Nanomodified Rapid Hardening Concretes

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Abstract. One of the priority areas of modern construction production is the introduction of high-performance high-speed concrete with improved technological and construction-technical properties for the design, erection and repair of engineering structures. Modern studies have made it possible to view concrete from the nanoscale point of view as a material characterized by a complex hetero-scale structure of hydrated cement phases and mineral additives. The properties of concrete are determined by the type, size and nature of the interaction of the components of each structural level, which creates the possibility of nanotechnological regulation of the processes of structure formation and control of operational characteristics. The main task of nanomodification is to provide a managed structure with more nanoscale hydration products. Typical nanowires in Portland cement systems are micro- and nanosilica SiO2, nanoglosses, TiO2, Al2O3, Fe2O3, CaCO3, carbon nanomaterials (carbon nanotubes and nanofibers). The introduction of C-S-H nanoparticles is the most effective way of accelerating the hydration of cement compared to other nanowires, by ensuring the growth of hydration products without an energy barrier in the pore space between the cement grains. The presented studies are devoted to the study of the nanomodification efficiency of concrete with a complex additive containing a polycarboxylate superplasticizer and synthesized nanoscale C-S-H particles. Based on the analysis of the results of early and design strength of nanomodified concrete, it is established that it is characterized by rapid strength gain and high durability after 28 days. The construction and technical properties of nanomodified concretes were investigated after 1 and 28 days of curing.

1. Introduction
One of the priority areas of modern construction production is the introduction of high-performance high-speed concrete with improved technological and construction-technical properties for the design, erection and repair of engineering structures and structures of residential, public, industrial construction to ensure the commissioning of objects in operation reliable work throughout the life cycle. High performances of concrete mix and durability in early and design age of innovative structural materials determine their technological efficiency. As a result, energy and resource consumption of their production, laying, curing, as well as the required pace of construction under different temperature conditions are ensured.
Modern studies have made it possible to view concrete from the nanoscale point of view as a material characterized by a complex hetero-scale structure of hydrated cement phases and mineral additives. The properties of concrete are determined by the type, size and nature of the interaction of the components of each structural level, which creates the possibility of nanotechnological regulation of the processes of structure formation and control of operational characteristics [1, 2]. Nanotechnology covers the area of science and technology relating to elements smaller than 100 nm, in construction this area expands to 200 nm and associated nano-interactions (phenomena) [3]. The main task of nanomodification is to provide managed structure with more nanoscale hydration products.

A considerable number of surface atoms in nanoparticles, which are determined by excess surface energy, increases the activity, reactivity of the material and determines its bulk properties, while the role of the interfacial surface increases significantly [2, 3]. The introduction of nanoparticles can significantly alter the physico-chemical interactions in the cementitious matrix, playing the role of catalysts or crystallization centers depending on the chemical composition of the surface and the concentration. Typical nanowires in Portland cement systems are micro- and nanosilica SiO₂, nanoglasses, TiO₂, Al₂O₃, Fe₂O₃, CaCO₃, carbon nanomaterials (carbon nanotubes and nanofibers) [3-5]. The introduction of C-S-H nanoparticles is the most effective way of accelerating the hydration of cement compared to other nanowires, by ensuring the growth of hydration products without an energy barrier in the pore space between the cement grains [6].

The modern development of concrete technologies is based on the use of highly mobile mixtures, that requires their modification by highly effective superplasticizing additives to reduce the water-cement ratio [7]. Nanotechnology approach of creation of high-tech binders with high early strength is based on composite modification of complex additives on the basis of nanocarried molecular polycarboxylate (RCE) additives [8].

Accelerated construction schedules that determine the reduction in the holding time of concrete in formwork, are related to the economic effect, require knowledge of the behavior of concrete at an early age to ensure safety during construction, as well as the proper durability and long-lasting properties [9, 10].

The purpose of these studies was to investigate the kinetics of the strength and construction properties of concrete modified by a complex nanomodifier based on the PCE superplasticizer and an innovative hardening accelerator containing C-S-H nanoparticles.

2. Materials, methods and procedure

Portland cement CEM I–42.5R of "Ivano-Frankivsk Cement" (Ukraine) was used to prepare the concrete. The compressive strength of Portland cement after 1, 2, 7 and 28 days according to EN 196-1 is 18.4 respectively; 28.9; 40.6 and 47.5 MPa and meets the requirements of EN 197. Natural quartz sand with a fineness modulus of 1.83 (maximum grain size of 2.5 mm) and granite crushed stone of the fraction of 5-20 mm were used as fillers. The concrete of nominal composition 1:1.37:2.79 was designed, with the consumption of binder 430 kg/m³ of mark on the slump class of the concrete mixture S5.

