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DEVELOPMENT OF NANOMODIFIED RAPID HARDENING CLINKER-EFFICIENT CONCRETES BASED ON COMPOSITE PORTLAND CEMENTS

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Показано, що значне зниження «вуглецевого сліду» у технології будівельного виробництва досягається за рахунок виготовлення клінкер-ефективних бетонів на основі портландцементів композиційних. Проведеними дослідженнями встановлено, що нерівномірний розподіл зернових фракцій суміші заповнювачів та їх підвищена загальна питома поверхня призводять до збільшення водопотреби, розшарування, водовідділення бетонної суміші та зниження міцності бетону. Для досягнення більш високої щільності упаковки зерен реалізовано підхід, який ґрунтується на оптимізації гранулометричного складу компонентів бетонної суміші. Встановлено, що підвищені показники ранньої міцності бетонів на основі низькоемісійних композиційних цементів досягаються за рахунок введення суперпластифікаторів на основі ефіру полікарбоксилату (PCE) та лужно-сульфатної активації. Для встановлення зв'язку між екологічними та технічними властивостями бетону визначено ефективність клінкеру в бетоні. При збільшенні міцності модифікованого бетону на основі портландцементу композиційного CEM II/B-M 32,5 R (клінкер-фактор 0,65) створюється можливість суттєвого зниження питомої витрати клінкеру на одиницю міцності до 4,5…3,0 кг/(м^3·МПа); відповідно CO_2-інтенсивність складає 3,9…2,6 кг CO_2/(м^3·МПа). Значна інтенсифікація процесів раннього структуроутворення наномодифікованих клінкер-ефективних бетонів забезпечується за рахунок комплексного підходу: оптимізації суміші компонентів, введення суперпластифікатора PCE та наномодифікаторів. З використанням методу лазерної дифракції доведено, що основний вклад у розвиток питомої поверхні наномодифікованої цементуючої матриці вносять ультратонкі частинки (K_{isa}=761,2 мкм$^{-1}$·vol. %) нано-SiO_2. Встановлено, що синергетичне поєднання мінеральних добавок в портландцементі композиційному та комплексного наномодифікатора «PCE+нано-SiO_2+C-S-H» забезпечує підвищені показники особливо ранньої міцності ($R_{c12год}$=6,4 МПа) та одержання бетонів класу C50/60 із швидким наростанням міцності (f_{cm2}/f_{cm28}=0,51). Таким чином, є підстави стверджувати про доцільність розроблення наномодифікованих клінкер-ефективних бетонів з метою забезпечення швидких темпів будівництва та вирішення проблем, пов'язаних з необхідністю реалізації стратегії низьковуглецевого розвитку

Ключові слова: клінкер-ефективний бетон, портландцемент композиційний, суперпластифікатор полікарбоксилатного типу, лужний активатор, наносиліка, рання міцність, показник емісії CO_2

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1. Introduction

Concrete as a composite building material is widely used in construction due to its relatively low cost, variety of applications, high durability and environmental friendliness [1, 2]. It is the second most used material on the planet after water. Current trends lean towards increasing the cement content in concrete. Between 2004 and 2019 cement consumption per square meter of flat increased from 204 to 219 kg/m^2. According to the UN, regarding continuous progress of industrialization, concrete share in construction of infrastructure, transport systems and implementation of ecofriendly energy projects will increase. However, widespread use of concrete leads to increased air pollution and requires higher amounts of resources and energy [3].

Modern technologies are being developed to improve efficiency of resource use [4]. The main environmental factor in concrete production is the CO_2 emissions. Due to population growth, urbanization and infrastructure development estimated global cement production of 4.6 billion tons is steadily increasing. Cement industry ranks third in energy consumption accounting to 6–7 % of all anthropogenic CO_2 emissions. Concrete will remain the main and irreplaceable material in construction. Portland cement that contains clinker will continue to be a required material for concrete production. Estimates show that till 2050 the production of concrete will increase by 12–15 % compared to 2014. Proposed Roadmap 2050 anticipates reduction of negative impact of cement production on the environment by as much as 80 %. The program introduces 5 equally important notions. It is also assumed that the efficiency of using materials that can replace cement will increase. Improved components will allow to produce new, low-emission cements and concretes.

Therefore, it is important to reduce the amount of Portland cement in ordinary concretes. Currently almost 98 % of concretes are produced belongs to C35/45 class. For ordinary concretes, the amount of clinker per MPa of compressive strength can reach between 8 and 12 kg/m^3. Increased use of cement in manufacturing of high-performance concretes can lead to increased shrinkage deformations and internal stresses, accumulation of microdefects aggravating risk of brittle fracture of structures [5, 6]. One of the ideas for development of concrete technology is the use of highly dispersed materials that significantly enhance the work of super- and hyperplasticizers. High-tech materials with advanced propertiesare one of the solutions for producing new-generation concretes with low specific consumption of clinker per unit strength within 3–5 kg/(m^3·MPa) [7].

The most effective way to reduce CO_2 emissions is to reduce the clinker content in Portland cement. Average amount of clinker in cement was estimated at 80 % in 2014. According to CEMBUREAU, it is expected that clinker to cement ratio will be drop to 70 % by 2050). Therefore, use of composite Portland cements with reduced clinker amount is an innovative approach to overall trend for reducing the anthropogenic carbon footprint. Benefits of eco-friendly cements include reduction of resource- and energy consumption as well as reduction in CO_2 emissions. Simultaneously, concrete elements gaing enhanced performance and durability. However, it should be noted that reduction of clinker content in cements inhibits the accretion of early strength and rate of concrete hardening. Significant acceleration of hardening of clinker-efficient concretes based on composite cements can be achieved by alkaline activation and nanomodification. This will ensure transition to new types of alkaline-activated composite cements with reduced clinker factor and nanomodified clinker-efficient concretes based on them. The development of alkali-activated composite cements is the next step in improvement of modern concretes. Studies focused on the development of nanomodified clinker-efficient concretes with increased early strength are of great importance.

2. Literature review and problem statement

The cement and construction industries face the problem of reducing the carbon footprint [3]. One of the most efficient ways is to replace the Portland cement clinker with additives of hydraulic or pozzolanic properties as well as microfillers. Replacement of cement by supplementary cementitious materials can reduce CO_2 emissions by 0.6–1.0 kg per kilogram of cement [2]. Principles of development of low carbon concretes are presented in [8]. The principles require the use of high- quality multicomponent cements (not less than 42.5 N/mm^2 of compressive strength), reduction of the clinker content in the mix and ensuring a sufficient volume of cement paste with densely packed grains.

To achieve higher packing density, authors of [9, 10] used multimodal multicomposite cements with intermittent granulometric composition. By introducing separate fractions of mineral additives with different grain size, the mix is densely packed. A significant potential for reducing CO_2 emissions is achieved by using multimodal composite Portland cements with addition of natural pozzolans and limestone [11–13]. It should be noted that with an increase volume of fine mineral additives, porosity of the matrix in concrete decreases. However, when maximum of filling the packing with a mineral additive is reached, concrete strength is reduced because of decrease in adhesion of cement stone with filler [14]. On the other hand, granulometric composition of fillers has a significant influence on technological properties of concrete mix and durability of concrete.

