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*The use of layered double hydroxides (LDHs) is a new direction in chemistry of cement. The influence of calcium/aluminum double hydroxides (Ca-Al LDHs) and polycarboxylate ethers (PCE) on the strength development of Portland limestone cement has been investigated. It has been shown that Ca-Al LDHs form in cement slurry with the introduction of alkaline aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$ . It was determined that this contributes to a significant increase in the early strength of cement stone. However, this reduces the setting time of hardening, and there is a decrease in strength with age. At an early stage of structuring in cement paste with the addition of  $\text{Na}[\text{Al}(\text{OH})_4]$ , metastable high-water hydrate phases of Ca-Al LDHs of type  $\text{C}_4\text{AH}_{19}$  ( $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ ) are formed, which, due to the conversion phenomenon, transform to cubic  $\text{C}_3\text{AH}_6$ . Such processes are accompanied by an increase in overall porosity and decreases in the strength of cement stone. Stabilization of the Ca-Al LDH structure is achieved by introducing anions  $[\text{NO}_3]^-$  into the interlayer space with the formation of Ca-Al- $\text{NO}_3$  LDHs through the use of sol-gel technology. X-ray phase analysis, IR spectroscopy, and electron microscopy proved the fact of synthesis of AFm-phases of type  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . When modifying such hydrates with polycarboxylate ethers, a nanocomposite Ca-Al- $\text{NO}_3$  LDHs-PCE is formed. It was found that when the Ca-Al- $\text{NO}_3$  LDHs-PCE nanocomposite was introduced to CEM II/A-LL 42,5 R, the strength over the period of 8...24 hours increases by 2.0–1.5 times, and, after 2 and 28 days, 58 and 144 % of the standard strength is achieved ( $R_{c28}=62.5$  MPa). The obtained nanomodified Portland limestone cement refers to extra rapid-hardening and high-strength cement, which makes it possible to solve the task of carrying out work on the rapid restoration of reinforced concrete structures' elements*

**Keywords:** Portland limestone cement, layered double hydroxides, polycarboxylate ethers, nanocomposite Ca-Al- $\text{NO}_3$  LDHs–PCE, strength

# EFFECT OF LAYERED DOUBLE HYDROXIDES Ca-Al LDHs AND POLYCARBOXYLATE ETHERS ON THE HARDENING OF PORTLAND LIMESTONE CEMENT

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## 1. Introduction

Concrete is the most widely used building material in civil engineering worldwide. At the same time, according to the principles of sustainable development, reinforced concrete structures must meet functional requirements during a given life cycle [1, 2]. However, under external loads and environmental influences, concrete structures are prone to damage. Various kinds of damage not only reduce the durability of structures but also lead to their unsuitability during operation. Therefore, there is an acute issue to restore building structures using special repair mixtures. At the same time, the main criteria are the high speed of repair and restoration work, as well as the durability and operational reliability of buildings and structures [3, 4].

One of the methods for adjusting the hardening of cement repair mixtures, especially increasing their early strength and water resistance, is the use of alkaline-activated cements [5, 6]. Mixtures based on them are used for the overhaul of the most complex structures that are under a variety of operating conditions. At the same time, when using alkaline accelerators, problems often arise associated with a sharp acceleration of the setting time, an increase the water demand of the binder, which leads to a decrease in the resulting strength of concrete and the durability of building structures [7, 8].

The solution to the problem of obtaining effective cement repair mixtures can largely be achieved through a combination of alkaline and aluminum-containing additives for the purpose of intensive generation of ultrafine AF<sub>t</sub>- and

AF<sub>m</sub>-phases in the early period of Portland cement hardening [9, 10]. This approach is relevant and provides significant prospects in the design of new compositions of repair mixtures. In order to resolve this issue, it is necessary to identify the peculiarities of the influence of alkaline aluminate accelerators on the processes of early structure formation of Portland cement systems.

