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DEVELOPMENT OF NANOMODIFIED RAPID HARDENING FIBER-REINFORCED CONCRETES FOR SPECIAL-PURPOSE FACILITIES

Розроблено наномодифіковані швидкотверднучі бетони для фортифікаційних споруд з врахуванням принципів композиційної побудови, які ґрунтуються на багаторівневому модифікуванні структури органомінеральним наномодифікатором та дисперсними волокнами. Досліджено кінетику тверднення, особливості порової структури, деформативні властивості та стійкість до дії високошвидкісного удару швидкотвердючих фібробетонів, модифікованих органо-мінеральними добавками на основі полікарбоксилатного суперпластифікатора, мікро- і нанокремнезему

Ключові слова: наномодифікування, дисперсне армування, органо-мінеральна добавка, швидкотверднучий бетон, деформативні властивості, високошвидкісний удар

Разработаны наномодифицированные быстротвердеющие бетоны для фортификационных сооружений с учетом принципов композиционного построения, основанных на многоуровневом модифицировании структуры органо-минеральным наномодификатором и дисперсными волокнами. Исследована кинетика твердения, особенности поровой структуры, деформативные свойства и устойчивость к действию высокоскоростного удара быстротвердеющих фибробетонов, модифицированных органо-минеральными добавками на основе поликарбоксилатного суперпластификатора, микро- и нанокремнезема

Ключевые слова: наномодифицирование, дисперсное армирование, органо-минеральная добавка, быстротвердеющий бетон, деформативные свойства, высокоскоростной удар

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1. Introduction

Concrete is used for the construction of fortifications, hangars, protective shelters, dugouts, firing positions and other types of specially designed structures subjected to impact loads. This is predetermined by its increased mechanical properties, a low coefficient of penetration compliance, discharge compliance, and a low required protective thickness from bullet action [1, 2].

There are often high requirements set for the time allocated for construction and repair of building structures. That is why such construction or repair works require using rapid-hardening concrete with necessary technical and technological properties. At the same time, a disadvantage of normal-weight high-strength concretes is low impact strength and increasing sensitivity to cracking and brittleness, which manifests itself by reducing plastic deformations in concrete under load. As a result, boundary loads destroy high-strength concrete almost instantaneously. Such a feature poses a threat to safe operation and reliability of buildings and structures when loads in compressed elements are exceeded.

In this regard, the actual task is the development of modern building composites, which have high indicators of early and final strength, increased level of crack resistance, resistance to various types of power influences and stable operational properties throughout a life cycle. The application of such concretes makes it possible to perform fast repair and renovation works, construction of protective structures of fortifications and shelters both for protection of the personnel of the armed forces and for civil protection of population.

2. Literature review and problem statement

Primarily, regulated compressive strength determines the resistance to destruction of building structural materials. However, the ability of a concrete structure to prevent formation, growth, and a spread of cracks, as well as the ability to control mentioned processes ensure the effective operation and durability of concrete structures under conditions of impact action [3].

According to authors of paper [4], concrete has a hierarchically organized multilevel structure. A cause of structural heterogeneity is the presence of discrete inclusions placed in a continuous matrix and initial defects at various scale levels. Accumulation of cracks and formation of a main crack begins from them at a load including an impact load. Given this, the authors made a conclusion about the need to eliminate structural defects, to increase static strength of concrete to ensure the ability to withstand extreme actions of external loads [5]. However, high strength of concrete worsens its brittle nature of destruction and increases sensitivity to cracking.

It is possible to apply metal reinforcement to eliminate the mentioned disadvantages. Authors of papers [6–10] confirm the expediency of using reinforced concrete as a constructive material for reinforcements and protective structures for various underground shelters and hangars. However, properties of reinforced concrete depend on the level of the stressed-deformed state significantly. Inhomogeneity, anisotropy, essential nonlinearity, cracks formation of reinforced concrete appear already at the early stage of formation of a structure. Papers show that a difference between deformation properties of concrete and reinforcement causes a redistribution of tension from concrete to reinforcement with increase in a load level [6–8]. This leads to a reduction in integral stiffness of cross sections and internal forces redistribution between parts of a construction at structural changes in a system. Based on the conducted studies, authors of paper [10] recommend using concrete slabs reinforced with double mesh, transverse reinforcement or a whole steel sheet for structures operating under a high-velocity impact. This circumstance relates to the over-consumption of steel reinforcement that leads to an increase in energy intensity and the structure cost.

Papers [11–15] propose methods for modification and improvement of a structure to overcome problems of control of cracks formation and compensation for defects of concrete, such as low tension strength and high brittleness. Such methods are associated with the introduction of new structural elements that block the development of cracks in concrete, specifically viscoelastic components and dispersed reinforcing fibers.

Authors of work [11] developed and applied steel fiber concrete with a compressive strength of 80–100 MPa. They established that the use of steel fiber concrete makes it possible to increase crack resistance of structures by 1.5 times [12]. However, an important problem when using steel fiber concrete is a possibility of formation of so-called «hedgehogs» and uneven distribution of steel fiber. It requires applying special devices for a uniform supply of fibers to a concrete mixture, as well as using forced mixers with high energy consumption, which leads to a rise in the price of concrete.

