Проведено оцінку ефективності ультрадисперсних мінеральних добавок за диференційним коефіцієнтом поверхневої активності. Встановлено, що наномодифіковані портландцементні композиції, які містять ультрадисперсні мінеральні добавки, полікарбоксилатний суперпластифікатор, луговмісний прискорювач тверднення, а також нанорозмірні частинки гідросилікату кальцію, характеризуються інтенсивним набором ранньої міцності. Визначено особливості формування фазового складу, мікроструктури та синтезу міцності наномодифікованого цементного каменю

Ключові слова: наномодифікування, портландцементна композиція, ультрадисперсні мінеральні добавки, рання міцність, гідратація, лужна активація

Проведена оценка эффективности ультрадисперсных минеральных добавок по дифференциальному коэффициенту поверхностной активности. Установлено, что наномодифицированные портландцементные композиции, содержащие ультрадисперсные минеральные добавки, поликарбоксилатный суперпластификатор, щелочесодержащий ускоритель твердения, а также наноразмерные частицы гидросиликата кальция, характеризуются интенсивным набором ранней прочности. Определены особенности формирования фазового состава, микроструктуры и синтеза прочности наномодифицированного цементного камня

Ключевые слова: наномодифицирование, портландцементная композиция, ультрадисперсные минеральные добавки, ранняя прочность, гидратация, щелочная активация

RESEARCH OF NANOMODIFIED PORTLAND CEMENT COMPOSITIONS WITH HIGH EARLY AGE STRENGTH

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1. Introduction

The intensity and prospects of development of innovative technologies for the production of concretes as composite materials with specific parameters are predetermined by the necessity to implement complex architectural shapes and functionally new types of structures, to reduce energy and capital intensity of modern construction, to increase the life cycle of facilities and buildings in line with the concept of "sustainable development". To achieve this, strict requirements are often set regarding the time allocated for the production or erection of building structures, which necessitates using rapid hardening concretes with the required technical and technological properties. Competitive advantages of using compositions with high strength at their early age are improving the efficiency of erection of monolithic structures, road infrastructure objects, as well as production of precast reinforced concrete products, carrying out repair and restoration works, including those under different temperature conditions.

Regulated construction and technical properties of rapid hardening building materials for different operating conditions are largely achieved through targeted control and control over the processes of early structure formation of cementitious matrix at the micro-, submicro- and nanostructural levels. The main task of nanomodification is to control the process of structure formation of the material from the bottom up (from the nanolevel to concrete macrostructure), as well as kinetics and mechanism of chemical interactions at the early stages of the cement matrix hardening process [1, 2].

2. Literature review and problem statement

Nanoscience and nanotechnologies are a new revolutionary approach in the building production for creating concretes with specified properties, including rapid hardening concretes. They apply a scientific approach, which is based on using the potential of particles of nanometric scale $(1–100)\cdot10^{-9}$ m, which is determined by the dimensional effect and is spread in the range of 1–100 of atomic-molecular diameters [3, 4]. In this case, it is noted that hydrosilicate gel (particles smaller than 100 nm) defines the nanostructural level of concretes and their main durability properties. It is demonstrated that controlling the nanostructure of concrete makes it possible to receive high-tech materials whose structure may be designed according to functional criteria for strength, durability, reduced level of impact on the environment [5].

Using of nanotechnologies in construction industry is carried out by two strategies: addition of the synthetically produced nanodimensional modifiers (primary nanomateri-

als) into material and synthesis of nanoelements in material in the process of its manufacturing [6]. The first strategy implies an adding to the hardening system of nanoparticles of different nature, in particular nanosilica, taurit, shungite and carbon nanomaterials (fullerenes, nanotubes and nanofibers), etc. [7, 8]. Modifying effects and mechanisms of influence of the introduced nanomaterials on the hydration peculiarities and properties of cement materials consist in the implementation of the so-called seeding effect, packing effect, increasing of chemical activity. Due to these effects, the early strength of Portland cements significantly accelerates [9]. At the same time, the problem of their homogeneous distribution in the medium of cement matrix was not solved sufficiently [10]. That is why practical interest is the technology of hardening accelerator X-SEED (Crystal Speed Hardening concept), which is based on the introduction of synthetically produced crystalline CSH-nanoparticles in the form of suspension and provides for uniform product distribution [11].

The second strategy of nanomodification of building materials is implemented at the introduction of energetically active ultrafine mineral additives, the nanoparticles, which are characterized by high non-compensated surface energy. Such nanoparticles are capable to significantly change physic-chemical interactions in concrete, playing the role of catalysts or centres of crystallization depending on the surface chemical composition and concentration, in this case there is an effect of a filler in the initial period and early pozzolanic reaction with the formation of nanoscale CSH phases [12, 13].