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## 2. Literature review and problem statement

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The production of Portland limestone cement is accompanied by lower energy consumption and the release of carbon dioxide [11, 12], that is, it has better environmental performance than other types of cement. At the same time, when using repair mixtures, it becomes necessary to increase the kinetics of hardening of Portland limestone cement in the early period of hydration. An option to overcome the corresponding difficulties may be the use of alkaline aluminate Na[Al(OH)<sub>4</sub>]. The advantages of the alkaline aluminate accelerator are to increase the strength at the initial stage of hardening, as well as the water resistance of concrete and leveling the corrosion of reinforcement. The reason for the action of such an admixture is the formation of metastable submicrocrystalline hydrate phases [13, 14].

However, issues regarding the regulation of the setting time of cementitious materials remained unresolved. Effective water-reducing admixtures that provide the technological properties of cementitious materials are superplasticizers based on polycarboxylate ethers (PCE). At the same time, the introduction of PCE causes some inhibition of hydration processes in cement paste. Therefore, the combination of Na[Al(OH)<sub>4</sub>] and PCE admixtures to adjust the processes of early structure formation and to increase the strength of cements is of significant interest for the development of research. Thus, complex admixtures based on alkali metal salts and PCE provide optimization of properties and acceleration of hardening of mixtures of different compositions [15, 16]. The introduction of alkaline aluminate Na[Al(OH)<sub>4</sub>] in combination with PCE makes it possible to obtain high-strength concrete, which is characterized by increased durability in aggressive environments [17, 18]. The disadvantage of such cementitious systems is that there may be some decline in their strength with the age of hardening. The unresolved part of the problem is related to the identification of features of structural-phase transformations of nanodispersed hydrate phases.

Recently, the development of nanotechnology determines increasing prospects in the chemistry of cement [19, 20]. Studies of nanoparticles such as nano-SiO<sub>2</sub> have made a significant breakthrough in improving the performance of cement-based materials. Ultrafine nano-SiO<sub>2</sub> particles with an extremely high specific surface area add a large number of nucleation centers to precipitate hydration products. These effects lead to the so-called seeding effect or nucleation effect of nano-SiO<sub>2</sub>, which can speed up the hydration process and reduce the setting time at an early age of hardening of clinker-efficient cements [21, 22]. Particular importance is also the use of sol-gel technologies in the direction of synthesis of C-S-H-PCE nanocomposites, which are characterized by a significant surface area. During the hydration of the alite phase, the barrier of origin of products is reduced, and the growth of large crystals is inhibited, which leads to a significant increase in the early strength of Portland

cement [23, 24]. Alkaline N-C-S-H-PCE nanomodifiers make it possible to obtain ultra-high-performance concretes of a new generation of increased durability, in particular under extreme operating conditions [25]. Specific interest in building materials science is the use of various kinds of nanocomposites [26]. At the same time, issues related to the development of nanocomposites as hardening accelerator of cements are not sufficiently resolved.

Such admixture as calcium nitrate effectively accelerates the hydration of Portland limestone cement and thus activates the crystallization processes of hydrates; it contains the same cations as clinker minerals [27]. One should also note the importance of using complex admixtures based on calcium nitrate and superplasticizers in concretes. This makes it possible to accelerate the hardening of concretes, as well as increase the efficiency of concreting at negative temperatures. At the same time, the formation of a new phase of type 3CaOAl<sub>2</sub>O<sub>3</sub>·0.83Ca(NO<sub>3</sub>)<sub>2</sub>·0.17Ca(OH)<sub>2</sub>·9.5H<sub>2</sub>O contributes to the early strength of cementitious systems [28, 29]. The use of calcium nitrate in the compositions of repair materials minimizes the progress of chloride corrosion of steel reinforcement, which is one of the main types of damage to reinforced concrete structures [30, 31].