An increase in stiffness parameters, strength, and energy characteristics of crack resistance of high-strength concrete [13, 14] confirm the expediency of a disperse reinforcement with synthetic fiber, which improves deformative properties. According to results of paper [15], it is possible to observe a main reinforcing effect of introduction of polypropylene fibers in a subcritical stage of destruction from the moment of development of a main crack to its complete defragmentation. Despite the practical significance of such results, the paper did not consider the kinetics of hardening of the studied fiber-reinforced concrete.

Work [16] shows that it is possible to solve the problem of cracks inhibition at one structural level only at traditional disperse reinforcement. However, the hierarchy of cracks formation and an aggregate of cracks indicates the presence of defects of various sizes in concrete and belonging to the corresponding scale level – nano-, sub-micro, micro, meso- and macro levels. According to authors of paper [17], it is possible to obtain disperse reinforced concrete with improved operational properties by a multilevel modification of its structure by additives of various functional purposes in combination with reinforcing fibers of the so-called hybrid reinforcement. Reinforcing elements are mineral fibers at the macro- and the mesoscale levels, and at the microscale level – they are highly dispersed mineral additions [18]. The disadvantage of fiber concrete made of the mentioned composition is that the concrete reinforcement occurs at the macro- and the micro-levels without changes in a structure of a cement stone at the nanolevel.

A new direction appeared in the disperse reinforcement of concrete with the development of nanotechnology. It is a dynamic disperse self-reinforcement of a cement stone [19]. It implies introduction of dispersion-strengthening additives such as basaltic microfiber, carbon microfibers modified with fulleroid, nanotubes and astralenes [20–22]. In this case, carbon nanotubes act as «nano-reinforcement» due to a high tension strength [20]. There is a significant change in properties of a cement matrix when using nanotubes with a diameter close to the thickness of C-S-H layers. At the same time, compressive and bending strength increases and cracking reduces, especially in surface layers of high-performance cement composites [20, 21]. In addition, papers [19, 22] note that carbon nanomaterials can change the microstructure of a cement matrix by increasing a content of calcium hydrosilicates of high density and reducing porosity. However, the introduction of carbon nanomaterials may cause difficulties from a practical point of view due to the problems of homogeneous distribution in the medium of a cement matrix and determination of the optimal amount of additives.

In order to increase deformation characteristics of cementing materials, authors of work [23] proposed the introduction of energetically active ultra- and nanofine active mineral additives. Nanoparticles of additives have high surface energy and can change physical and chemical interactions in concrete significantly. They play a role of crystallization centers of hydrosilicates in a pore space between cement grains. At the same time, they provide an effect of a filler at the initial period and the early pozzolan reaction with the formation of nanosized scale fibrous C-S-H phases [24, 25]. However, one should note that ultrafine additives have high dispersion, which causes increased water demand and reduced workability of concrete mixtures. Work [26] shows that using organo-mineral nanocomposites – materials of mineral and polymeric components based on silica additives of various origin and polycarboxylate superplasticizers is effective for the production of high strength cement stone. However, there are no detailed studies on features of the early formation of cement-silica-based compositions, as well as their crack resistance.

Therefore, there are reasons to assume that insufficient understanding of the influence of a multilevel modification of a concrete structure on the hardening kinetics; deformation parameters and behavior under an action of high-velocity impact necessitate studies into development of concretes for special-purpose facilities.

3.The aim and objectives of the study

The objective of present study is the development of nanomodified rapid-hardening fiber-reinforced concretes with regulated operational properties, specifically with high resistance to a high-velocity impact for special purpose facilities.

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

– to investigate influence of complex nanomodifier and disperse reinforcement on the kinetics of strength development of nanomodified fiber-reinforced concretes based on highly flowing concrete mixtures;

– to determine parameters of a pore structure and deformation properties of nanomodified fiber-reinforced concretes;

– to determine behavior of developed nanomodified rapid-hardening fiber-reinforced concretes under an influence of a high-velocity impact.

4. Materials and methods to study rapid-hardening nanomodified fiber-reinforced concretes

4. 1. Examined materials and equipment used in the study

The development of rapid-hardening high-strength concrete as a composite polystructure material involves a multistage organization where a structure of any lower level is an integral element of higher-level structural in homogeneities based on «composite in composite» principle. We used common Portland cement with high early strength CEM I 42.5R PJSC Ivano-Frankivskcement (Ukraine) according to EN 197-1 based on a clinker of mineralogical composition, wt. %: C_3S – 64.20; C_2S – 12.88; C_3A–5.65; C_4AF – 14.62, for the development of nanomodified rapid-hardening fiber- reinforced concretes. According to the particle size distribution of Portland cement CEM I 42.5R (Table 1), the content of 10.0; 50.0 and 90.0 wt. % correspond to particles of 5.75; 19.42 and 56.29 μm, respectively.

We used natural quartz sand from Zhovkva deposit with a fineness modulus of M_F=2.1 as a fine aggregate for concrete; and granite crushed stone of 5–20 mm fraction as a coarse aggregate.