Clinker-efficient concrete technology is based on a concept of optimizing the «water to cement» and «water to binder» ratios [8]. The principle is to reduce the distance between cement particles in paste at initial period of the hydration process. This method results in reduced porosity, increased density and improved mechanical properties of concrete. One solution for acquiring such concretes is to modify the concrete mix with new generation of highly efficient superplasticizers based on polycarboxylate ether with nanodesigned chains (PCE). At maximum reduction of water content (up to 40 %) in concrete mix, such modifiers provide required workability which in turn provides high density and significant increase in concrete durability [15]. Use of highly efficient superplasticizers enables higher actual packing density of solid particles in cement powder. This allows to apply composite Portland cements with reduced clinker factor and high content of mineral additives [10, 11]. It should be noted that PCE modifiers and mineral fillers are of particular importance in acquisition of «green» self-compacting concrete (eco-SCC) mixes. Considering increase in the consumption of composite Portland cements, mineral additives, fillers, nanomaterials and other products that significantly improve adsorption capacity of the solid phase the use PCE seems necessary. Use of superplasticizers and highly active composite cements, optimization of particle size distribution and decreasing of the mix water demand contribute to reduction of clinker-factor.

However, the issues related to slow rate of early strength gain in concretes with composite cements remain unresolved [16]. This is caused by low reactivity of mineral additives in the cementitious matrix compared to Portland cement clinker phases. In order to overcome these shortcomings and increase reactivity of main components, various approaches have been developed. The aim is to create high-strength clinker-efficient concretes based on composite cements. Authors of [17, 18] note that one of main approaches to acceleration of concrete hardening consists in increasing specific surface area of composite cements and density of particle packing by introducing water-reducing admixtures. On the other hand, effect of accelerating early strength gain can also be achieved by alkaline-sulfate activation [19–21]. Presence of active mineral additives (granulated blast furnace slag, natural pozzolan and fly ash) in the cementitious matrix of concrete when adding an alkaline-sulfate hardening activator ensures exchange reaction and formation of structurally active AF_m phases. At the same time, due to the pozzolanic activity, amount of low-basicity calcium hydrosilicates C-S-H (I) grows and hydrogelenite belonging to AF_m phases is also formed. This approach to improving efficiency of alkali-activated cements and concretes was used in [22, 23].

Study [24] shows that cementitious matrix of concrete is a complex nanostructured multiphase composite material consisting of a gel-like phase, crystals of various dimensional levels and bound water. Concrete structure can be divided into four levels: from macrostructure (10^{-2} m) through mesostructure of mortar and microstructure of the cement stone to the level of solid phase C-S-H (10^{-10} m) which represents the nanostructural level. An effective way to accelerate the early period of structure formation in a cement matrix consists in the use a bottom-up nanotechnological approach. Nanomodification is based on introduction of nanosized additives (SiO_2, TiO_2, Al_2O_3, etc.) and carbon nanotubes [25, 26]. The study results show that the use of nanosilica accelerates early pozzolanic reaction in the cement matrix due to its high solubility in alkaline media. During introduction of nano-SiO_2 to concrete, paste microstructure is compacted due to synthesis of C-S-H (I) phases. Increase in strength of the cementing matrix is provided [27, 28].

To accelerate the process of hydration of mixed cements (after 6–12 hours), the latest Crystal Speed Hardening™ technology is used which consists in introduction of suspension of the C-S-H phase seeds. In this case, hydrated calcium silicates form additional centers of crystallization, especially in the intergranular space which leads to rapid development of structure of the cement matrix. It was found in study [29] that complex introduction of active C-S-H nanoparticles and polycarboxylate superplasticizer PCE increases the early strength of Portland cements.

Thus, comprehensive evaluation of granulometric distribution of components in cement allows to fully utilize nanoparticles potential to form specified properties of fast-hardening clinker-efficient concretes and formulate a new nanotechnological approach. Despite practical relevance of such results, studies on effect of hardening activator, nanosilica and C-S-H nanocrystals on early strength of concretes based on composite Portland cements has not yet been considered. Therefore, development of fast-hardening clinker-efficient concretes modified with alkaline-sulfate activator – nano-SiO_2 – C-S-H-PCE complex additive and study of the processes of their structure formation are promising.

3. The aim and objectives of the study

The study objective was to develop a rapid-hardening concrete based on composite Portland cement according to the criteria of early strength and clinker efficiency and establish features of their structure formation at nano-, micro-, meso- and macro-levels.

To achieve this objective, following goals were set:

– to optimize grain composition of aggregates and fillers of various grading composition taking into account distribution of their specific surface;

– to design compositions of rapid-hardening concretes with certain level of consumption of a composite Portland cement and a PCE superplasticizer that meet the strength and clinker efficiency criteria. The goal will be reached using the method of mathematical experiment planning;

– to study influence of complex nanomodifier of Na_2SO_4–nano-SiO_2–C-S-H-PCE type on hardening rate and quality parameters of clinker-efficient concrete based on composite Portland cements.

4. Materials and methods

4. 1. Materials and equipment used in the study

Composite Portland cement CEM II/B-M (S-P-L) 32.5 R with high early strength produced according to DSTU B EN 197-1 by PJSC Ivano-Frankivskcement, Ukraine, was used in designing rapid-hardening concretes. Its main characteristics are given in Table 1.

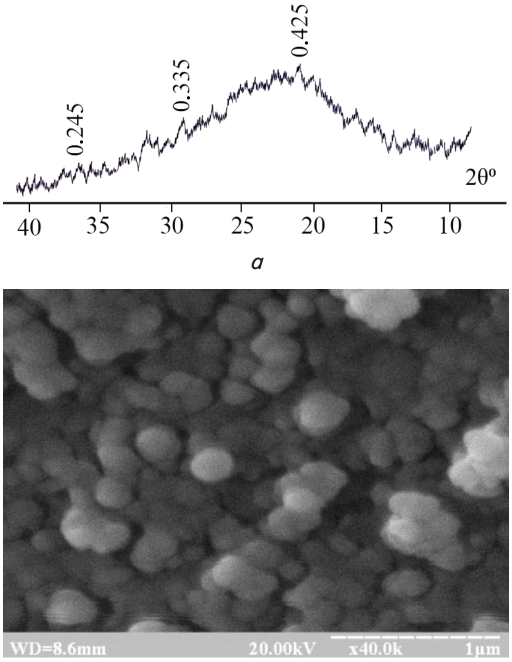
Table 1

Main characteristics of composite Portland cement CEM II B-M (S-P-L) 32.5 R with high early strength produced according to DSTU B EN 197-1