A new direction in the chemistry of cements is the use of layered double hydroxides (LDHs) [32, 33]. Materials with modifiers based on LDHs also have a wide range of applications in various fields of the environment, chemistry, biology and energy [34, 35]. At the same time, calcium hydroaluminate phases of the Ca-Al LDHs type play an important role in cementitious systems. Synthesis of Ca-Al LDHs is achieved by various methods (co-deposition, sol-gel, hydrothermal synthesis, ion exchange, structure reconstruction, mechanochemical, etc.) [36]. In this case, the particle size, crystallinity, and adsorption properties of LDH of different synthesis methods will also differ [37]. It is characteristic that the relationship between the particle size and the dosage of LDHs largely determines the resistance of concrete to chloride penetration [38, 39]. At the same time, research should be undertaken to increase the efficiency of nanocomposites based on the layered double hydroxides Ca-Al-LDHs to accelerate the hydration of cement, as well as to optimize their parameters. This will make it possible to implement a number of their significant effects, which will provide a significant acceleration of the hardening of cementitious systems, as well as increase the operational properties of concrete.

The study of the effectiveness of cementitious systems modified by Ca-Al LDHs predetermines the possibility of designing multifunctional rapid-hardening repair mixtures of a new generation, which provide high mechanical characteristics and durability of building structures under different operating conditions. All this suggests that it is expedient to conduct a study on the processes of adjusting the Ca-Al LDHs nanocomposites and PCE polycarboxylate ethers.

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## 3. The aim and objectives of the study

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The aim of this work is to study the influence of layered double hydroxides Ca-Al LDHs and polycarboxylate ethers on the processes of structure formation, kinetics of hardening, and strength development of Portland limestone cement. This will make it possible to obtain extra rapid-hardening modified Portland limestone cements for repair mixtures and increase their operational properties and durability.

To achieve the set aim, the following tasks have been solved:

- to establish the effect of alkaline aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$  and polycarboxylate superplasticizer PCE on the physical and mechanical properties of Portland limestone cement;

- to synthesize double hydroxides calcium/aluminum Ca-Al LDHs modified by PCE and establish their structural features using a complex of methods of physicochemical analysis;

- to determine the strength development and establish the processes of structure formation of Portland limestone cement, modified with a nanocomposite of the Ca-Al- $\text{NO}_3$  LDHs–PCE type.

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#### 4. The study materials and methods

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##### 4.1. The object and hypothesis of research

The object of our research is the processes of adjustment of the properties of modified Portland limestone cement through the use designing effective repair materials of the new generation.

The main hypothesis of the study is to identify the possibility of a complex combination of layered double calcium/aluminum hydroxides Ca-Al LDHs and polycarboxylate ethers for the development of extra rapid-hardening modified Portland cements with high strength. This assumption is justified by the provision on the effectiveness of the introduction at an early stage of hydration of artificially synthesized nanomodified crystallization centers based on structurally active  $\text{AF}_m$ -phases. The practical implementation of such a simplified phenomenon makes it possible to determine the ways of obtaining effective mixtures for the rapid repair and restoration of reinforced concrete structures with improved operational properties and durability.

##### 4.2. Research materials and equipment used in the experiment

In the study, we used Portland limestone cement CEM II/A-LL 42.5 R with high early strength, produced by JSC Ivano-Frankivskcement (Ukraine). A comprehensive dispersion assessment of CEM II/A-LL 42.5 R found that the specific surface area reaches  $3900 \text{ cm}^2/\text{g}$ ; sieve residue,  $A_{0.045}=5.2\%$ . It should be noted that the specific surface area of the Portland limestone cement CEM II/A-LL 42.5 R is determined mainly by the fine limestone fraction, which largely contributes to its higher reaction-chemical activity [11].

Sodium tetrahydroxoaluminate  $\text{Na}[\text{Al}(\text{OH})_4]$  was used to accelerate the rate of hardening of cementitious systems. This alkaline-aluminate activator  $\text{Na}[\text{Al}(\text{OH})_4]$  adjusts the kinetics of the processes of cement setting and hardening;  $\text{pH}=13.4$ . As a highly efficient modifier, a highly reducing superplasticizer based on polycarboxylate ethers (PCE) was used.