One of the widely used methods of nanotechnology in the production of concretes and solutions is the modification by the surface active substances additives. The action of these modifiers is manifested by the change in chemical processes on the surface interphase by creating adsorption layers that are hindering the growth of crystals, affect their habitus, the degree of particles wetting, which reduces the degree of hydration of Portland cement. Highly efficient polycarboxylate superplasticizers with the nano-designed molecular chains make it possible to increase strength due to significant reduction of water-cement ratio [14]. A phenomenon of hydration speed micellar nanocatalysis of Portland cement hydration by combined micelles, which consist of micellar surface active substances and usual molecular surface active substance, was found. Micellar nanocatalysis provides the increasing of Reactive powder concrete strength, but there are no details regarding its early strength [15].

A nanotechnological approach to creating high-tech concretes with high early strength is the technologies of high quality binding nanomaterials and organic-mineral nanocomposites – materials from mineral and polymer components. It is efficient to use a complex organic and mineral additives based on silica additives of different origin and polycarboxylate superplasticizers for obtaining of high cement strength [16]. However, the features of early structure formation of cement-silica compositions are insufficiently explored. Nanocement with increased quantity of mineral silica additives can be obtained by mechano-chemical activation in the presence of a polymer modifier of the naphthalene-sulfonate type to specific surface of $300–900$ m^2/kg [17]. In this case, solid nanoshells (capsules with thickness of $20–100$ nm), structured by calcium cations, are formed on the grains of Portland cement. This nanocement is characterized by an accelerated rate of hardening and improved building and technical properties compared to Portland cement. Another technology of nanocements bases on use of Fine Cement with the nanoparticles contents of 24.0 % and Ultra Fine Cement with the 39.0 % content of particles less than 1 μm, which are obtained in high-energy mills [18]. Concretes based on such nanocements are characterized by $1.5–2.0$ times higher early and standard strength. However, these technologies require the use of special equipment, which increases the cost of the finished material.

In this regard, a promising task is the development of Portland cement compositions with high strength at an early age through a comprehensive use of nanotechnological approaches to the organization of structure and formation of properties by addition of ultrafine mineral components. In this case, it is important to methodically explore the effect of energetically active part of the fractions with excess surface energy and complex chemical admixtures of plasticizing and accelerating action, as well as calcium hydrosilicate nanoparticles on the processes of structure formation and crystallization in cement matrix.

3. Aim and objectives of research

The aim of the research is to determine characteristics of the processes of hardening and structure formation of nanomodified Portland cement compositions containing ultrafine mineral additives, complex chemical admixtures, CSH-nanoparticles.

To achieve the set aim, it is necessary to solve the following tasks:

– to determine indicators of particle size distribution of disperse systems;

– to investigate physical and mechanical properties of nanomodified Portland cement compositions;

– to establish peculiarities of the processes of structure and phase formation of Portland cement compositions, modified at the nanostructure level.

4. Materials and methods of research of rapid hardening nanomodified Portland cement compositions

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

The study was carried out using the Portland cement CEM I-42.5 R from JSC "Ivano-Frankivskcement" (Ukraine) based on the clinker of normalized mineralogical composition, % by weight: C_3S – 64.20; C_2S – 12.88; C_3A – 5.65; C_4AF – 14.62. Low-calcium fly ash (FA), highly active metakaolin (MK) and silica fume (SF) were used as supplementary cementitious materials. Chemical composition of the raw materials is given in Table 1.

Table 1

Chemical composition of Portland cement and mineral additives

Material	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	R$_2$O	SO$_3$
CEM I-42.5 R	21.44	5.22	4.84	64.68	0.55	0.95	2.32
Fly ash	43.75	21.79	21.34	4.83	2.15	1.80	0.35
Silica fume	94.71	–	5.29	–	–	–	–
Highly active metakaolin	54.21	44.59	0.75	0.45	–	–	–

According to granulometric analysis of the Portland cement CEM I-42.5 (Table 2), the content of 10.0; 50.0 and 90.0 % by weight is equal to 5.75; 19.42, and 56.29 μm respectively. In this case, value of D_{10} for fly ash, metakaolin and silica fume is 9.01; 2.20 and 0.07 μm respectively.

Table 2

Particle size distribution of
Portland cement and mineral additives

Material	D_{10}, μm	D_{50}, μm	D_{90}, μm
CEM I-42.5 R	5.75	19.42	56.29
Fly ash	9.01	40.21	46.59
Silica fume	0.07	0.15	0.30
Highly active metakaolin	2.20	10.30	13.70

According to the particle size distribution of the applied ultrafine additives the content of active particles less than 1 μm for fly ash, highly active metakaolin and microsilica is 9.0; 5.2 and 100 % respectively (Fig. 1). These particles complement particle size distribution of Portland cement and provide the gap-graded particle size distribution in the Portland cement compositions.

The innovative superplasticizer GLENIUM ACE 430 based on polycarboxylate esters (PCE), sodium sulphate Na_2SO_4 as alkaline hardening accelerator, as well as the additive X-SEED 100 (BASF), which contains CSH-nanoparticles were used as nanomodifiers of Portland cement systems.