We used concrete of C 35/45 strength class of nominal composition 1:1.35:2.71 with the consumption of CEM I 42.5R 430 kg per 1 m^3 of concrete mixture as control. We used an organo-mineral nano-additive to provide polystructure modification of a concrete matrix (nanomodified concrete – NC). As a admixture of a plasticizing action, we used a superplasticizer of the new generation based on polycarboxylates with nanodesigned chains MasterGlenium Ace 430 (PCE). This makes it possible to achieve a high water-reducing effect at obtaining a given workability of concrete mixtures. A rational design of a dense matrix is based on the principle of optimized filling of the Portland cement system with a provision of gap-graded particle size distribution with a use of ultrafine mineral additives that complement the granulometric composition of Portland cement [27]. As mineral components of organo-mineral nanomodifier, we used an ultrafine additive – silica fume (SF) of Elkem Microsilica Grade 940-U trademark containing SiO_2 of 94.71 %, as well as Aerosil-380 (NS) nano-silica containing 99.8 % of SiO_2. According to the granulometric analysis (Table 1), microsilica contains 50 % of active particles of nanometric size (less than 0.15 μm) and has specific surface S_{sa} = 15,000 m^2/kg. The specific surface of NS additive is 380±30 m^2/g with an average particle size of 4–7 nm.

Table 1

Particle size distribution of Portland cement and mineral additives

Material	D_{10}, μm	D_{50}, μm	D_{90}, μm
CEM I42.5R	5.75	19.42	56.29
Silica fume	0.07	0.15	0.30
Aerosil-380	0.006	0.008	0.015

We carried out disperse reinforcement at the macro- and the meso-scale levels with alkaline-resistant modified basalt fiber (36 mm in length, 18 μm in diameter) to increase an impact viscosity of nanomodified concrete. The degree of disperse reinforcement of fiber concrete (FRC) and nanomodified rapid-hardening fiber reinforcement concrete (NFRC) with basaltic fiber was 1.0 %.

We determined a particle size distribution of Portland cement and ultrafine mineral additives using the laser granulometer Mastersizer 3000.

4. 2. Procedure for determining the properties of samples

We determined consistence of modified concrete mixtures by the slump test according to EN 12350-2, as well as by flow table test according to EN 12350-5. We carried out tests for compressive strength of control and nanomodified concretes on sample-cubes of 10×10×10 cm after 1, 2, 7 and 28 days. We carried out the evaluation of defects of a surface layer of the developed composites to their porosity parameters. We studied peculiarities of a porous structure of nanomodified concrete according to the kinetics of water absorption of samples of 7.07×7.07×7.07 cm, which hardened for 28 days. We used the method of discrete weighing of pre-dried samples carried out after 0.25; 1.0 and 24 hours after immersion in water. Absorption curves of polycapillary materials are approximated by a three-parameter exponential function of type:

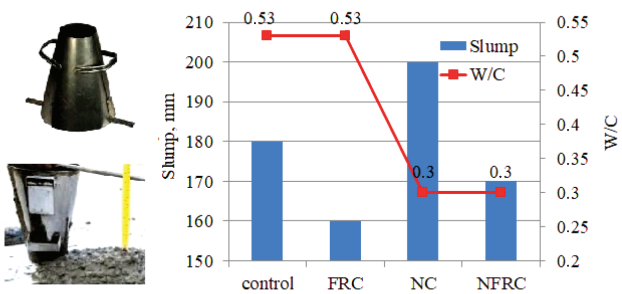
$$W_t = W_{\max}\left[1 - e^{-\overline{(\lambda t)}\alpha}\right],$$

where W_t is the water absorption of a sample at t time in percentage by weight; $W_{\max}$ is the water absorption of a sample determined after 24 hours in a percentage by weight; t is the time of water absorption, hours; λ_1 is a parameter of an average size of open capillary pores determined by nomograms [28]; α is a parameter of homogeneity of sizes of open capillary pores determined by nomograms [28].

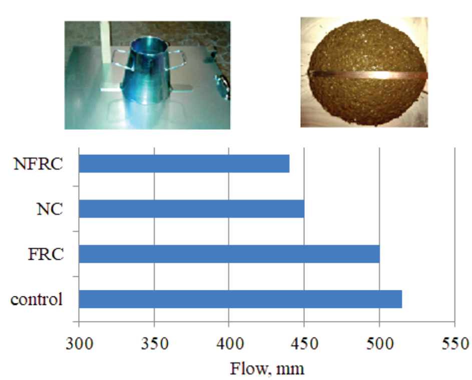
After 28 days of hardening, we used samples of developed nanomodified fiber-reinforcement concretes to determine deformation properties, and we also exposed them to a high-velocity impact. We determined a prism strength, an elasticity modulus, and the Poisson coefficient of nanomodified rapid-hardening concretes on sample-prisms of 10×10×40 cm at a load level of 30 % from the destructive one. We fired samples of concrete with single shots from a distance of 25 m using ordinary bullets of 5.45 caliber from a Kalashnikov assault rifle for the implementation of impact tests. The initial velocity of a bullet was 915 m/s with kinetic energy at the time of departure of about 2.8 kJ. We carried out a microscopic analysis of the surface of samples of control and nanomodified concrete after a high-velocity impact using a portable optical microscope USB 1.3 MPix 25x-500x with CS02-500 stand.