The composition of concrete without additives was used as a control (RC). Adjustment of the rheological behavior of concrete mixtures was carried out by polycarboxylate superplasticizer Master Glenium ACE 430 (PCE) in the amount of 1.5 wt.%. In order to ensure high parameters of strength development, a Master X-SEED® 100 curing accelerator (nanoscale calcium hydroxilicate particles suspension) was introduced according to the Crystal Speed Hardening concept. The amount of accelerator in the concrete mixture was 2 wt.%. The components of the concrete mixture were mixed in a laboratory concrete mixer. Superplasticizer and curing accelerator were introduced with mixing water. The consistence of modified concrete mixtures was determined by cone sedimentation according to EN 12350-2 and flow test according to EN 12350-5. Specimens-cubes of concrete 100 x 100 x 100 mm for up to 1 day were cured at room temperature, after dissolution they were immediately tested for strength. After 1 day of curing, the samples were dissolved and stored under normal conditions (t = 20 ± 3°C, φ = 95%).
The compressive strength tests of the developed concretes were carried out after 6, 12, 18 h and 1, 2, 7 and 28 days of curing. Indicators of deformativ properties (prism strength, an elasticity modulus, and the Poisson coefficient) of modified concretes were determined after 1 and 28 days of curing on specimens-prisms of size 10 × 10 × 40 cm at a loading level of 30% of destructive.

The features of the porous structure of nanomodified concretes were investigated by the water absorption kinetics of the samples 7.07 × 7.07 × 7.07 cm, which hardened for 1 and 28 days. In addition to this, the method of discrete weighing of pre-dried samples is used, that is carried out after 0.25; 1.0 and 24 h after immersion.

3. The results of the research

The consistency of the control concrete mixture without additives, that corresponds to the slump class S5, is achieved at B/C = 0.53. The flow diameter of concrete according to EN 12350-5 was 510 mm.

The use of a polycarboxylate superplasticizer and a complex additive, on basis of the superplasticizer and curing accelerator, allows to obtain a precipitate of a slump of a concrete mixture of 21-23 cm at B/C = 0.29 with providing a water-reducing effect ΔB/C = 45.3%. The flow diameter is somewhat reduced (up to 500 mm).

The concrete of the control composition is characterized by strengths of 1 and 2 days 19.6 MPa and 30.5 MPa, respectively. After 28 days of curing, the concrete strength is 57.6 MPa, which corresponds to the class strength C 40/50. The results of testing the strength of concrete with the complex nanocomposition of PCE + X-SEED showed a high intensity of early strength set (up to 1 day). Thus, after 6 and 12 hours the strength of such concrete is respectively 11.8 and 39.4 MPa (figure 1). At the same time, the compressive strength of plasticized concrete after 6 and 12 h corresponds to 1.5 and 31.2 MPa, respectively.

![Figure 1. Compressive strength of modified concretes.](image)

The intensive synthesis of concrete strength at an early date in the presence of a complex nanomodifier is due to the high water-reducing effect of the polycarboxylate superplasticizer with the provision of intergranular compaction, and to accelerate the processes of Portland cement hydration by introducing ready-made crystallization centers with uniform [8, 9]. The nanomodified developed concretes meet the requirements for high-speed concrete according to the "Technical Requirements for Materials and Mixtures for the Repair and Maintenance of Concrete Pavements" – TL BEB-StB (achieve concrete strength of 20 MPa in 5-24 hours). According to EN 206-1, nanomodified concretes are characterized by a rapid strength development (f_{cm}/f_{cm28} = 0.72), with a yield of 66.6 MPa after 2 days.
After 28 days the strength of high-strength nanomodified concrete is 92.3 MPa (compressive strength class C 70/85) and meets the requirements for high strength.

To evaluate the effectiveness of the additives introduced, the relative strength of the concrete was calculated. The strength of the control concrete after 28 days was chosen as the reference. As can be seen from figure 2, the character of the increase in the early strength of the control and modified concretes is different. Thus, the intensification of curing of admixture concrete occurs after 12 h, while the modified concrete - after 6 h. It should be noted that the strength of concrete modified with the addition of PCE + X-SEED, after 6 h is 20% of the strength of the control concrete after 28 days. At the same time, the strength of plasticized concrete after 6 h is only 3% of the strength, which indicates some blocking of the hydration processes of Portland cement in the presence of polycarboxyl superplasticizer. After 28 days the strength of concrete with the addition of RCE exceeds the strength of the control composition by 1.43 times, and with a complex nanomodifier 1.6 times.