The particle size distribution of Portland cement and mineral additives was determined by a laser granulometer Mastersizer 2000. Portland cement compositions were prepared by mechanical activation of components in a laboratory vibromill.
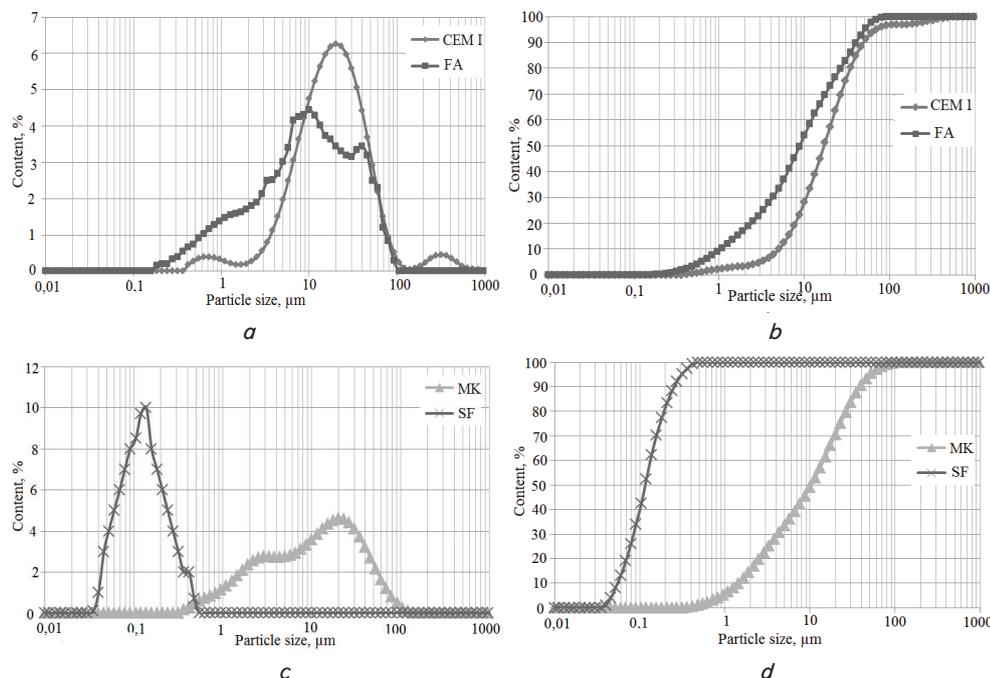
ed methods. Physical and chemical analysis methods (X-ray phase, electron microscopy analysis a. o.) were used for investigation of hydration processes of cementitious composites. Chemical compositions of materials were determined by the X-ray spectrometer ARL 9800 XP. The pH index of the liquid phase of model systems with the ultrafine additives were examined using the portable pH meter Meter PP-201K.

5. Results of studying the indicators of nanomodified Portland cement compositions with high strength at an early age

Dispersity as a quantative characteristic of microheterogeneous systems is defined by the existence of interphase surface (capacity factor) and is characterized by geometrical dimensions. To evaluate the interphase surface of mineral components coefficient of surface activity K_{sa} was calculated as the ratio of the surface area of the particles to their volume. Thus, for the particles of Portland cement of average size 19.42 μm, K_{sa} is 0.31 $μm^{-1}$, for fly ash with an average size of particles 8.71 μm, $K_{sa}=0.69$ $μm^{-1}$. The K_{sa} indicator of highly active metakaolin for $D_{50}=10.3$ μm is 0.58 $μm^{-1}$ and of microsilica with the particles of average size 0.15 μm is 40.0 $μm^{-1}$ (Table 3).

With the decrease of the particles size their specific surface significantly increases. Therefore, to assess the contribution of individual particles of polydisperse systems to general specific surface, it was proposed a differential coefficient of surface activity (K_{isa}), which is determined by multiplying the coefficient of surface activity by the content of each fraction of the material [19]. The maximum value of differential coefficient of surface activity K_{isa} of fly ash, highly active metakaolin and microsilica is 10.1; 15.82 and 531.8 $μm^{-1}·vol. %$ respectively, whereas for CEM I-42.5 is 3.81 $μm^{-1}·vol. %$ (Fig. 2). Data of the curves of differential coefficient shows that interphase surface determines mainly by the particles of size less than 1 μm.