5. Results of studying the parameters of nanomodified rapid-hardening concretes reinforced with disperse fibers

According to the results of workability determination, we established that the concrete mixture of the control composition has a parameter of a slump of 180 mm that meets the requirements for the slump class S4 (Fig. 1, *a*). We should note that the introduction of organo-mineral SF+NS+PCE nanomodifier provides a significant water-reducing effect ($\Delta W/C = 43.4$ %) when providing workability parameters of NC and NFRC concrete mixtures for the slump class of S4. We also should note that a use of disperse reinforcing elements causes some decrease in workability of concrete mixtures ($S = 160$–170 mm).



a



b

Fig. 1. Workability of concrete mixtures: *a* — slump test; *b* — flow table test

As we can see from Fig. 1, *b*, workability parameters determined by flow table test change more. Thus, the control concrete has a flow of 515 mm, which corresponds to F4 class. According to the flow parameter, nanomodified NC and NFRC concrete mixtures have high viscosity and relate to F3 class ($F = 440$–450 mm).

According to the results of determining strength at the design age, the concrete of the control composition corresponds to the strength class C 35/45 ($f_{cm28} = 52.6$ MPa), and has a medium strength development ($f_{cm2}/f_{cm28} = 0.42$) (Fig. 2). At disperse reinforcement with basalt fiber, the strength of concrete increases by 6–14 % and meets the requirements for concrete with medium strength development ($f_{cm2}/f_{cm28} = 0.46$). Nanomodification of concrete by organo-mineral nano-additive provides growth of its strength at the early age and after 28 days. Thus, the strength of nanomodified concrete NC without fibers after 2 days is 78.1 MPa, which exceeds by 3.6 times the strength of concrete with control composition. The compressive strength of such concrete after 28 days is 111.2 MPa, which corresponds to the strength class C 80/95.

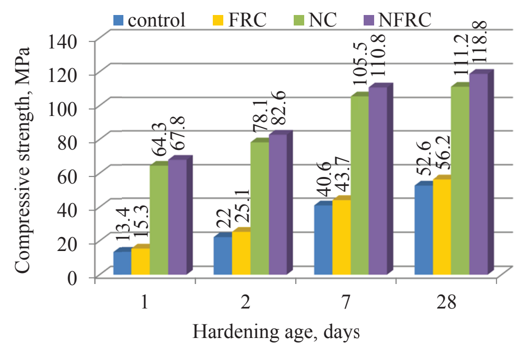


Fig. 2. Compressive strength of nanomodified fiber-reinforced concretes

The early strength of fiber-reinforcement concrete increases by 5.7–12.6 % compared to non-reinforced nanomodified concrete. The strength of nanomodified fiber-reinforced concrete is 118.8 MPa after in 28 days, which corresponds to strength class C 90/105. Nanomodified concretes NC and NFRC correspond to the requirements for concrete with a rapid strength development according to the specific strength parameter ($f_{cm2}/f_{cm28} = 0.7$) and are categorized as high strength concrete.

According to experimental data, we obtained curves of water absorption kinetics of samples of control and nanomodified rapid-hardening concrete (Fig. 3), which have a smooth character of an exponential type. At the same time, concrete of the control composition has a higher velocity of water saturation in the initial period compared with nanomodified concretes.

As we can see from Table 2, nanomodification of concrete by an organo-mineral additive makes possible to adjust parameters of both integral and differential porosity (parameters of an average pore size – λ_1 and homogeneity of pore sizes α). Thus, volumetric water absorption of nanomodified NC concrete and NFRC fiber-reinforced concrete, which characterizes open capillary porosity (W_o), reduces by 6.2 times compared with control.

An analysis of differential porosity parameters showed that the pore homogeneity parameter is 0.55 by the size of the control concrete and is higher than the parameter of nanomodified composites. However, a size of the pores shifts to the macrocapillary region, as shown by the mean pore size of 2.62 and the low microporosity parameter (K_m=0.47). The introduction of basalt fiber to concrete control composition improves a pore structure substantially. The parameter of an average pore size of NC nanomodified concrete and NFRC fiber-reinforced concrete reduces to 0.53 and 0.50, respectively. The number of macropores in nanomodified concrete reduces, as evidenced by the increased microporosity parameters of 0.77 and 0.85, respectively, for NC and NFRC.