The increased water demand of the control concrete mixture to obtain the required consistency causes the increased porosity of the concrete, both at an early age and after 28 days. Thus, the parameter of average size of pores size of the control concrete after 1 day is 22.2, and after 28 days it decreases to 10.6 (table 1), with the overall porosity decreases from 21.7% to 11.8%. Reducing water consumption by 44.6% with the introduction of a superplasticizer PCE reduces the pore size to 4.2 after 1 day and 1.05 after 28 days.

The overall porosity of plasticized concrete samples at an early age decreased by 2.4 times, and after 28 days - by 1.6 times compared to the control. Parameter of average size of pores of concrete modified with the additive PCE + X-SEED is 1.3 in 1 day and 0.53 in 28 days. This is due to the rapid formation of the cement stone structure with a uniform distribution of hydration products. The change in concrete water absorption over time confirms the rapid formation of the composite structure with the introduction of the PCE + X-SEED complex modifier.

The modulus of elasticity is the basic property of concrete; indicating the ability of the concrete to be resiliently deformable and related to its stability, it is important in assessing the deformation of structural elements in service conditions [8]. Prism strength of concrete modified with additives PCE + X-SEED, in 1 and 28 days reaches respectively 72.3 and 92.6% cube strength. In terms of deformative indices after 1 day (prism strength 36÷37 MPa, modulus of elasticity 33.1÷35.4 GPa) nanomodified concretes meet the normative values for C32/40 class concrete, and indicate their ability to withstand
higher stresses with the same relative deformations. It should be noted that after 1 day of curing for nanomodified concrete, 66% of the modulus of elasticity is reached. The high deformation properties of fast-curing nanomodified concrete are due to the rapid formation of a dense, low-defective structure.

**Table 1. Construction and technical properties of concrete.**

| Parameter                          | Value for concrete, aged, days |
|------------------------------------|---------------------------------|
|                                    | control                         | P I-500P+PCE | PC I-500P+PCE+X-SEED |
|                                    | 1  | 28  | 1  | 28  | 1  | 28  |
| Density of concrete, ρc, kg/m3      | 2280 | 2310 | 2380 | 2420 | 2420 | 2480 |
| Porosity of concrete, P, %          | 21.7 | 11.8 | 9.1 | 7.6 | 7.6 | 5.3 |
| Parameter of average size of pores  | 22.2 | 10.6 | 2.5 | 1.2 | 1.3 | 0.53 |
| Water absorption, Wm, %             | 9.1  | 4.5  | 3.4  | 2.3  | 2.8  | 1.2  |
| Mean compressive strength, f, MPa   | 19.6 | 57.6 | 41.6 | 82.2 | 50.2 | 92.3 |
| Prism strength, fprism, MPa         | 10.3 | 48.5 | 36.2 | 63.3 | 36.3 | 85.5 |
| Elasticity modulus, Em, GPa         | 12.2 | 41.5 | 33.1 | 52.2 | 35.4 | 53.6 |
| Poisson coefficient                 | 0.25 | 0.16 | 0.24 | 0.17 | 0.20 | 0.17 |
| Concrete shrinkage, εc, mm/m        | 0.2  | 0.32 | 0.12 | 0.21 | 0.07 | 0.15 |

Shrinkage of concrete in the early terms may cause cracking and deterioration of concrete performance [11]. According to the results of tests, it is found that as a result of high water-reducing effect, fast binding of water to hydrate compounds, as well as accelerated synthesis of strength of cement stone with reduction of specific binder flow rate, fast-setting nanomodified concrete is characterized by reduced values of shrinkage deformations (after 1 day – 0.09 mm/m). After 28 days, the shrinkage of such concrete is 0.15 mm / m, while the control concrete is 0.32 mm/m.

**4. Conclusions**

Complex nanomodification of concrete with an additive containing polycarboxylate superplasticizer and synthetic calcium hydroxilicate particles, provides high-tech concrete mixtures (mobility class S5), as well as high-strength concrete (class C70/85) with a rapid growth of strength (fcm2/fcm28=0.72). Sealing the system with the introduction of a complex modifier causes a decrease in the porosity of 1.6-2.4 times. The growth of deformatory indices of nanomodified high-strength concretes is caused by the rapid formation of a maldefective structure with the formation of fibrous products of hydration, which increases the ability of concrete to resist destructive deformations and to perceive the active loading of such betonites. Increased building and technical properties of rapid hardening high-strength concrete provide reliable concrete performance in building structures during operation.

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