With the decreasing of particles size of microheterogeneous systems the thickness of the effective layer of solid phase ($δ_{ef}$), which is calculated for the unit of weight of dispersion (1 g) and characterizes its behavior when mixing with water. Thus, for CEM I-42.5 with specific surface of 340 m^2/kg, $δ_{ef}$ equals 0.95 μm, and for microsilica – 0.03 μm (SSA=15000 m^2/kg). In this case, thickness of the layer of water ($δ_w$) on the particles of suspension with

Fig. 1. Particle size distribution of Portland cement and mineral additives:
a, b — incremental volume; *c, d* — cumulative volume

4. 2. Technique for determining indicators of the samples' properties

Physical and mechanical properties of nanomodified Portland cement compositions were determined in accordance with applicable valid standards and generally accept-

W/S=0.3 for Portland cement is equal to 0.88 μm that is correlated with the thickness of effective layer as 1:0.9 (Table 3). With an decreasing of particle size thickness of the water layer is reduced to 0.67 μm for fly ash and 0.23 μm for highly active metakaolin, and the ratio of thickness of

the solid phase and water is 1:0 and 1:0.74 for fly ash and metakaolin, respectively.

Table 3

Characteristic of disperse systems

Material	SSA, m^2/kg	K_{sa}, μm^{-1}	K_{isa}, $\mu m^{-1} \cdot$vol. %	δ_{ef}, μm	δ_w^*, μm	d^*, μm
CEM I-42.5 R	340	0.31	3.81	0.95	0.88	1.06
Fly ash	450	0.69	10.1	0.74	0.67	0.80
Highly active metakaolin	1300	0.58	15.82	0.31	0.23	0.27
Silica fume	15000	40.00	531.8	0.03	0.02	0.02

*Note: * – at W/S=0.3*

Excessive energy supply of the systems with ultrafine additives causes active adsorption of molecules of water mixing on the interphase surface with spontaneous redistribution of the system components between a surface layer and a volumetric phase. At the uniform distribution of mixing water, on the surface of the solid phase of disperse systems, the water shell thickness decreases significantly with an increase in specific surface. In this case, the distance between the particles in the pastes (d) decreases, which causes the growth of forces of interaction in such systems, the formation of a strong spatial structure, causes significant increase in viscosity and acceleration of the processes of early structure formation.

It should be noted that during the Portland cement hydration there occurs a dispergation of the hydration products with transition to the ultramicrodispersed region. Thus, effective diameters D_{50} and D_{90} for rapid hardening Portland cement are 12.68 and 45.90 μm, respectively, whereas for the products of its hydration are 3.27 and 9.3 μm. In this case, the content of particles smaller than 10 μm for Portland cement and its hydration products reach 41.93 and 97.27 %, respectively, while geometric surface increases by 4.1 times and the system becomes dispersion-bound [20].

Results of testing the Portland cement composition CEM II/A-Q "Portland cement CEM I – highly active metakaolin – superplasticizer of the polycarboxylate type PCE – alkali containing hardening accelerator" according to DSTU EN 196-1:2007 (W/C=0.50) established that with the plasticizing effect (ΔF=85 %), early strength of the system grows by 1.6 times compared with CEM I-42.5 and standard strength is R_{c28}=55.5 MPa (Fig. 3). Due to a significant water-reducing effect, the CEM II/A-Q standard strength reaches 66.9 MPa. Rapid hardening Portland cement compositions, modified with a complex additive based on highly active metakaolin, are characterized by high rates of early strength development (R_{c1}/R_{c28}=58.2 %; R_{c2}/R_{c28}=70.1 %) and by the indicators of standard strength are related to those of high strength.
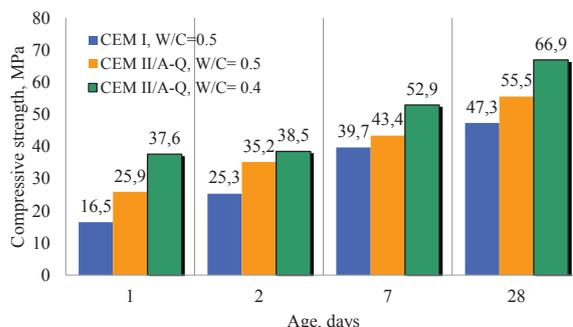

Fig. 3. Compressive strength of CEM I-42.5 R and rapid hardening Portland cement compositions (DSTU EN 196-1:2007)