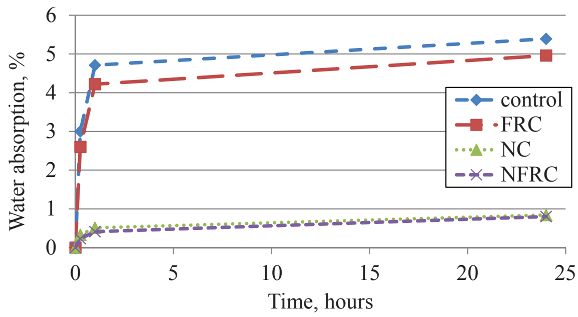


Fig. 3. Kinetics of water absorption of nanomodified concretes

Table 2

Basic parameters of a porous structure of nanomodified concretes

Concrete marking	Water absorption, %			Microporosity coefficient, K_m	Parameter of average size of pores, λ_1	Parameter of homogeneity of pores by size, α
	weight, W_m	volume, W_o	equilibrium, W_p			
control	5.4	12.4	2.54	0.47	2.62	0.55
FRC	4.9	11.4	2.14	0.44	2.48	0.52
NC	0.8	2.0	0.74	0.77	0.53	0.41
NFRC	0.8	2.0	0.65	0.85	0.50	0.45

The results of study into deformation properties of the control concrete indicate that its prism strength is 40.3 MPa, while the prism strength of NC nanomodified concrete of isoworkability mixtures increases to 86.0 MPa (Table 3). The prism strength of nanomodified rapid-hardening concrete increases to 96.2 MPa at fiber reinforcement and providing a water-reducing effect. The modulus of elasticity, which characterizes a degree of stiffness of material, of nanomodified NC concrete increases by 1.5 times compared with the control concrete based on highly flowing mixtures. Disperse reinforcement of nanomodified concrete provides an increase of its modulus of elasticity by 7.6 % compared to the non-reinforced one and is 63.9 GPa, while the Poisson's coefficient is equal to 0.17.

According to Table 3, the displacement modulus of nanomodified concrete and fiber concrete increases by 1.5–1.6 times in comparison with the control one. Nanomodification and disperse reinforcement of a control concrete matrix also gives possibility to increase ability of a material to resist a volume change that is not accompanied by a change in a shape, as evidenced by an increase in the modulus of volume elasticity.

A breakdown damage occurs under the action of a impact wave of a high-velocity impact in a sample of the control concrete (Fig. 4, *a*). A pronounced zone of radial cracks appears around a crater of an impact. It corresponds to the thickness of the sample. The microstructural analysis of concrete samples confirms the presence of deep cracks with the opening width of more than 5 mm (Fig. 4, *b*).

Table 3

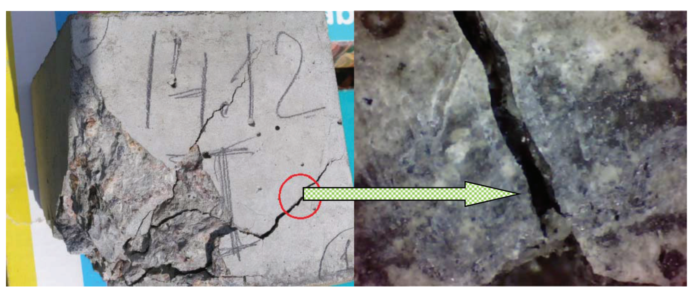
Parameters of deformability of concretes

Concrete marking	Prism strength, MPa	Elasticity modulus, GPa	Poisson's ratio	Shear modulus, GPa	Modulus of volume elasticity, GPa
control	40.3	39.4	0.18	16.7	20.5
FRC	41.5	38.6	0.18	16.3	20.1
NC	86.0	59.4	0.17	25.4	30.9
NFRC	96.2	63.9	0.17	27.3	33.3

Samples of nanomodified concrete reinforced with disperse fibers have separate broken particles caused by a concentrated bullet impact after the action of a high-velocity impact. A destruction load of axial compression and bending went in three main directions. Cracks on a surface of the intact part of the cube are almost absent (Fig. 5, *a*).

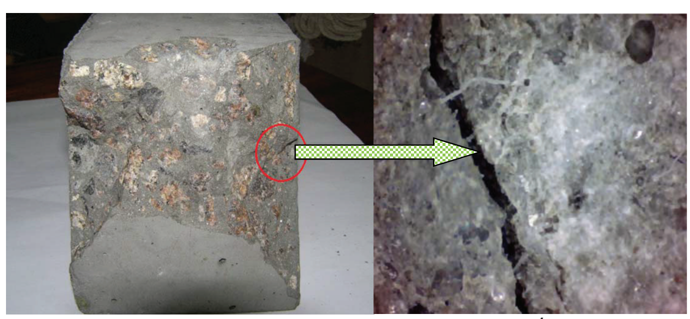
The results of microscopic investigations of a surface of samples of nanomodified rapid-hardening concrete reinforced with a disperse fiber show a homogeneous structure of a hardened cementing matrix (Fig. 5, *b*).