The method of sol-gel technology [36] was employed to synthesize calcium hydronitroaluminate  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  due to an exchange reaction in the liquid phase of alkaline aluminate  $\text{Na}[\text{Al}(\text{OH})_4]$  and calcium nitrate  $\text{Ca}(\text{NO}_3)_2$ . Two types of seeds were obtained by mixing aqueous solutions of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Na}[\text{Al}(\text{OH})_4]$  (sample N 1), as well as aqueous solutions of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Na}[\text{Al}(\text{OH})_4]$  in the presence of polycarboxylate ethers (sample N 2).

Studies of the chemical composition of Portland cements were carried out using the ARL 9800 XP X-ray spectrom-

eter (Thermo Electron SA, Switzerland). The specific surface area of cements was determined by the Blaine method of air permeability. In determining the pH of the medium, a pH meter of the pH-150MI type (Ukraine) was used. Ca-Al- $\text{NO}_3$  LDHs IR spectra were acquired using an FT-IR-Nicolet 8700A spectrometer. The types of hydrate phases were determined using X-ray diffractometry and microscopic analysis. The microstructure of seeding and nano-modified Portland cement was investigated using the scanning electron microscope SEM 106II (SEIMI, Ukraine). The scanning electron microscope is equipped with a micro-analyzer of chemical composition acting in X-ray range; it makes it possible to obtain more complete information about the surface layer of the object.

##### 4.3. Procedure for determining the properties of samples

The parameters of Portland limestone cement were determined in accordance with DSTU B EN 196–1:2015, DSTU B EN 196–3:2015, DSTU B EN 196–6:2015. The impact of  $\text{Na}[\text{Al}(\text{OH})_4]$  and PCE was determined on cement-sand mortar based on Portland limestone cement using monofractional quartz sand. Studies of the effect of synthesized aluminum-containing seeding Ca-Al- $\text{NO}_3$ -LDHs and Ca-Al- $\text{NO}_3$ -LDHs–PCE on the strength development of Portland cement were carried out using polyfractional quartz sand in accordance with DSTU B EN 196-1.

The criteria for the effectiveness of modifier additives (plasticizing and water-reducing effects) were determined in accordance with DSTU B V.2.7-69. The technical effect was determined by the criterion of increasing the compressive strength of modified Portland cements relative to the standard strength  $R_{c28}$  of the Portland limestone cement CEM II/A-LL 42.5 R.

To study the structural groups by IR spectroscopy in the range of  $3800\text{--}300 \text{ cm}^{-1}$ , samples in the form of a colloidal gel were applied to plates  $\text{CaF}_2$  and thallium iodide-bromine in the form of a dry film. To compensate for the absorption of these materials, the same plates were placed in the comparison channels of the Specord M-30 device.

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#### 5. Results of studies on the influence of layered double hydroxides and polycarboxylate ethers on the properties of Portland limestone cement

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##### 5.1. Investigation of the effect of alkaline aluminate accelerator and polycarboxylate ethers on the physical and mechanical properties of Portland limestone cement

The influence of alkaline aluminum-containing hardening accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$  on the properties of the Portland limestone cement CEM II/A-LL was investigated. Figure 1a shows that for cement-sand mortar (C:S=1:3, W/C=0.50) based on CEM II/A-LL 42.5 R, the initial and final setting time are 240 and 285 min, respectively. With the introduction of 3.0 wt%  $\text{Na}[\text{Al}(\text{OH})_4]$ , the initial setting time is reduced to 30 min, and the final setting time – to 40 min. Increase in the amount of  $\text{Na}[\text{Al}(\text{OH})_4]$  to 5.0 wt% leads to a reduction in the initial setting time to 20 min, and the final setting time to 30 min. For the Portland limestone cement CEM II/A-LL, the flowability at W/C=0.50 is 200 mm. With the introduction of  $\text{Na}[\text{Al}(\text{OH})_4]$ , there is a decrease in the flowability of cement-sand mortar. On the other hand, to achieve flowability – 200 mm with the introduction of  $\text{Na}[\text{Al}(\text{OH})_4]$ , water-cement ratio increases