To study the kinetics of strength development of the rapid hardening Portland cement compositions CEM II/A-Q in the initial period of structure formation fine-grained concrete (C:S=1:3, W/C=0.39) was formed. Fine-grained concrete from high flowability mixture (W/C=0.39; flowability F=168 mm) based on CEM II/A-Q is characterized by high intensity of strength development in the early period of hardening (Fig. 4). Thus, strength of the modified fine-grained concrete after 10 hours grows by 2.7 times and after 15 hours by 2 times compared with the concrete based on CEM I. Due to water reducing effect, strength of the fine-grained concrete based on the nanomodified Portland cement composition CEM II/A-Q after age of 10 and 15 hours of hardening increases by 3.3 and 2.3 times, respectively, compared with the fine-grained concrete based on CEM I. After age of 48 hours, strength of the fine-grained concrete based on CEM II/A-Q is R_{c2}=30.1 MPa. Due to a significant water reducing effect (ΔW/C=23 %), strength
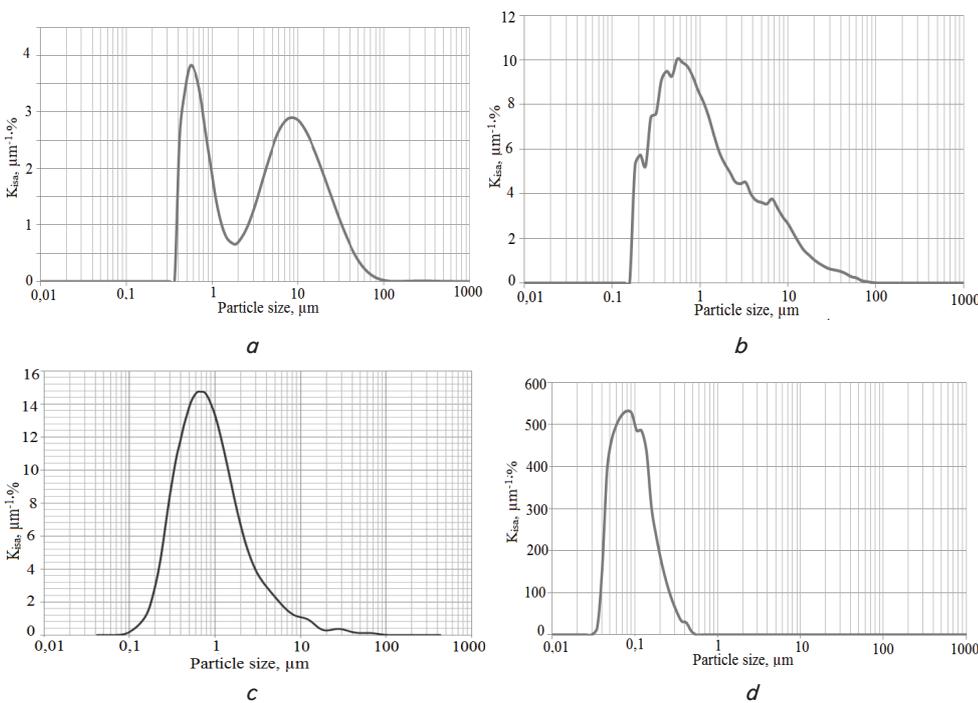

Fig. 2. Incremental coefficient of surface activity: *a* — Portland cement; *b* — fly ash; *c* — highly active metakaolin; *d* — microsilica

of the modified rapid hardening concrete (W/C=0.3) after 2 days increases to 36.8 MPa (technical effect ΔR_{c2}=68 %), and strength after 28 days of hardening is 55.2 MPa. In this case, fine grained concrete modified with ultrafine additive based on highly active metakaolin is characterized by significant increase in early strength after age of 24 hours – R_{c1}/R_{c28}=63.0 % and after age of 48 hours – R_{c2}/R_{c28}=66.7 %.
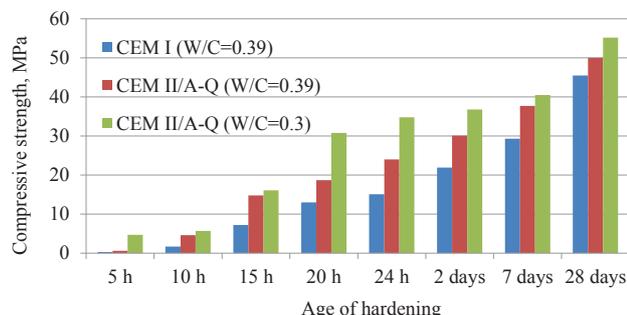

Fig. 4. Compressive strength of fine-grained concretes based on rapid hardening Portland cement compositions

When implementing a strategy of nanomodification with specially synthesized nanoparticles, Portland cement compositions, modified with a superplasticizer of the polycarboxylate type and CSH-nanoparticles, were examined. An addition of nanomodifiers provides an intensive increasing of early strength of isoflowing fine-grained concretes (F=140–145 mm) during 24 hours (Fig. 5). Thus, after age of 10 hours strength of nanomodified Portland cement composition increases by 3.4 times compared to the control composition and after age of 24 hours it reaches 54 % of the 28-day strength that allows to categorize it as super rapid hardening. By the indicator of standard strength R_{c28}=84.8 MPa, a nanomodified Portland cement composition refers to high strength binder.
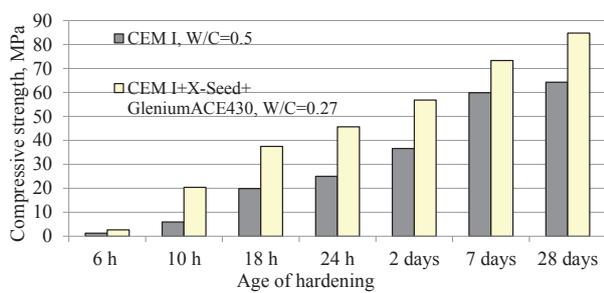

Fig. 5. Compressive strength of nanomodified Portland cement compositions according to DSTU EN 196-1:2007

Peculiarities of mechanism of cement compositions hydration were revealed by examining the processes of interaction in the model systems $CaO+Na_2SO_4$+highly active metakaolin, $CaO+Na_2SO_4$+fly ash, and $CaO+Na_2SO_4$+microsilica with water. A pH index of liquid phase of the model systems containing high aluminium mineral additives – fly ash and metakaolin, increases (Fig. 6). At the same time, in the presence of microsilica pH values of liquid phase of the model systems are the lowest over all periods of hydration.