Main characteristics		Requirements by EN 197-1	Value
Additive content, %		21–35	35
Specific surface, m^2/kg		–	395
Water demand, %		–	29.5
Setting time, min	initial	≥75	160
	end	–	240
Volume change uniformity, mm		≤10.0	0
Compressive strength, MPa	2 days	≥10.0	19.8
	28 days	≥32.5≤52.5	40.5
	90 days	–	52.7
	360 days	–	63.2
Average activity in steam treatment, MPa by DSTU B C.2.7-112		–	30.7
C_3A content in clinker, %		≤8.0	6.8

Dispersion of Levasil CB8 colloidal solution of nano-SiO_2 (dry solids content: 50 wt %) with 10–150 nm particles of spherical shape was used as a nanoadditive (Fig. 1); true density $\rho=1.4$ g/cm^3; pH=9.5. A nano-modifier based on the C-S-H Master X-Seed 100 colloidal suspension (manufactured by BASF, Germany) was used to accelerate the concrete hardening process. Sodium sulfate (Na_2SO_4) was used as an alkaline-sulfate activator of hardening nanomodified concretes. Polycarboxylate type (PCE) MasterGlenium ACE 430 superplasticizer (manufactured by BASF, Germany) was used as a highly effective water-reducing additive. Fine sand of Zhovkva deposit, Ukraine, and aggregates of two fractions (2–5 mm and 5–20 mm) of Virovske deposit, Ukraine, were used to design of mixture compositions.

Chemical composition of nano-SiO_2 and CEM II/B-M (S-P-L) 32.5 R Portland cement was determined using ARL 9800 XP X-ray spectrometer (Thermo Electron SA, Switzerland). To determine particle size distribution of nano-SiO_2 and CEM II/B-M (S-P-L) 32.5 R, Master Sizer 3000 laser analyzer (Malvern Panalytical, GB) was used. Its operation is based on the principle of electromagnetic wave scatter.



a

b

Fig. 1. Characteristics of nano-SiO_2: phase composition (*a*); microstructure (*b*)

Shape and size of nano-SiO_2 particles were studied using REM 106I scanning electron microscope (SELMI, Ukraine). Specific surface area of composite Portland cement was determined by the Blaine air permeability method. Microstructure of nanomodified concrete was examined using REM 106I scanning electron microscope and mesostructure and macrostructure were examined using Bresser ETD-101 stereoscopic microscope (Germany). Porosity of concretes with nanomodifiers was determined using a device by TESTING (Germany). Distribution of air voids in concrete was determined using RapidAir 457 automated image analysis system (Denmark). Pixel resolution of the RapidAir system is 2.18 μm at 100×magnification. HS 280/75 climatic chamber (Czech Republic) was used to determine frost resistance of nanomodified concretes.

4. 2. Properties of prepared concretes

Main characteristics of composite Portland cement CEM II/B-M (S-P-L) 32.5 R with high early strength were determined according to DSTU B EN 196. Particle size distribution of colloidal nano-SiO_2 solution was determined by laser diffraction. The particle size distribution is calculated using theory of light scattering M_i using a model of equivalent volume sphere. According to the results of laser diffraction, differential coefficient of particle distribution, K_{isa}, over specific surface was calculated according to the methodology developed in [10]. This coefficient is determined by the product of multiplying A/V (ratio of surface area of particles to their volume characterizes specific surface SSA, $\mu m^2/\mu m^3=\mu m^{-1}$) by content of each material fraction.

Grain composition of fine and coarse aggregates of the concrete mixture was determined by the method of dry sieving through a set of sieves according to EN 933-1:2012-03. After sieving, fractions on individual sieves were weighed and grading curve was developed. The grading curve obtained in the study (designed curve) was compared with standard curves. The method of orthogonal central compositional planning was used to study the effect of consumption of composite Portland cement and amount of PCE on concrete strength and clinker efficiency. To establish relationship between ecological and technical properties of concrete, clinker efficiency in concrete was determined by the ratio of cement consumption to compressive strength in a certain age [kg/(m^3·MPa)].

Compressive strength of nanomodified concretes was determined on cubic specimens (100×100×100 mm) after 1, 2 and 28 days according to DSTU B C.2.7-214:2009. To determine nature of porous structure of the cement matrix of concrete, a Powers index was applied showing maximum distance from any point in the cement matrix to the edge of the nearest void [30]. Determination of deformation properties (compressive strength, modulus of elasticity, Poisson's ratio) of concrete was performed according to DSTU B C.2.7-217:2009. Compressive strength, modulus of elasticity, and Poisson's ratio of nanomodified concretes were calculated from determined N_u and $0.3N_u$ loads and relative elastic-instantaneous deformations ε_{1el} and ε_{2el}. Freeze-thaw resistance was determined by accelerated procedure according to DSTU B C.2.7-49-96.

5. Results

The results of grading curve determination conducted in accordance with EN 933-1:2012-03 allowed to calculate the contribution of nanomaterial in the mix. The sieve analysis of fillers revealed that the highest content of sand fractions (calculated by partial residues of 29.6 and 54.0 wt. %) was concentrated on 0.50- and 0.25-mm sieves indicating an increased content of fine fraction. For crushed stone fractions of 2–4 mm, maximum filler size on 4.0- and 2.0-mm sieves was 69.1 and 24.7 wt. %, respectively. When sieving crushed stone of fraction 4–16 mm, the highest content of 30.2 and 61.9 wt. % was found on 16.0- and 8.0-mm sieves respectively. According to the results of calculation of the total mass, a grading curve was constructed. As can be seen in Fig. 2, the designed curve of the mix fits between standard curves. At the same time, for fractions from 0.30 to 1.70 mm, there was a slight deviation of the design mix curve from the control one which can lead to some increase in water consumption. In general, the curve of the designed aggregate was satisfactory which guarantees appropriate workability and consistency of the concrete mix with the least amount of water and cement (mortar) as well as minimum air content.

Important factors affecting quality of concrete include grain composition of fillers and their specific surface area which largely determines amount of water consumed to moisten the grain surface as well as relative volume of fillers occupied by grains. These factors also affect workability of the concrete mix and tendency to segregation. For example, for basic concrete composition No. 2 with cement amount of 370 kg/m^3 (Fig. 3, *a*), total specific surface area of is equal to 159,600 m^2 per 1 m^3 with share of cement grains accounting for 92.7 % and the water-cement ratio W/C=0.55.

