount of 0.14 wt.% with a fiber length of 12 mm which ensures the production of concrete whose porosity does not exceed 5%, and water absorption - 4 wt.%.

The durability of the developed concrete compositions was studied by studying their kinetics of strength gain (Table 2), wear resistance, frost resistance, atmospheric resistance, and corrosion resistance. It was established that the introduction of a sulfate-carbonate additive to the composition of fly ash-cement systems contributes to a more uniform set of strength of concrete at all stages of hardening. The increase in strength of modified concrete samples is: at the age of 7 days – 105.88%, at the age of 28 days – 141.17% and at the age of 90 days – 117.53%, the value of compressive strength is 8.05, respectively MPa, 24.6 MPa and 33.5 MPa.

The developed fine-grained concretes based on modified ash-containing binders are characterized by a denser and more uniform structure of artificial stone, which is evidenced by a decrease in the wear rates of concretes based on modified systems by 50% and by 54.8% for dispersed reinforced concrete compared to compositions without additives. -but. The use of dispersed reinforcement allows for a 22.2% increase in the abrasion resistance of ready-made concrete, while its absence - only by 13.8% compared to fine-grained concrete based on OPC.

Table 2 – Strength gain of developed compositions of fine-grained concretes on the modified fly ash-cement basis

Composition on 1t of composition, wt.%						Compressive/flexural strength, MPa, after hardening, days				
OPC	Fly ash	Sulfate admixture	Carbonate admixture	aggregates	fiber (over 100%)	3	7	28	90	365
20	11	-	-	69	-	3.52/ 13.86	4.62/ 22.6	5.12/ 33.4	5.62/ 36.4	6.62/ 38.6
10	21	-	-	69	-	0.31/ 2.44	1.24/ 3.91	2.69/ 10.2	3.62/ 15.4	3.82/ 18.4
10	19.2	1.2	0.6	69	-	1.0/ 5.53	1.79/ 8.05	4.51/ 24.3	5.12/ 33.5	5.62/ 43.4
10	19.2	1.2	0.6	69	0.14	3.6/ 10.4	4.35/ 17.69	5.1/ 27.0	6.62/ 45.4	6.5/ 46.2

Remark: all compositions, modified by Sika admixture, in quantity 0.5 wt% from the binder

After 100 cycles of testing for frost resistance, concrete samples based on fly ash-cement compositions modified with sulfate-carbonate additives increase strength by 16...33%. This indicates the continuation of the hydration processes of the binder and the possibility of obtaining concrete with higher frost resistance (F200 and higher).

In the process of researching the weather resistance of the developed compositions based on modified binders, a stable increase in strength by 13...15% was established after 350 cycles of alternating wetting and drying of fine-grained concrete samples, which indicates the continuation of the processes of structure formation in artificial stone and allows predicting high operational properties of the developed materials.

To implement the technology of complex processing of ash with the aim of obtaining composite materials with increased operational characteristics based on technologies developed at KNUBA and NDIVM, ALIT-BUD LLC produced a batch of fine-grained dispersed reinforced concrete using the technology of dry construction mixtures based on the developed fly ash-cement binding composition, modified with sulfate and carbonate additives, which contained: 58 wt.% fly ash, 30% OPC, 6% calcium carbonate (chalk) and 6 wt.% calcium anhydrite. Fine-grained dispersed-reinforced concrete was prepared on a technological line for the production of dry building mixtures by simultaneous mixing of the initial components in a mixer of the CMC-1 type. The fiber was fed to the mixer manually, since the line does not have equipment for its dosing and feeding in automatic mode. The consumption of components necessary for the production of a dry mixture of fine-grained concrete is given in the table. 3.

Table 3 – Composition on 1t of dry mix to prepare fine-grained concrete for obtain mortars class Ц.I.CT3 according to DSTU B V.2.7-126:2006

Components	Component composition on 1t of fine-grained concrete	
	OPC	Modified fly ash-cement
OPC Type I M500	0.27	0.081
chalk MMC-1	-	0.00162
gypsum anhydride	-	0.00216
fly ash	0.15	0.31
sand	0.327	0.327
granite dropouts	0.25	0.25
superplasticizer	0.001	0.001
water retarder	0.001	0.001
defoamer	0.001	0.001
polypropylene fiber	-	0.6

After the production of fine-grained concrete, in order to study its operational properties and the possibility of using it in the installation of screeds, a series of beam samples with a size of 4x4x16 cm were made based on the proposed material, which were stored at a temperature of +180C and humidity of 55%, and their operational properties were tested. The results of the research are presented in table. 4.

Conducted studies of the technological and operational characteristics of the proposed fine-grained concrete for laying floors confirm the effectiveness of replacing OPC with composite cement. The use of the developed binder in the composition of fine-grained concrete allows to reduce the consumption of OPC without deteriorating its properties, improve adhesion, ease of laying and increase such physical and mechanical characteristics as strength, as well as reduce water absorption and shrinkage.