The pH increasing of the liquid phase causes alkaline activation of mineral additive, resulting in the destruction of the outer layer on the surface of particles and facilitating active interaction with $Ca(OH)_2$ with the formation of additional hydration products. According to XRD data of paste

based on the model system $Ca(OH)_2$: metakaolin=1:1 after 48 hours (Fig. 7, a) slight lines of hexagonal hydroaluminate calcium of the type AF_m-phase (d/n=0.810; 0.395; 0.288; 0.247 nm) appear. In the presence of aluminum-containing additives (metakaolin, fly ash) and sodium sulfate in the model system the intensity of lines $Ca(OH)_2$ (d/n=0.493; 0.263; 0.193 nm) significantly reduces and there appear lines of ettringite (d/n=0.971; 0.556 nm). After 28 days of hardening of the model system in the presence of sodium sulfate intensity of portlandite lines significantly reduces. In this case, intensity of the lines of ettringite increases (Fig. 7, b). At the same time, the system $Ca(OH)_2$:highly active metakaolin=1:1 after 28 days of hardening is characterized by the existence of non-bound portlandite, while the products of interaction between the components are hexagonal calcium hydroaluminates, in particular hydrohelenite $2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$ (d/n=1.250; 0.418; 0.285 nm).
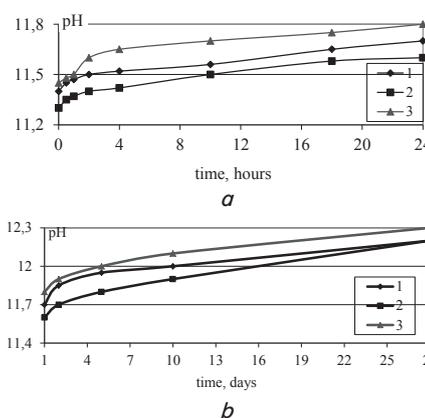
Fig. 6. Kinetics of pH change in the model systems during: a — 1 day; b — 28 days: 1 — $CaO:FA:Na_2SO_4$=(1:1:0.5); 2 — $CaO:MK:SF:Na_2SO_4$=(1:0.5:0.5:0.5); 3 — $CaO:MK:Na_2SO_4$=(1:1:0.5)
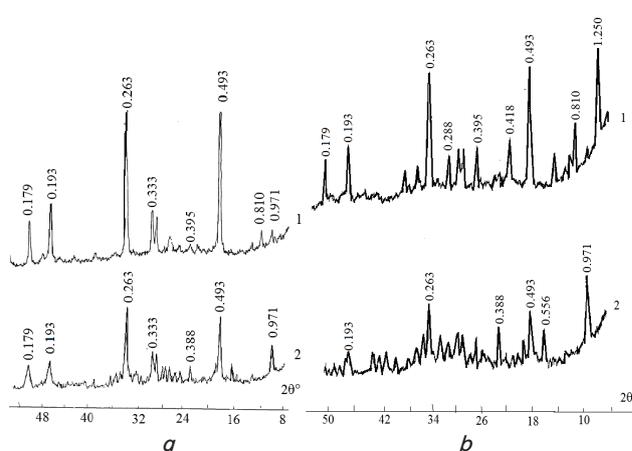
Fig. 7. XRD patterns of model systems, hydrated: a — 24 hours; b — 28 days; 1 — $Ca(OH)_2$:MK=(1:1); 2 — $Ca(OH)_2$:MK:Na_2SO_4=(1:1:0.5)

The XRD patterns of Portland cement CEM I paste after 24 hours demonstrates main lines of ettringite (d/n=0.973; 0.561; 0.388; 0.348; 0.256 nm) and $Ca(OH)_2$ (d/n=0.493; 0.263; 0.193; 0.179 nm) (Fig. 8, a). At the same time, the XRD patterns of the Portland cement composition paste displays higher intensity of the lines of ettringite while that of the lines of $Ca(OH)_2$ is lower, that indicates acceleration of the processes of hydration and structure formation. Thus,

early strength of the paste based on the modified Portland cement composition increases by 2.5 times compared with ordinary Portland cement CEM I. After 28 days intensity of the lines of calcium hydroxide increases, that indicates active progress of hydration processes of the Portland cement CEM I (Fig. 8, *b*).