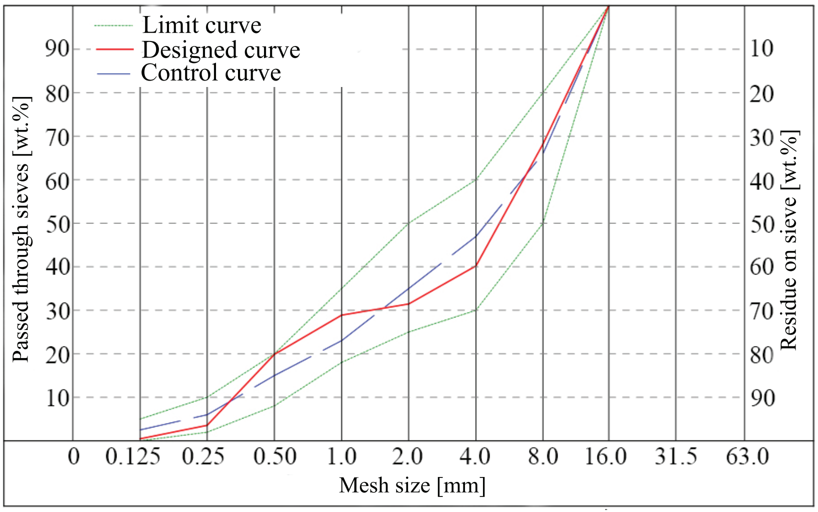
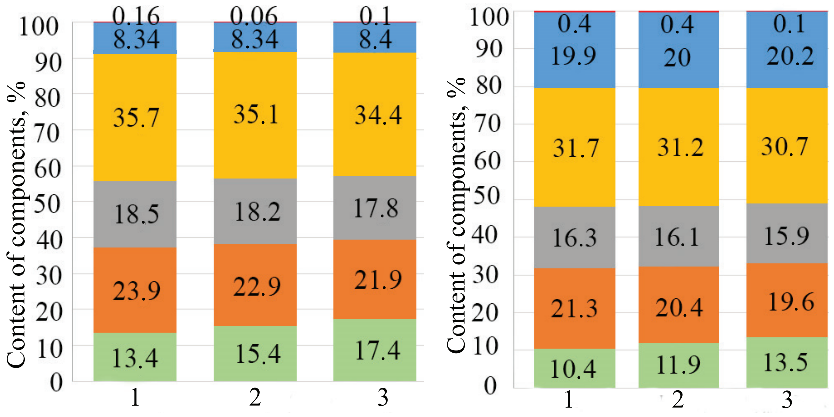


Fig. 2. Grading curve of designed aggregate (sand of 0.125–2.0 mm fraction, crushed stone of 2–4 and 4–16 mm fractions)



a *b*

Fig. 3. Composition of concrete based on composite Portland cement CEM II/B-M 42.5 R: by weight (*a*); by volume (*b*)

At the same time, only 20 % of water is bound with hydration products of the concrete cementing matrix and the rest evaporates which results in a growth of concrete porosity. As can be seen from Fig. 3, *b*, volume ratio of water/cement is 1.68 with average film thickness of H_2O molecules d=1.3 μm. Therefore, dense packing of concrete components is ensured by a significant reduction of the water-cement ratio. The effect can be obtained by introduction of high-performance PCE superplasticizers.

To determine the effect of formulation and technological factors, concrete mixtures composition was designed using mathematical experiment planning. Experimental studies of impact of composite Portland cement CEM II/B-M 42.5 R and PCE superplasticizer consumption on early strength as well as clinker efficiency in concrete were performed according to a two-factor three-level experiment. Consumption of CEM II/B-M 32.5 R (X_1=320; 370; 420 kg/m^3) and amount of PCE (X_2=0; 0.8; 1.6 wt. %) were chosen as variable factors. To accelerate gain of early strength, hardening activator (Na_2SO_4) was introduced to the mix in amount of 2.0 wt. %. As a result of processing plans and their corresponding experimental data, regression equations for water demand (Y_w), compressive strength after 1 and 2 days (Y_{fc1}, Y_{fc2}) and clinker efficiency in concrete (Y_{c2}) were obtained by the method of least squares that adequately describe dependence of indicators as system optimization criteria on variable factors.

$$Y_w=0.46-0.047\cdot X_1-0.085\cdot X_2+$$
$$+0.007\cdot X_1^2+0.042\cdot X_2^2+0.020\cdot X_{12}^2;$$

$$Y_{fc1}=14.93+2.86\cdot X_1+6.88\cdot X_2-$$
$$-0.30\cdot X_1^2-3.65\cdot X_2^2+1.02\cdot X_{12}^2;$$

$$Y_{fc2}=36.70+4.88\cdot X_1+11.38\cdot X_2-$$
$$-2.35\cdot X_1^2-6.05\cdot X_2^2+2.60\cdot X_{12}^2;$$

$$Y_{c2}=6.43-0.05\cdot X_1-3.80\cdot X_2+$$
$$+0.65\cdot X_1^2+2.90\cdot X_2^2-0.30\cdot X_{12}^2.$$

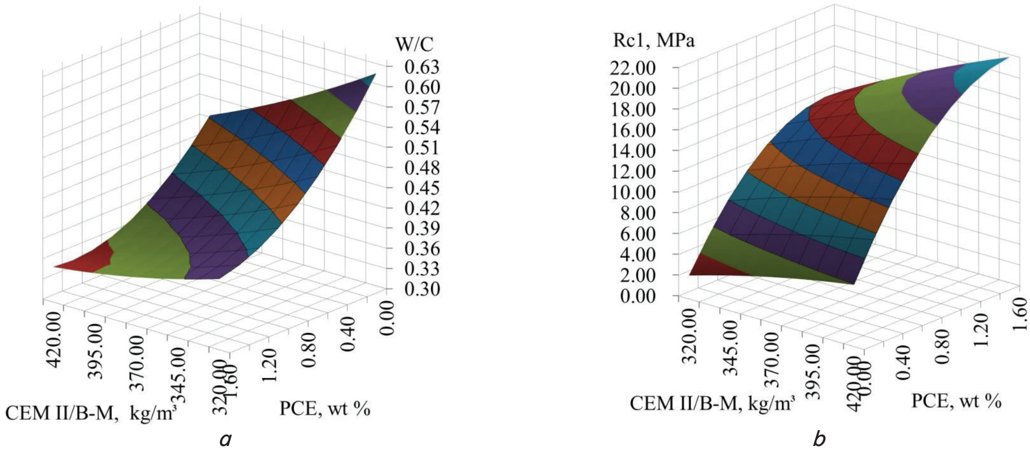
Analysis of the obtained polynomial regression equations and experimental-statistical models of concretes revealed that with the increase of cement usage from 320 to 420 kg per m^3 in presence of 2.0 wt. % Na_2SO_4 to achieve flow table diameter 16–18 cm, a decrease in W/C from 0.62 to 0.48 (Fig. 4, *a*) was observed. Concrete exhibited decrease in the early strength (from 3.1 to 5.8 MPa after 1 day). With the introduction of 1.0–1.5 wt. % PCE, due to significant water-reducing effect (by 34–27 %), the strength of the modified concrete significantly increased (4.6–3.5 times) and reaches values of 14.4; 18.3 and 21.5 MPa. As can be seen from Fig. 4, *b*, after 2 days of curing, modified concrete with cement amount of 420 kg/m^3 and PCE of 1.6 wt. % had the highest strength (f_{c2}=47.0 MPa).

It should be noted that the greatest increase in strength (1.8–2.0 times) was observed for the modified concrete and increased cement amount of 380 kg/m^3 and PCE from 0.2 to 1.0 wt. %. The smallest increase in strength (1.1–1.2 times) was found for cement amount of 420 kg/m^3 and PCE from 1.2 to 1.6 wt. %. Calculations of concrete clinker efficiency revealed that with an increase in strength of concrete based on CEM II/B-M cement, specific consumption of clinker per unit of strength decreased by 3.75 times from 15 to 4 kg/m^3 MPa (Fig. 5, *b*) after 2 days and 3.5...3.1 kg/m^3 MPa after 28 days.