Table 4 – Comparison of exploitation properties of fine-grained concrete on the OPC basis (basic variant) and on fly ash-cement basis, modified with sulfate-carbonate admixture

Name	Demands DSTU BV.2.7-126:2006			Composition of fly ash concrete on the basis:	
				OPC (reference)	Modified fly ash-cement
Marking	CT1	CT2	CT3		
Slump, cm	Not less than 8			8…9	8…9
Water retention, %	Not less than 95			95	100
Workability, min	Not less than 60			120	120
Compressive strength, MPa					
- 3 days	5	7	10	15.0	12.53
- 28 days	15	25	35	36.8	34.6
Flexural strength, MPa					
- 3 days	2	2.5	3.0	2.5	3.8
- 28 days	3.5	4.5	6.0	5.5	6.8
Adhesion after 28 days, MPa	Not less than 0.5			0.5…0.6	0.6…0.7
Shrinkage, mm	Not less than 8			1.0	0.8
Frost resistance, cycles	-	-	50	75	100

CONCLUSIONS

The composition of the fly ash-cement binder modified with a sulfate-carbonate additive in the presence of a super-plasticizer was developed and optimized. The phase composition of new formations of cement stone, which is mainly represented by solid solutions based on hydrosulfoaluminates and calcium hydrosilicates, was established;

The peculiarities of the structure-formation of the developed binding compositions in the presence of micro-silica at different ambient temperatures were investigated and it was established that its presence does not cause synthesis in the composition of thaumasite hydration products. The phase composition of neoplasms is mainly represented by solid solutions based on ettringite and compounds similar to scoutite, epistilbite, and hydrogarnets.

The use of the developed binder will allow the utilization of waste from the fuel and energy industry in the composition of fine-grained concrete, on the one hand, and on the other hand, it will reduce emissions of carbon dioxide into the atmosphere by reducing the consumption of OPC clinker in the composition of binders.

he developed compositions of fine-grained concrete in terms of their operational characteristics differ little from the properties of concrete based on pure OPC. It is advisable to manufacture them using the technology of producing dry building mixtures with the maximum content of waste from the fuel and energy complex, which will allow saving material and energy resources, including reducing costs for OPC by 20-40%, and the use of such mixtures in the national economy will contribute to improving the environmental situation.

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Дрібнозернисті бетони на основі модифікованих золоцементних в'яжучих речовин з покращеними властивостями

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Анотація. Стаття присвячена дослідженню дрібнозернистих бетонів, на основі модифікованих золоцементних в'яжучих речовин, що містять у своєму складі не менше 55 % за масою золи-винесення. Використання даного в'яжучого дозволить з одного боку утилізувати відходи паливно-енергетичного комплексу у складі дрібнозернистого бетону, а з іншого – зменшить викиди вуглекислого газу в атмосферу за рахунок зменшення витрати

портландцементного клінкеру в складі в'яжучих речовин.

В ході досліджень доведено позитивний вплив комплексної модифікації золоцементної композиції сульфатними та карбонатними добавками та вивчено фазовий склад новоутворень штучного каменю. Встановлено, що при одночасній модифікації золоцементної композиції синтез міцності забезпечується за рахунок утворення у складі продуктів гідратації на ранніх стадіях твердіння етрингіту та його аналогів з вмістом карбонатної та залізистої складової.

Досліджено експлуатаційні та технологічні властивості розроблених в'яжучих речовин та бетонів на їх основі. В процесі дослідження атмосферостійкості розроблених складів на основі модифікованих в'яжучих речовин встановлено стабільний приріст міцності на 13…15% після 350 циклів навперемінного зволоження та висушування зразків дрібнозернистого бетону, що свідчить про продовження процесів структуроутворення у штучному камені та дозволяє прогнозувати високі експлуатаційні властивості розроблених матеріалів.

Встановлено, що розроблені дрібнозернисті бетони на основі модифікованих золовмісних в'яжучих речовин відрізняються більш щільною та однорідною структурою штучного каменю

Про це свідчить зниження показників стираності бетонів на основі модифікованих систем на 50% та на 54,8% для дисперсноармованого бетону порівняно з бездобавочними композиціями відповідно.

Вивчено довговічність розроблених складів бетонів шляхом дослідження їх кінетики набору міцності, зносо-, морозо-, атмосферо- та корозійної стійкості. Встановлено, що введення сульфатно-карбонатної добавки до складу золоцементних систем сприяє більш рівномірному набору міцності бетонів на всіх етапах тверднення. Приріст міцності зразків модифікованого бетону становить: у віці 7 діб – 105,88%, у віці 28 діб – 141,17% та у віці 90 діб – 117,53%, значення міцності при стиску - відповідно 8,05 МПа, 24,6 МПа та 33,5 МПа.

Ключові слова: дрібнозернистий бетон, зола, пластифікуючі добавки, довговічність, модифіковані золоцементні в'яжучі речовини.