to  $W/C=0.56-0.60$ . Fig. 1, *b* shows that with the addition of 1.5; 3.0; and 5.0 wt%  $Na[Al(OH)_4]$ , flowability decreases to 172; 148 and 130 mm, respectively. Note that an increase in the content of alkaline aluminum-containing activator  $Na[Al(OH)_4]$  to 5.0 wt% leads to an intense loss of workability over time: after 20 min, the average base diameter – 130 mm. At the same time, compressive strength after 14 and 24 h increases by 25–30 % compared to Portland cement without additives and amounts to 7.5–7.0 MPa. It is characteristic that after the introduction of 1.5–5.0 wt%  $Na[Al(OH)_4]$ , hardening in 7 and 28 days leads to a decrease in compressive strength by 1.9–2.3 times. At the same time, the porosity of cement with 3.0–5.0 wt%  $Na[Al(OH)_4]$  increases by 20.1–22.3 %, in particular, open porosity increases by 1.4–1.6 times compared to Portland cement without admixtures.

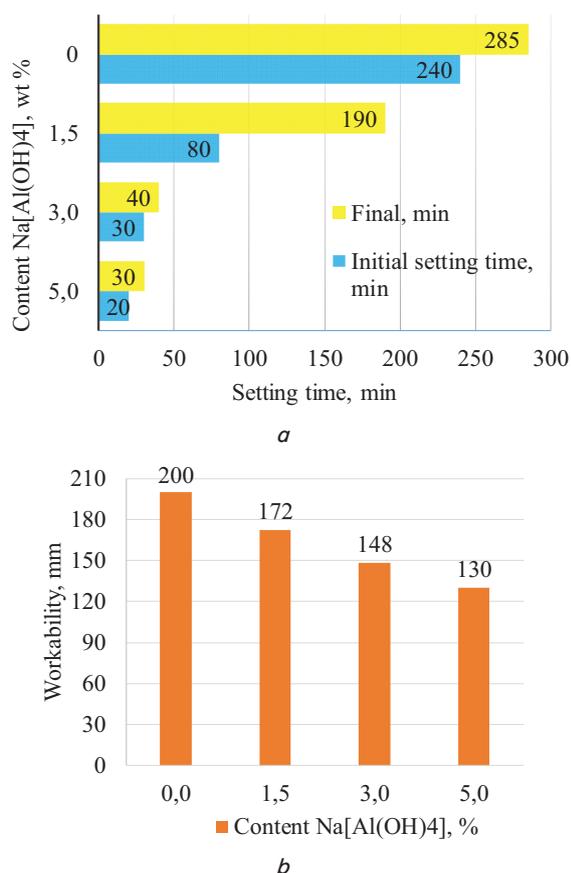


Fig. 1. Effect of  $Na[Al(OH)_4]$  on the Portland limestone cement CEM II/A-LL 42.5 R: *a* – setting time; *b* – workability

To reduce the destructive effect of the alkaline-aluminate activator  $Na[Al(OH)_4]$  on the strength development of Portland cement, a highly reducing superplasticizer of the polycarboxylate type PCE was used. It was established that the introduction of 3.0–5.0 wt%  $Na[Al(OH)_4]$  and 1.0 wt% PCE leads to a sharp reduction in the initial setting time (to 30–20 minutes). At the same time, the PCE provides a reduction in  $W/C$  from 0.50 to 0.38 while ensuring stable flowability 185–190 mm. Note that when polycarboxylate ethers are introduced into the CEM II/A-LL 42.5 R+ $Na[Al(OH)_4]$  system, flowability preservation is