At the same time, there is a strengthening of a contact area between cement matrix and a aggregate, as well as versatile orientation and even distribution of reinforcing fibers in a cement matrix.



a *b*

Fig. 4. Sample-cubes of concrete of the control composite after tests for a high-velocity impact: *a* – general view; *b* – microstructure



a *b*

Fig. 5. Sample-cubes of nanomodified fiber-reinforced concrete after tests for a high-velocity impact: *a* – general view; *b* – microstructure

6. Discussion of results of studying the properties of nanomodified rapid-hardening fiber-reinforced concrete

We showed the possibility of obtaining high-tech concrete mixture. It follows from the obtained results (Fig. 1) when determining the effectiveness of nanomodification of concrete by the organo-mineral SF+NS+PCE additive. We established a high water-reducing effect of the organo-mineral nano-modifier ($\Delta W/C = 43.4$ %) with the provision of the slump class of S4 of a concrete mixture, because of a high dispersant action of a polycarboxylate-based superplasticizer. We should note that a use of reinforcing elements leads to a decrease in consistence of concrete mixtures from 200 to 170 mm. Apparently such mechanism of influence is related to a structure of a mixture with fibers, a growth of a phase separation surface and a need to increase an amount of water for wetting, an increase in internal friction of components of a matrix in the presence of fibers.

The study showed that the introduction of an organo-mineral nanomodifier causes an increase in the initial density of a system, which determines a growth in the number of contacts and acceleration of structure formation processes. We can explain this with implementation of a water-reducing effect of a superplasticizer, optimization of packing of particles of a cementing system by ultrafine mineral additives (micro- and nano-silica) [27]. A content of nanofractions in the composition of mineral additives leads to development of excess surface energy and is crucial for achievement of technological and technical macro-effects. The mechanism of increase in the strength of nanomodified concrete works due to the obtaining of an additional number of submicro-reinforcing hydrosilicate phases in the early stages of hydration (the phenomenon of «self-reinforcement») as a result of the interaction of ultra- and nanofine particles of a mineral additive with $Ca(OH)_2$ [29, 30]. In this regard, an interest is estimation of strength of nanomodified fiber-reinforced concretes in the early periods given in Fig. 2. After 1 and 2 days, the strength of nano-modified fiber-reinforced concrete NFRC is 67.8 and 82.6 MPa, respectively, with a strength ratio value after 1 day – $f_{cm1}/f_{cm28} = 0.57$ and after 2 days – $f_{cm2}/f_{cm28} = 0.70$, which meets the requirements for ultra-rapid hardening concretes. The strength of nanomodified rapid hardening fiber-reinforced concrete after 28 days is 118.8 MPa.

The results of the test of strength are well correlated with the results of determination of parameters of a pore structure of the control and the nanomodified concretes. The number of macropores in nanomodified concretes decreases, as evidenced by increased microporosity parameters (0.77–0.85), open porosity at the same time decreases in 6.2 times. Increasing homogeneity, reducing defects of the structure of a surface layer and a transition zone of nanomodified concrete by reducing a number and a size of pores that are the initiators of a growth of a stress leads to an increase in stiffness of a matrix component. In this case, the elastic modulus increases from 39.4 GPa for the control concrete and to 59.4 GPa for the nanomodified concrete. Reinforcement with basalt fibers, which have a high modulus of elasticity, provides further growth in deformation characteristics. Thus, the modulus of elasticity of nanomodified fiber-reinforced concrete rises by 7.6 % compared to non-reinforced one.

An analysis of the results of the tests of concretes under the influence of a high-velocity impact indicates that stratification of the control concrete passes through a surface of a contact zone «cement matrix – aggregate» and is determined by a brittle destruction.Coarse aggregate remains almost intact indicating its weak adhesion with a cement matrix. We should note that the breaking off of separate particles of nanomodified and disperse reinforced concretes took place not on a contact surface of a cement matrix and an aggregate, but along the area of the greatest impact load, and grains of crushed stone were destroyed in the direction of the force. At the same time there is a point breakdown of a nanomodified cement matrix, and the bulk of a cube remains solid and almost intact. This indicates an increased impact strength of the developed nanomodified rapid-hardening fiber-reinforced concretes and the ability of a structure to withstand tension and compressive stresses that arise at impact waves action.

We can consider the obtained results of the tests of the developed nanomodified rapid-hardening fiber-reinforced concretes as expedient ones from a practical point of view, as they give possibility to build fortification, protective and other types of constructions of a special purpose in short terms. They ensure their effective operation under an action of a high-velocity impact.

From a theoretical point of view, they make possible to state the establishment of a set of principles for multilevel modeling of a structure of rapid-hardening fiber-reinforced concrete with increased impact viscosity, including the nano-, micro-, meso- and macroscale levels. And these are certain advantages of the study. It is advisable to carry out further studies on the effect of a high-velocity impact on nanomodified rapid-hardening concretes reinforced with different types of fibers at an early age.

7. Conclusions

1. We developed nanomodified rapid-hardening fiber-reinforced concretes resistant to a high-velocity impact based on the study into strength, porosity and deformation properties. We established that nanomodification of concrete by organo-mineral additives based on micro, nano-silica and polycarboxylate superplasticizer ensures obtaining of highly-flowing fiber-reinforced concrete mixtures of slump class S4 with a significant water-reducing effect $\Delta W/C = 43.4\%$. Peculiarities of the acceleration of kinetics of hardening of nanomodified concrete are optimization of packing of particles of a cementing system, provision of initial density, stimulation of nucleation processes in an intergranular space due to heterogeneous nucleation, acceleration of pozzolana reactions. Nanomodified fiber-reinforced concrete relates to ultra-rapid-hardening high strength concretes by the strength development ($f_{cm1}/f_{cm28} = 0.74$ and $f_{cm2}/f_{cm28} = 0.7$) and 28 days-strength ($f_{cm28} = 118$ MPa).