Results showed a regularity associated with simultaneous influence of clinker efficiency in a concrete on its technical and environmental indicators. Based on graphical interpretation of mathematical models, it was found that the greatest increase in concrete strength was for of the amounf of Portland cement between 350...380 kg/m^3 and amount of PCE 0.8...1.2 wt. %. In this case, in terms of specific strength, clinker-efficient modified C25/30...C35/45 concrete classes are characterized by their average growth (f_{cm2}/f_{cm28}=0.32...0.39).

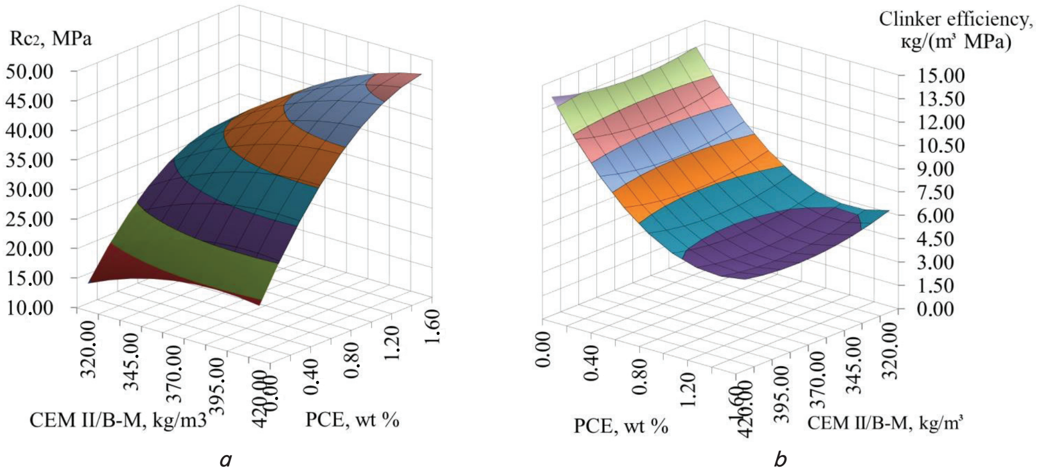
It should be noted that particle size distribution of main components which determines packing density of grains is crucial for obtaining high early strength of clinker-efficient concretes [8]. Therefore, granulometric composition of the fillers, composite Portland cement and nanomodifier were optimized. To increase the content of reactive particles in the cement matrix of clinker-efficient concrete, a colloidal suspension of nano-SiO_2 was used. As can be seen from Fig. 6, main components of concrete mix are distributed by size classes.

The study results show that for aggregates fractions 4–16 and 2–4 mm, 50 % of grains correspond to sizes of 10.1 and 2.8 mm and to 0.290 mm for sand. At the same time, for composite Portland cement and nano-SiO_2, 50 % of volume of particles correspond to sizes of 11.82 and 0.19 µm. Studies of particle size distribution by laser diffraction have established that for CEM II/BM 32.5 R, average diameter by volume $D[4; 3]$ and specific surface $D[3; 2]$ corresponds to 25.9 and 4.38 µm (Table 2). At the same time, these diameters for nano-SiO_2 are reduced to 0.209 and 0.200 µm, respectively.



a *b*

Fig. 4. Response surfaces: water/cement ratio of the concrete mixture (*a*), concrete strength after 1 day of hardening (*b*)



a *b*

Fig. 5. Response surfaces after 2 days of hardening: concrete strength (*a*), clinker efficiency in concrete (*b*)

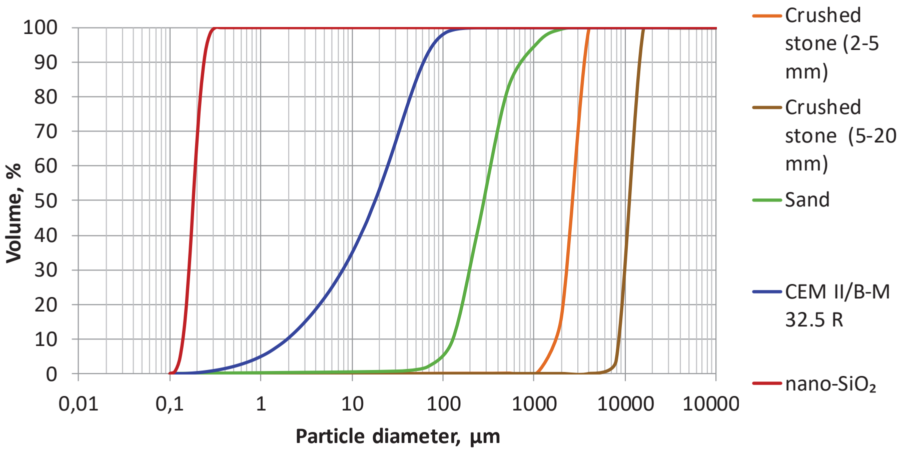


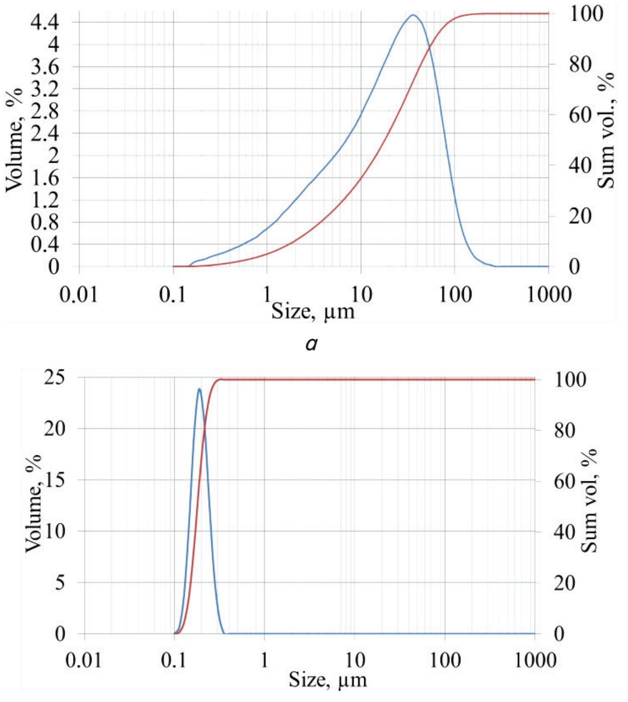
Fig. 6. Integral distribution of grains of main components in a clinker-efficient concrete and a nanomodifier

Table 2

Granulometric composition of composite Portland cement CEM II/B-M 32.5 R and nano-SiO_2

Material	∅<0.5 µm, %	∅<1 µm, %	∅<5 µm, %	∅<10 µm, %	∅<20 µm, %	$D[3;2]$, µm	$D[4;3]$, µm	d_{50}, µm
CEM II/B	2.05	5.74	21.44	35.43	57.35	4.38	25.9	17.9
nano-SiO_2	100.0	100.0	100.0	100.0	100.0	0.200	0.209	0.204

It should be noted that a highly dispersed 0.2...1.0 µm fraction with a content of 5.4 vol. % (Fig. 7, *a*) displays itself for CEM II/B-M 32.5 R with a high content of mineral additives. At the same time, for nano-SiO_2, despite partial agglomeration, all particles (100.0 vol. %) are in the range up to 0.3 µm (Fig. 7, *b*).