On the diffractograms of paste based on the modified Portland cement composition "Portland cement CEM I – highly active metakaolin – superplasticizer of the polycarboxylate type PCE – alkaline-containing hardening accelerator" peaks of $Ca(OH)_2$ decreases as a result of its binding by the mineral additives, in particular active Al_2O_3 and SiO_2 of highly active metakaolin with the formation of ettringite, hexagonal calcium hydroaluminates and calcium hydrosilicates.
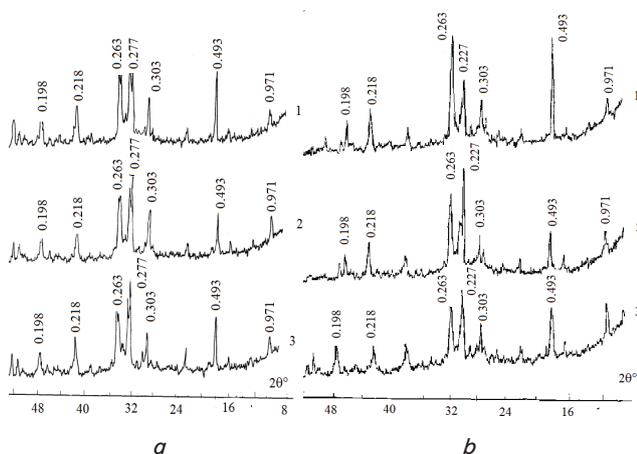

Fig. 8. XRD patterns of modified Portland cement composition pastes, hydrated: *a* — 24 h; *b* — 28 days; 1 — CEM I; 2 — CEM II/A–Q; 3 — CEM II/A–Q+PCE

Results of SEM of modified Portland cement composition show that ultrafine mineral additives provides formation of AF_t- and CSH-phases of acicular and fibrous habitus in the non-linker part of cementitious system in the early periods of hydration (Fig. 9, *a*), resulting in the accelerated processes of strength synthesis and realization of the phenomenon of "self-reinforcement" at the microstructure level [21].
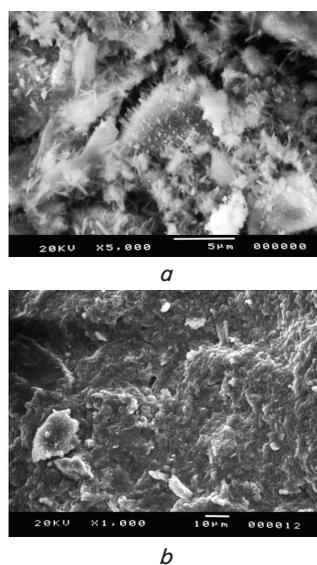

Fig. 9. SEM of paste based on the nanomodified Portland cement composition, hydrated: *a* — 24 hours; *b* — 28 days

After 28 days of hardening microstructure of paste based on CEM II/A-Q is characterized by density and uniformity (Fig. 9, *b*). In this case, defects and cracks at the micro- and mesolevel disappear, which leads to the growth of strength of the nanomodified Portland cement compositions.

6. Discussion of results of research of the properties and phase structure of nanomodified Portland cement compositions

Differential coefficient of surface activity characterizes the impact of certain fractions on the values of the interphase surface. Assessing of particle size distribution of ultrafine systems by the values of differential coefficient of surface activity was shown that reducing the size of particles to 0.1 μm dramatically increases their surface activity. Thus, for microsilica with average size of particles 0.15 μm, maximum differential coefficient of surface activity is 531.8 $μm^{-1}·$%, which is two orders of values larger than this indicator for Portland cement.

An analysis of results of physical and mechanical tests of the nanomodified Portland cement compositions according to DSTU EN 196-1:2007 and fine-grained concrete on their base demonstrated a significant increase of strength in early (to 24 hours) and later periods of hardening. An strength increasing of modified cement matrix is due to an increase of the content of ultrafine energy–active fractions in the Portland cement compositions, providing of optimization of particles packing, creation of the initial density of the system, growth of the interfacial active area, improvement of the rheological action of superplasticizers, formation of additional amount of hydrates in the non–clinker part of the binder [20–22].

Using the ultrafine highly active metakaolin, which characterized by an enhanced content of aluminum Al_2O_3 (42 % by weight) and surface activity (K_{isa}=15.82 $μm^{-1}·$vol. %) compared with fly ash (the content of Al_2O_3 is 21–23 % by weight, K_{isa}=10.1 $μm^{-1}·$vol. %) provides reaction between $Ca(OH)_2$ and Na_2SO_4 with the formation of dihydrate gypsum and sodium hydroxide at the early stages of hardening, which leads to an increase in alkalinity of the liquid phase. In this case, there is alkaline activation of the mineral additive, resulting in the destruction of the outer layer at the surface of the particles and facilitating active interaction with $Ca(OH)_2$ with the formation of additional hydration products. According to the XRD analysis (Fig. 7, 8) interaction between the components of the Portland cement system CEM II/A-Q at the early stages of hydration results in the formation of AF_t- and CSH-phases in the non-clinker part with the formation of fine crystalline dense structure.