delayed in time up to 25 min compared to the composition of CEM II/A-LL 42.5 R+ $Na[Al(OH)_4]$ . Studies of strength indicators (Fig. 2, *a*) established that for CEM II/A-LL 42.5 R ( $W/C=0.50$ ), compressive strength after 14 h; 1, 2, 7, and 28 days is 5.6; 14.0; 20.8; 30.0; and 41.2 MPa, respectively. Complex admixture of 1.5 wt%  $Na[Al(OH)_4]$  and 1.0 wt% PCE to CEM II/A-LL 42.5 R provides a water-reducing effect  $\Delta W/C=31.6\%$  (flowability – 190 mm) and an increase in strength after 14 h of hardening by 1.6 times ( $R_c=9.6$  MPa); after 1, 2, and 28 days – 1.1–1.2 times ( $R_c$  is 17, 24, and 48 MPa, respectively), compared to Portland cement without modifiers. With the introduction of 3.0...5.0 wt%  $Na[Al(OH)_4]$  and 1.0 wt% PCE to provide flowability – 190 mm, water-reducing effect is  $\Delta W/C=16.2...8.5\%$ , strength after 14 h reaches 7.2 and 5.6 MPa. At the same time, in all other terms of hardening, the strength decreases by 20–35 %. The effect of modifiers on the kinetics of flexural strength development in the mortars is shown in Fig. 2, *b*.

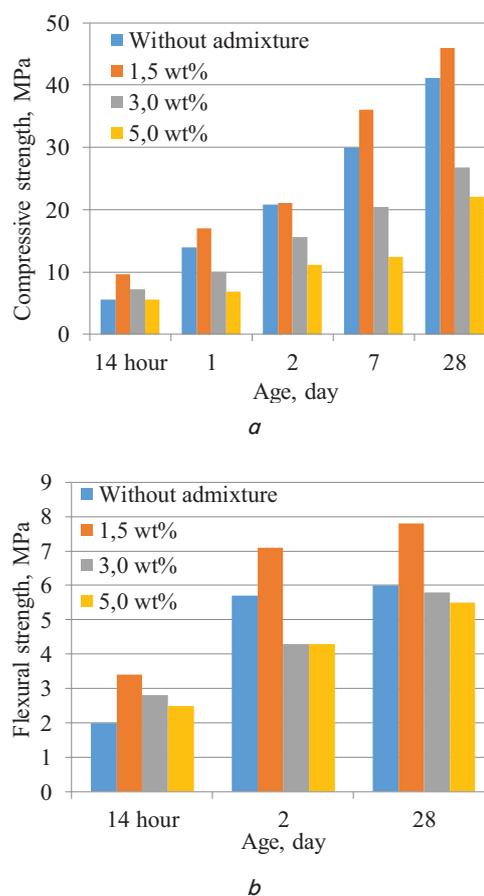


Fig. 2. Strength development of the Portland limestone cement CEM II/A-LL with admixtures  $Na[Al(OH)_4]$  and polycarboxylate ethers: *a* – compressive strength; *b* – flexural strength

It should be noted that the bleeding of the Portland limestone cement CEM II/A-LL 42.5 R, modified by  $Na[Al(OH)_4]$ +PCE, decreased from 15.2 to 1.5 % while heat release accelerated by 40 min compared to Portland cement without modifiers. Our results regarding the physical and mechanical parameters of the Portland limestone cement

CEM II/A-LL, modified with  $\text{Na}[\text{Al}(\text{OH})_4]$  and PCE, testify to the feasibility of designing a complex aluminum-containing nanomodifier C-A-H-PSE as an effective hardening accelerator.

**5. 2. Synthesis of nanocomposite based on layered double hydroxides Ca-Al-LDHs and polycarboxylate ethers**

To obtain particularly hardening cementing systems using the sol-gel technology method, an aluminum-containing nanocomposite was synthesized. Using a complex of methods of physico-chemical analysis, the resulting phases were determined [40]. Studies of samples N 1 and N 2 by IR spectroscopy have established (Fig. 3) that the samples N 1 and N 2 have absorption bands in the IR spectrum, which are characteristic of the calcium nitrate fragment  $\text{Ca}(\text{NO}_3)_2 - 3472$  (3464), 1635, 1447, 1390, 1360, 1050, 872, and  $832 \text{ cm}^{-1}$ . Weak absorption at  $1780 \text{ cm}^{-1}$  indicates a small number of free anions  $[\text{NO}_3^-]$ .