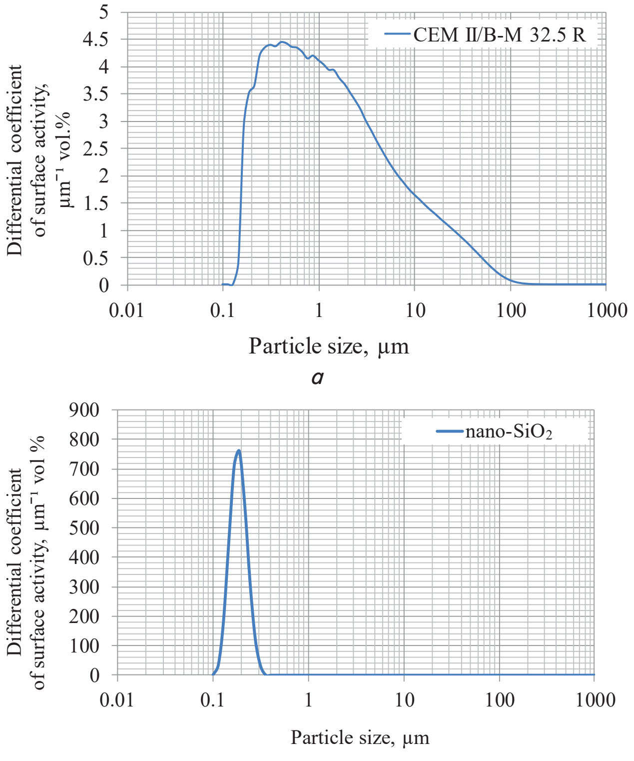
b

Fig. 7. Particle size distribution: composite Portland cement CEM II/B-M (*a*); nano-SiO_2 (*b*)

For a more complete assessment of dispersity of composite Portland cement and nano-SiO_2, the particle surface distribution coefficient was determined using granulometric distributions. It was found that the highest surface area in CEM II/B-M 32.5 R (K_{isa}=4.45 μm^{-1} vol. %) is exhibited by 0.42 µm particle size. For the 5...10 µm fraction, this coefficient decreases by 2.1...2.8 times and by an order of magnitude as the particle size increases (Fig. 8, *a*). At the same time, for most the reactive, smallest nano-SiO_2 particles with a size of 0.188 µm, maximum K_{isa} value is 761.2 μm^{-1} vol. % which is 128 times higher compared to CEM II/B-M (Fig. 8, *b*), that is the contribution of this fraction to specific surface of the cementing system reaches 45 %. In the processes of early structure formation, the smallest fractions make major contribution to development of specific surface of the cementitious matrix. This largely determines rate of early strength gain in clinker-efficient concretes.

Effect of the superplasticizer (PCE), hardening activator (Na_2SO_4), nano-SiO_2, and X-Seed accelerator (nano-C-S-H) on the properties and strength of clinker-efficient concretes was studied on an optimized composition of the component mix. The mix design per 1 m^3 was as follows: cement – 370 kg, sand – 407 kg, aggregate 2–4 mm – 527 kg, aggregate 4–16 mm – 824 kg; slump flow of S4 was assumed. The results of the experimental tests have shown that to achieve slump flow of S4 for a concrete mix without additives, water-cement ratio has to be 0.68, average density 2,400 kg/m^3, air content 3.2 %.

As can be seen from Fig. 9, early strength after 12 and 24 h was 0.8 and 10.2 MPa, respectively, and standard strength was 40.5 MPa that corresponds to the C25/30 class. With the introduction of PCE+Na_2SO_4 additive, the water content was reduced by 40 % while slump test resulted in the 160 mm of flow (ρ=2,420 kg/m^3, V_p=2.2 %). According to assessment of specific strength by EN 206-1, such modified concrete is characterized by its average increase (f_{cm2}/f_{cm28}==0.39). Introduction of Na_2SO_4+nano-SiO_2+C-S-H-PCE complex additive in the concrete mixture (W/C=0.40, ρ=2410 kg/m^3, V_p=2.5 %) provides an 8-fold increase in early strength at 12 h and 2.3 times increase after 1 and 2 days. For nanomodified alkaline-sulfate-activated clinker-efficient concrete, standard strength is 73.9 MPa which corresponds to C50/60 strength class. According to the specific strength, nanomodified clinker-effective concrete belongs to rapid-hardening concretes (f_{cm2}/f_{cm28}=0.51).



b

Fig. 8. Coefficient of differential particle distribution by surface: composite Portland cement CEM II/B-M (*a*); nano-SiO_2 (*b*)

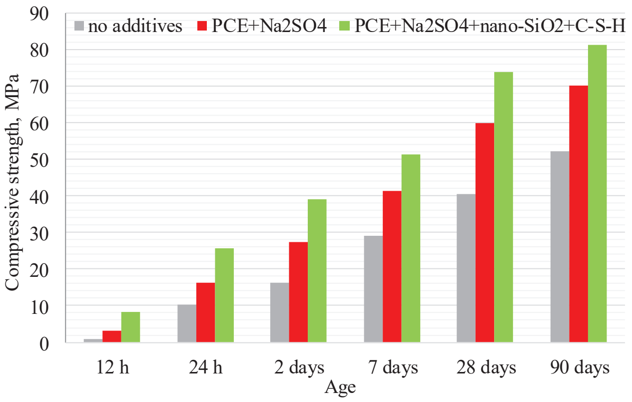
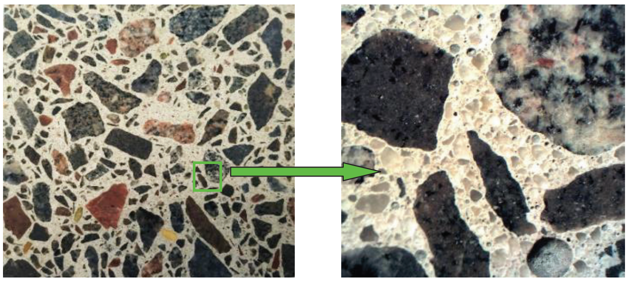


Fig. 9. Strength of clinker-efficient concretes without additives and with additives Na_2SO_4, nano-SiO_2, X-Seed, PCE

Nanomodified, rapid-hardening clinker-efficient concretes are characterized by formation of a dense interfacial transition zone between the coarse aggregate and the cement matrix at a macro level. As can be seen from Fig. 10, *a*, grains of aggregates of various sizes are distributed evenly in the cementitious matrix of concrete. At the same time, nanomodification of the cementitious matrix determines high strength of the interfacial transition zone at «matrix-aggregate» boundary at a meso level (Fig. 10, *b*).