Improved strength characteristics of the Portland cement compositions, modified with calcium hydrosilicate nanoparticles, at an early age (after age of 24 hours larger than 20 MPa) are achieved as a result of physical and chemical processes associated with the autocatalytic mechanism of hydrates deposition from the pore solution, the so-called seeding effect, with accelerated formation of CSH gel, which is the main binding phase in cement matrix. The addition of CSH-nanoparticles causes the formation of hydrate products in the porous space between the cement grains, which leads to the more uniform distribution of hydrates with the creation of dense microstructure and provides a possibility of obtaining high-strength composites with high strength at an early age. Nanotechnological control over properties

of Portland cement compositions opens up good opportunities for the production of new-generation concretes, in particular, High Performance Concrete, of High Strength Concrete, Self-compacting Concrete. It is expedient to carry out further research into the properties of concretes with different functional purposes based on the nanomodified Portland cement compositions, which would extend the idea about nanotechnological methods of creating rapid hardening composites with improved performance properties under different operating conditions.

7. Conclusions

1. An analysis of indicators of differential coefficient of surface activity allows making quantitative assessment of the contribution of individual particles to specific surface of the cementitious systems. It was found that the surface activity of ultrafine systems when changing the size of its particles in the range of $1.0-0.1$ µm grows by two orders of value. Nanoparticles, which have defined a supply of free surface energy, increase the interface that can accelerate chemical reactions, detect catalytic activity and significantly accelerate synthesis of strength of cement systems.

2. Results of the research of physical and mechanical properties of the nanomodified Portland cement compositions show that at plasticizing effect these compositions are characterized by fast development early strength (R_{c2}/R_{c28}=63 %) and by the value of activity they correspond to the strength class 52.5 R. Due to a significant water reducing effect nanomodified binders by the indicators of early strength belong to the rapid hardening (R_{c2}/R_{c28}=67–70 %) and by the criterion of standard strength (R_{c28}=66–88 MPa) they meet the requirements for high strength binder.

3. The results of physical and chemical analysis methods demonstrated that there is an increased quantity of hydration products in the non-clinker part of the cement matrix at the early stages of structure formation of nanomodified Portland cement composition due to the growth in alkalinity of the liquid phase, acceleration of the processes of nucleation in the inter-grain space and reactions associated with pozzolanic activity of ultrafine mineral additives. In this case, acceleration of the processes of hardening a modified cement matrix and obtaining its dense and high-strength structure are provided.

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Короткоживучий ізотоп ^{99m}Tc, похідний внаслідок розпаду радіоізотопу ^{99}Mo, є основним інструментом ядерної медицини, за допомогою якого здійснюється 85 % всіх діагностичних сканів у світі. Для вирішення проблеми виділення ізотопів ^{99}Mo запропоновані пробопідготовка та метод вилучення Mo, який входить в комплекси, що містять нітрат з трибутілфосфатом (ТБФ), з матриць, які містять молібден, методом надкритичної екстракції діоксидом вуглецю (СФЭ-CO_2). Запропонована теорія опису розчинення Mo в розбавленій азотній кислоті за допомогою моделі Русел і Джокерів

Ключові слова: надкритичний діоксид вуглецю, надкритична екстракція, ізотопи молібдену

Короткоживущий изотоп ^{99m}Tc, производный вследствие распада радиоизотопа ^{99}Mo, является основным инструментом ядерной медицины, с помощью которого осуществляется 85 % всех диагностических сканов в мире. Для решения проблемы выделения изотопов ^{99}Mo предложены пробоподготовка и метод извлечения Mo, входящего в нитратсодержащие комплексы с трибутилфосфатом (ТБФ), из молибденсодержащих матриц методом сверхкритической экстракции диоксидом углерода (СФЭ-CO_2). Предложена теория описания растворения Mo в разбавленной азотной кислоте с помощью модели Русел и Джокеров

Ключевые слова: сверхкритический диоксид углерода, сверхкритическая экстракция, изотопы молибдена

THE STUDY OF SUPERCRITICAL EXTRACTION OF COMPLEXES OF MOLYBDENUM WITH CARBON DIOXIDE

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1. Introduction

The importance of the activities in this field is connected with a necessity to search new, radiation safe methods of obtaining the medical isotopes of wide application. One of the candidates for such application is the Mo isotopes which serve as initial material for obtaining the Tc medical isotopes [1]. Due to this, the use of the method of super-critical extraction with carbon dioxide [2] for separation of metal isotopes [3] constitutes an interest. Ideally, this method allows obtaining the Tc medical isotope from the corresponding Mo isotope.

2. Literature review and problem statement

The method of uranium ions and lanthanides extraction from solid samples in the medium of supercritical carbon dioxide (SC-CO_2) with fluorinated β-dyketone was first