2. We established that using the principles of nanomodification with organo-mineral modifiers and disperse reinforcement, we provide optimization of a structure of nanomodified concretes on nano-, micro-, meso- and macro levels, which manifests itself in formation of a dense, finely-porous, less defective matrix. An increase in the number of contacts, reduction in size and the number of initial defects such as pores, microcracks, an increase in the homogeneity of nanomodified concrete leads to an increase in deformation characteristics. Thus, the stiffness of nanomodified fiber-reinforced concretes increases by 1.5–1.6 times, which makes it

possible to withstand greater stresses at a constant value of relative deformations.

3. An increase in the density of a cement matrix, formation of products of hydration of a fiber habitus, strengthening of a contact zone between cement stone and aggregate ensure resistance of nanomodified fiber-reinforced concretes to the action of a high-velocity impact at the micro level. At the macro- and meso-levels, we achieve inhibition of cracks and efficiency of a system operation under the action of impact loads by spatial three-dimensional reinforcement with a dispersed fiber.

References

1. Savickiy N. V., Nikiforova T. D. Ukreplennye rayony i mobil'nye blok-posty dlya oborony territorii i zashchity lichnogo sostava v zone provedeniya antiterroristicheskoy operacii // Mistobuduvannia ta terytorialne planuvannia. 2016. Issue 61. P. 92–100.
2. Perspektyvy zastosuvannia pryrodnykh ta shtuchnykh materialiv dlia dodatkovoho zakhystu inzhenernykh ukriplen ta sporud / Shabatura Yu. V. et. al. / Perspektyvy rozvytku ozbroiennia ta viyskovoi tekhniky sukhoputnykh viysk. Lviv: NASV, 2017. P. 291.
3. Murthy A., Palani G., Iyer N. Impact Analysis of Concrete Structural Components // Defence Science Journal. 2010. Vol. 60, Issue 3. P. 307–319. doi:10.14429/dsj.60.358
4. Analiz mekhanizmiv poetapnoi orhanizatsiyi mikrostruktury betoniv / Korobko O. O. et. al. // Resursoekonomni materialy, konstruktsiyi, budivli ta sporudy. 2013. Issue 25. P. 76–83.
5. Rana N., Tiwari A., Srivastava A. K. High performance concrete and its applications in the field of civil engineering construction // International Journal of Current Engineering and Technology. 2016. Vol. 6, Issue 3. P. 982–985.
6. Ubaidullaiev Yu. N. Model vyboru ratsionalnoi oriyentatsiyi armatury v zalizobetonnykh obolonkovykh konstruktsiyakh fortyfikatsiynykh sporud // Tsentr voienno-stratehichnykh doslidzhen Natsionalnoho universytetu oborony Ukrainy. 2013. Issue 2 (48). P. 96–99.
7. Afanasieva L. V. Zalizobetonni konstruktsiyi v umovakh vysokoshvydkisnoho udaru // Mistobuduvannia ta terytorialne planuvannia. 2016. Issue 61. P. 108–113.
8. 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
9. 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
10. Skoruk O. Mitsnist ta trishchynostiykist stalefibrobetonnykh plyt, opertykh po konturu pry povtornykh navantazhenniakh // Pidvodni tekhnolohiyi. Promyslova ta tsyvilna inzheneriya. 2016. Issue 3. P. 83–93.
11. Proektuvannia skladiv fibrobetonu iz zastosuvanniam eksperymentalno-statystychnykh modelei / Dvorkin L. Y. et. al. // Suchasni tekhnolohiyi ta metody rozrakhunku v budivnytstvi. 2016. Issue 5. P. 45–58.
12. Wille K., El-Tawil S., Naaman A. E. Properties of strain hardening ultra high performance fiber reinforced concrete (UHP-FRC) under direct tensile loading // Cement and Concrete Composites. 2014. Vol. 48. P. 53–66. doi:10.1016/j.cemconcomp.2013.12.015
13. Interaction of mineral and Polymer Fibers with Cement Stone and their Effect on the Physical-Mechanical Properties of Cement Composites / Plugin A. A. et. al. // International Journal of Engineering Research in Africa. 2017. Vol. 31. P. 59–68. doi:10.4028/www.scientific.net/JERA.31.59
14. Kyrychok V. I., Kryvenko P. V., Huziy S. H. Dyspersne armuvannia luzhnykh aliumosylikatnykh pokryttiv dlia zakhystu betonu vid koroziyi // Budivelni materialy ta vyroby. 2017. Issue 3-4. P. 30–33.
15. Solodky S. Y., Turba Y. V. Crack resistance of concrete, reinforced with fiber of different types // 18 Internationale Baustofftagung. Weimar: Ibausil, 2012. P. 0561–0567.
16. Korotkih D. N. Dispersnoe armirovanie struktury betona pri mnogourovnevom treshchinoobrazovanii // Stroitel'nye materialy. 2011. Issue 3. P. 96–99.
17. Modeling of Falling Weight Impact Behavior of Hybrid Basalt/Flax Vinylester Composites / Boria S., Pavlovic A., Fragassa C., Santulli C. // Procedia Engineering. 2016. Vol. 167. P. 223–230. doi:10.1016/j.proeng.2016.11.691
18. Vysokomitsni samoushchilniuvalni betony na osnovi dyspersno-armovanykh tsementuiuchykh system / Sanytskyi M. A., Marushchak U. D., Kirakevych I. I., Stechyshyn M. S. // Stroitel'nye materialy i izdeliya. 2015. Issue 1. P. 6–9.
19. Falikman V. R. Nanomaterialy i nanotekhnologii v sovremennyh betonah // Promyshlennoe i grazhdanskoe stroitel'stvo. 2013. Issue 1. P. 31–34.
20. 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
21. Pushkarova K., Sukhanevych M., Martsikh A. Using of Untreated Carbon Nanotubes in Cement Compositions // Materials Science Forum. 2016. Vol. 865. P. 6–11. doi:10.4028/www.scientific.net/msf.865.6
22. Tolmachev S. N., Belichenko E. A. Perspektivy primeneniya nanochastic v betonah transportnogo naznacheniya // Budivelni materialy ta vyroby. 2017. Issue 1-2. P. 38–41.
23. Sakulich A. R., Li V. C. Nanoscale characterization of engineered cementitious composites (ECC) // Cement and Concrete Research. 2011. Vol. 41, Issue 2. P. 169–175. doi:10.1016/j.cemconres.2010.11.001
24. 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
25. Influence of the new method of nanosilica addition on the mechanical properties of cement mortars / Horszczaruk E., Mijowska E., Cendrowski K., Sikora P. // Cement Wapno Beton. 2014. Issue 5. P. 308–316.