Studies of pore structure have established that nanomodified concrete was characterized by increased number of fine voids ($A_{300}=1.34$) evenly distributed in the cementitious matrix (Fig. 11). This was confirmed by larger specific surface area. In addition, the Powers index which determines the distance between voids measured 0.157 mm (norm is ≤0.2 mm) which determines increased freeze-thaw resistance.

The results proved an existence of an interesting mechanism associated with formation of microstructure in the cementitious matrix of a clinker-efficient concrete. In particular, electron microscopy has revealed that cementitious matrix of the concrete with no additives was had porous microstructure with weak adhesion between hydrated phases (Fig. 12, *a*). Nanosilica has exceptional reactivity compared to other types of silicate materials and improves performance of cementitious materials. The results obtained using the SEM and EDX methods indicate that addition of nanosilica particles with high surface reactivity to the cement paste improves microstructure of composite cements. In this case, leaching of calcium ions becomes much lower since nanosilica particles react with calcium hydroxide to form additional clusters and a denser C-S-H (I) gel at early stage of hardening (Fig. 12, *b*). Particularly early void clogging at microstructure level is explained by introduction of C-S-H nano-seeds that promote crosslinking of the cement matrix particles. The «accelerating effect» of nano-seeds of C-S-H and nano-SiO_2 in combination with PCE and alkaline activator (Na_2SO_4) can significantly compensate for the slow rate of hydration in the cementitious system of clinker-efficient concretes. Nanomodification of the cement matrix increases the content of fine grade particles resulting in more dense nature. The process increases the contact area between particles of gel-like low-basicity phases C-S-H (I) with formation of a composite cross-linked structure at micro- and nano-levels which significantly accelerates hardening of clinker-efficient concretes.



a *b*

Fig. 10. Nanomodified concrete: macrostructure (*a*); mesostructure (*b*)

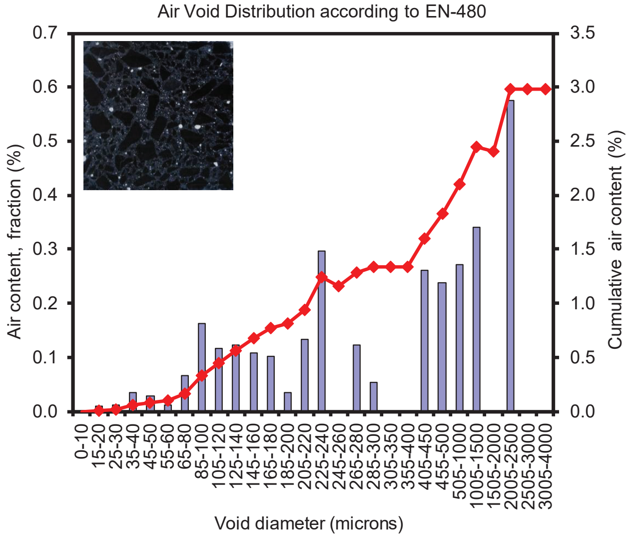
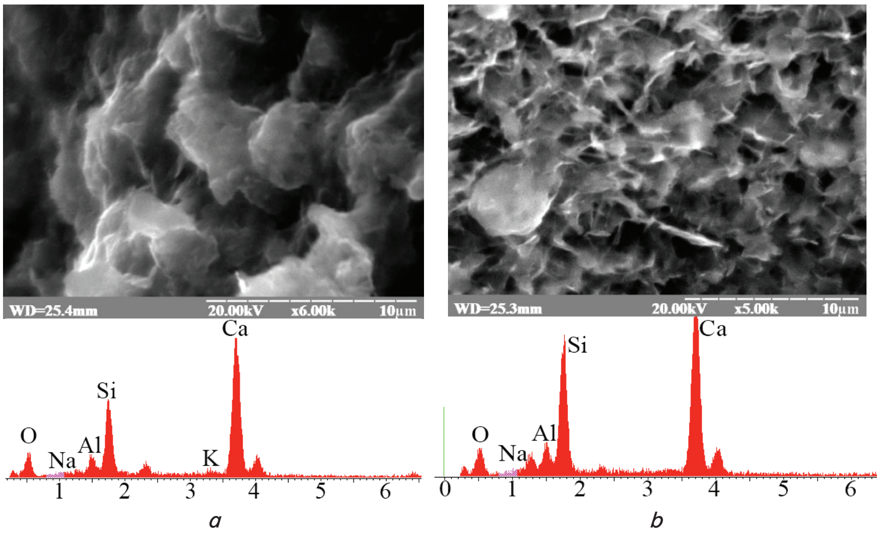


Fig. 11. Size distribution of air voids in a nanomodified concrete



a *b*

Fig. 12. Microstructure and spectra of characteristic X-ray spectra of cement matrix of clinker-effective concrete after 2 days of hardening: with no additives (*a*); with addition of Na_2SO_4+nano-SiO_2+C-S-H-PCE (*b*)

For nanomodified concrete of C50/60 class, prism strength $f_{c\,prism}$=62.5 MPa, modulus of elasticity E_{cm}=48.4 GPa, Poisson coefficient ν=0.17; frost resistance brand: F300.

6. Discussion

Concrete is a hierarchical composite material of disordered structure over a wide range of scale levels. At the sub-microscopic level, cement paste is the main component of concrete. It is formed as a result of reaction of the clinker minerals and water. Cement paste acts as a binder for other components and is responsible for concrete strength. Gel-like calcium hydrosilicates (C-S-H) and crystalline hydrates such as calcium hydroxide, AF_m and AF_t phases are main crystalline phases of the hydration products. The majority of cementitious matrix of a concrete based on composite Portland cement is produced by nanocrystalline calcium hydrosilicates (C-S-H). Therefore, to improve clinker efficiency of concrete, it is necessary to better understanding the chemical and physical nature of cement paste, study it at a molecular level and establish role of individual components.

According to obtained results, grain composition of aggregates and fillers and their specific surfacearea have a influence on water demand and consistency of concrete mixture. Uneven distribution of grain fractions results in decrease in the concrete mixture workability and quality of hardened concrete. In this case, the cumulative specific surface area of the composite determines the water demand to moisten the grain surface. The study results show that cumulative specific surface area of components (cement consumption in composition No. 2 is 370 kg/m^3) is equal to 159,600 m^2 (per 1 m^3) including a 92.7 % constitution of cement grains (Fig. 3). This causes an increase in water demand of the concrete mix (W/C=0.55, average film thickness of H_2O molecules is 1.3 µm) which leads to a decrease in strength and durability of concrete. It is noteworthy that in the manufacture of commercial concrete of C25/30 class, mainly clinker Portland cement CEM I 42.5 (C=370 kg/m^3) is used with addition of lignosulfonate plasticizers. In this case, specific consumption of clinker per unit strength in concrete is 9.25 kg/(m^3 MPa) which determines a significant indicator of intensity of CO_2 emissions in concrete (E_{CO2}=8.0 kg/m^3·MPa).