For samples N 1 and N 2, the carbonate phase is registered, as evidenced by intense absorption at  $2940-2800 \text{ cm}^{-1}$ ,  $1460$  ( $1480-1420$ )  $\text{cm}^{-1}$ , as well as medium and weak absorption; in this case, for sample N 2, absorption is more intense. At the same time, for sample 2, there is a significant expansion of the absorption spectrum in the region of  $1600-1200 \text{ cm}^{-1}$ . Anionic groups are observed in this region: carbonates, carboxylates  $\text{CO}_3^{2-}$  ( $1560-1630 \text{ cm}^{-1}$ ) and  $\text{COO}^-$  ( $1350-1420 \text{ cm}^{-1}$ ), and, at  $1450-1420 \text{ cm}^{-1}$  – uncoordinated carbonate groups. It is characteristic that intensive bands of 2880, 1460,  $872 \text{ cm}^{-1}$  (sample 2) indicate a significant content of the carbonate fragment. Polycarboxylate ethers are characterized by the following bands in the IR spectrum: 1570, 1460, 1340, 1279, 1240, 1140, 1104, 1060, 964,  $841 \text{ cm}^{-1}$ . In this case, the band of  $1570 \text{ cm}^{-1}$  may indicate the absorption of the  $\text{O-C-O-Na}^+$  group. Spectra in the region of  $1530-1450 \text{ cm}^{-1}$  arise from the absorption of  $\text{CO}_2$  calcium by hydroxide  $\text{Ca}(\text{OH})_2$ . This is also evidenced by the bands of 842, 1475,  $1420 \text{ cm}^{-1}$ . These oscillations are associated with valence and deformation oscillations of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^- - 3640-3400 \text{ cm}^{-1}$  valence  $\text{OH}$ -calcium hydroxide, aluminum hydroxide has bands at 3600, 3520, 3464 (3472),  $3370 \text{ cm}^{-1}$  – valence oscillations, and at 1020 and  $965 \text{ cm}^{-1}$  – deformation oscillations. Fluctuations in the range of  $3600-3300 \text{ cm}^{-1}$  and  $1670 \text{ cm}^{-1}$  belong to the  $\text{OH}$ -groups of molecular water (valence and deformation oscillations, respectively). Note that in the samples under study, a band of  $520 \text{ cm}^{-1}$  is registered with a valence oscillation of  $\nu_{\text{Al-O}}$ , which is characteristic of calcium hydroaluminates. According to X-ray phase analysis (Fig. 4), reflexes of hydrate new formations are recorded on diffracto-

grams: calcium hydroxide ( $d/n=0.493$ ;  $0.260 \text{ nm}$ ), calcium hydrocarboaluminate ( $d/n=0.76$ ;  $0.280 \text{ nm}$ ), hexagonal calcium hydronitroaluminate  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 12\text{H}_2\text{O}$  ( $d/n=0.890 \text{ nm}$ ). It is characteristic that with the introduction of PCE, the intensity of the reflexes of calcium hydronitroaluminate decreases while the width increases, that is, its structure is amorphized due to the formation of hydrated nanoembryos Ca-Al- $\text{NO}_3$  LDHs. This indicates that the seed embryos are highly dispersed calcium hydronitroaluminates  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (Ca-Al- $\text{NO}_3$  LDHs), as well as nanomodified calcium hydronitroaluminate with polycarboxylate PCE dispersant  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O} - \text{PCE}$  (Ca-Al- $\text{NO}_3$  LDHs – PCE).