26. Pushkarova K. K., Kaverin K. O., Kalantaevsky D. O. Research of high-strength cement compositions modified by complex organic-silica additives // Eastern-European Journal of Enterprise Technologies. 2015. Vol. 5, Issue 5 (77). P. 42–51. doi: 10.15587/1729-4061.2015.51836
27. Research of nanomodified portland cement compositions with high early age strength / Marushchak U., Sanytsky M., Mazurak T., Olevych Y. // Eastern-European Journal of Enterprise Technologies. 2016. Vol. 6, Issue 6. P. 50–57. doi:10.15587/1729-4061.2016.84175
28. Leshchinskiy M. Yu. Ispytanie betona: sprav. pos. Moscow: Stroyizdat, 1980. 360 p.
29. Marushchak U., Sanytsky M., Olevych Y. Effects of elevated temperatures on the properties of nanomodified rapid hardening concretes // MATEC Web of Conferences. 2017. Vol. 116. P. 01008. doi:10.1051/matecconf/201711601008
30. Marushchak U., Sanytsky M., Sydor N. Design of rapid hardening engineered cementitious composites for sustainable construction // Selected Scientific Papers – Journal of Civil Engineering. 2017. Vol. 12, Issue 2. doi:10.1515/sspjce-2017-0026

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DEVELOPMENT OF THE ELECTROCHEMICAL SYNTHESIS METHOD OF ULTRAFINE COBALT POWDER FOR A SUPERALLOY PRODUCTION

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Розроблено електрохімічний метод синтезу тонкодисперсного порошку кобальту, призначеного для виробництва твердих сплавів. Запропоновано введення аміаку в електроліт, доведено формування при цьому амінокомплексу Co^{+3}. Показано утворення при 100 А/дм^2 ультрадисперсних 35–150 мкм частинок Со коралоподібної форми, які легко піддаються розмолу до сфероїдних складових. Визначено максимальну температуру електроліту – 30 °C, розраховано катодний вихід за струмом 39 % та питома витрата електроенергії 48 кВт·год/кг

Ключові слова: амінокомплекс кобальту (+3), порошок кобальту, тверді сплави, дендрит

Разработан электрохимический метод синтеза тонкодисперсного порошка кобальта, предназначенного для производства твердых сплавов. Предложено вводить аммиак в электролит, доказано формирование при этом амминокомплекса Co^{+3}. Показано образование при 100 А/дм^2 ультрадисперсных 35–150 мкм частиц Со порошка кораллоподобной формы, легко размалывающихся на сфероидные составляющие. Определена максимальная температура электролита 30 °C, рассчитан катодный выход по току 39 % и удельный расходом электроэнергии 48 кВт·час/кг

Ключевые слова: аминокомплекс кобальта (+3), порошок кобальта, твердые сплавы, дендрит

1. Introduction

Ultrafine metal powders are widely used in various fields of engineering and manufacturing. Cobalt powder possesses high electrical conductivity, electrochemical and catalytic properties and is used for various purposes. For instance, it is used in chemical power sources [1], including hydrogenation [2] or as anodic material [3].