Therefore, effective solution of this problem consists in correct selection of the fillers and microfillers on the one hand and introduction of superplasticizers based on polycarboxylate ether on the other hand. This allows to obtain tight packing of the mix and to reduce the distance between cement particles in an initial period of the hydration process which contributes to growth of strength and durability. Fine-dispersed fractions of mineral additives improve porous structure resulting in a growth of water resistance and durability of concrete. The E_{CO2} emission index can be reduced by 70 % for the same concrete strength class.

Use of PCE superplasticizers leads to a slowdown of early strength gain in modified clinker-efficient concretes. Therefore, the effect of acceleration of early strength is largely achieved through alkaline-sulfate activation. The proposed solutions feature designing compositions of clinker-efficient concretes by the method of mathematical experiment planning. The method takes into account alkaline- sulfate activation (2.0 wt. % Na_2SO_4). Composite Portland cement CEM II B-M 32.5 R (X_1=320; 370; 420 kg/m^3) and PCE (X_2=0; 0.8; 1.6 wt. %) as variables. Obtained results showed that (Fig. 5, *a*), modified clinker-efficient concrete with cement amount between 320 and 380 kg/m^3 and PCE (from 0.2 to 1.0 wt. %) containing hardening activator exhibited highest (1.8–2.0 times) strength gain. This is due to alkaline-sulfate activation of the composite cementing system through synergistic interaction of its mineral components with formation of hydrogelenite C_2ASH_8 and alkaline hydro alumosilicates N-A-S-H, which is confirmed by study [22]. At the same time, a significant reduction of specific consumption of clinker per unit strength (up to 4 kg/m^3 MPa) in the early age of concrete should be noted (Fig. 5, *b*). According to specific strength, modified clinker-efficient concrete is characterized by its average growth (f_{cm2}/f_{cm28}=0.32...0.39) which is insufficient to ensure rapid pace of concrete pouring and repair works.

It was established that optimization of dispersity of cement and nanomodification have a significant impact on the rate of hardening of clinker-efficient concrete in the early period. For example, authors of [10] have developed a new approach to determine dispersity of powder materials using a differential coefficient of particle distribution over surface. The results show that the smallest particles mainly contribute to development of specific surface of nanomodified cementing system (K_{isa}=4.45 µm^{-1} vol. % for CEM II/B-M 32.5 R and K_{isa}=761.2 µm^{-1} vol. % for nano-SiO_2) (Fig. 8, *a, b*) which largely determines rate of early strength gain in clinker-efficient concretes. The early structure formation can be activated by increasing cumulative surface area of the cementing system by addition of ultrafine nano-SiO_2. This allows to accelerate formation of C-S-H (I) nanodispersed gel which improves phase interactions and strengthens the interfacial transition zone. On the other hand, the effect of acceleration of early strength gain significantly strengthens additional introduction of colloidal suspension of C-S-H nano-seeds using the X-Seed technology. This is evidenced by the results (Fig. 9) of increased early strength gain indices of nanomodified clinker-effective concrete: R_c=6.4 MPa after 12 hrs which is 8 times more than for a concrete without additives. Introduction of nano-SiO_2+C-S-H-PCE colloidal complex makes it possible to obtain concretes of C50/60 class with a rapid increase in strength gain (f_{cm2}/f_{cm28}=0.51).

The results of porosity study and electron microscopy shown in Fig. 11, 12 confirm the latter conclusions. The results show that small voids (A_{300}=1.34) are evenly distributed in the structure of the cementitious matrix of nanomodified concrete (Fig. 11). This is confirmed by the Powers index (L=0.157 mm) and determines increased freeze-thaw resistance. The method of microscopic analysis shows a compacted nanomodified microstructure of an alkaline-activated cement matrix (Fig. 12, *b*) based on low-basic C-S-H (I) phases reinforced by acicular AF_t phases.

Some studies [7, 24] describe the impact of nanoscale additives on accelerating processes in the early period of concrete structure formation. The data obtained indicate that colloidal solutions of nano-SiO_2 have a strong effect in the cementitious matrix of concretes based on Portland cement of CEM I type due to pozzolanic reaction and microstructure compaction. However, the results of studies of combined effect of hardening activators, nanoscale additives, in particular nano-SiO_2 and C-S-H-PCE, on the processes of early structure formation were not sufficiently elucidated. Finding out the mechanism behind it will open the possibility of effective rate regulation, especially rate of early hardening (12–24 hrs) of clinker-efficient concretes by using

Na_2SO_4–nano-SiO_2–C-S-H-PCE complex nanomodifier and new nanotechnological approaches.

Based on results of different studies, efficient technologies will be developed that will allow to create high-strength low-clinker concretes of high durability. The methods will apply nanotechnological approach, controlling synthesis of strength of the cementitious matrix and mechanisms for increasing efficiency of alkaline and sulfate activation. This will provide an opportunity to obtain rapid-hardening clinker-efficient concrete. The conclusions will give the engineers tools for solving problems related to the need of implementing the strategy of low carbon technology development.

7. Conclusions

1. The grading curve of aggregates and filler was designed for this study: 31.5 % of fine (0...2 mm) aggregate, 27.7 and 40.8 % of coarse (2...8 and 8...16 mm, respectively) aggregate. A grading curve was designed which fitting the composition range according to EN 933-1:2012-03. It was shown that cumulative specific surface area of all components at cement consumption C=370 kg/m^3 was 159,600 m^2 per 1 m^3 of the mix (92.7 % for cement grains). This determines increase in water consumption of the concrete mixture (W/C=0.55) which leads to an increase in concrete porosity. Optimization of the mix of aggregates and introduction of PCE super-plasticizers make it possible to obtain dense packing of grains and reduce distance between cement particles in the initial period of structure formation which raises durability of modified clinker-efficient concretes.

2. Composition of modified clinker-efficient concretes based on composite Portland cement with account of alkaline-sulfate activation was designed by the method of mathematical experiment planning. Based on graphical interpretation of mathematical models, it was established that the most effective consumption of composite Portland cement CEM II/B-M 32.5 R was within 350...380 kg/m^3 with content of PCE was 0.8....2 wt. %. The clinker-efficient concretes of C25/30...C35/45 classes were characterized by its average strength increase (f_{cm2}/f_{cm28}=0.32...0.39).

3. It was established that optimization of composition of a clinker-efficient concrete and nanomodification have a decisive influence on hardening rate. Introduction of the Na_2SO_4 – nano-SiO_2 – C-S-H-PCE complex nanomodifier into clinker-efficient concrete provides increased rates of particularly early strength R_c=6.4 MPa after 12 hrs and production of concretes of C50/60 class with rapid strength gain (f_{cm2}/f_{cm28}=0.51). Nanomodified clinker-efficient concrete is characterized by a fine porous structure (A_{300}=1.34) with evenly distributed voids in the cementitius matrix (Powers index L=0.157 mm) which determines increased freeze-thaw resistance (F300).

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