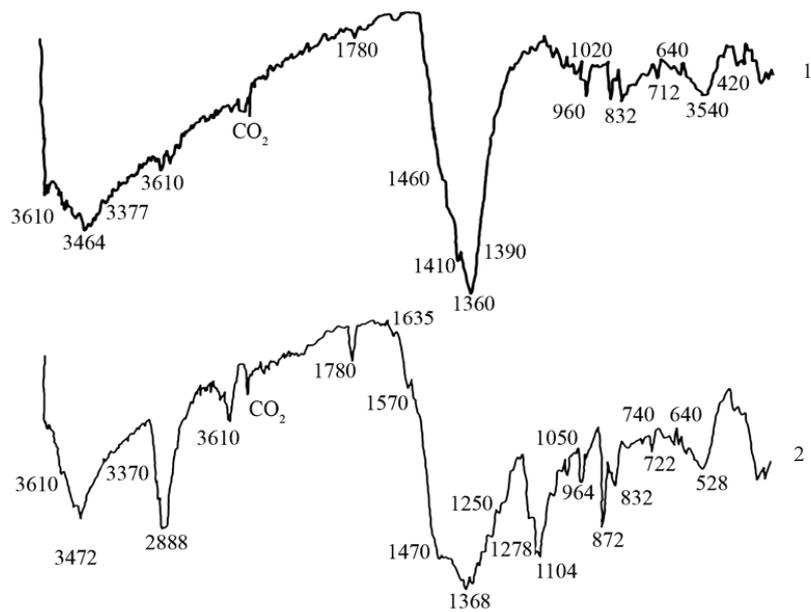


Fig. 3. IR spectra of aluminum-containing seed: 1 – gel  $\text{Ca}(\text{NO}_3)_2+\text{Na}[\text{Al}(\text{OH})_4]$  (sample N 1), 2 – gel  $\text{Ca}(\text{NO}_3)_2+\text{Na}[\text{Al}(\text{OH})_4]+\text{PCE}$  (sample N 2)

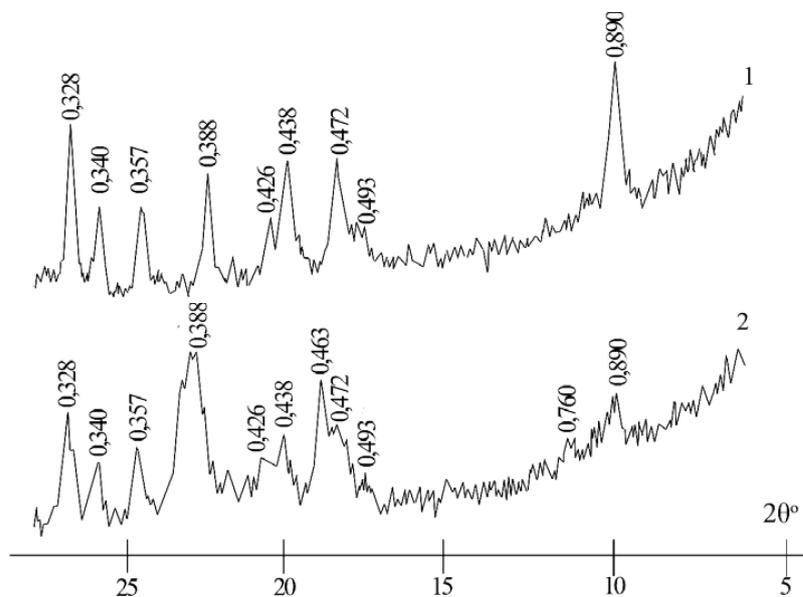


Fig. 4. Synthesized calcium/aluminum-containing nanocomposite diffractogram: sample 1 – Ca-Al- $\text{NO}_3$  LDHs; sample 2 – Ca-Al- $\text{NO}_3$  LDHs–PCE

The data from raster electron microscopy (Fig. 5, *a, b*) show that the synthesized aluminum-containing seed Ca-Al-NO<sub>3</sub> LDHs is characterized by a significant number of plate-like new formations – calcium hydroaluminates and hydronitroaluminates. When dispersing the seed with polycarboxylate ethers Ca-Al-NO<sub>3</sub> LDHs–PCE, due to adsorption modification, the formation of nanoembryos is observed. In this case, the seed is dispersed with the formation of fine aggregates the size of 500–800 nm (Fig. 5, *c, d*). It should be noted that the nano-embryos of phases Ca-Al-NO<sub>3</sub> LDHs can be a substrate for polycarboxylate molecules of PCE ethers. This contributes to the acceleration of the processes of early structuring formation and the intensive compaction of the microstructure of the cementitious matrix in the subsequent hardening periods.

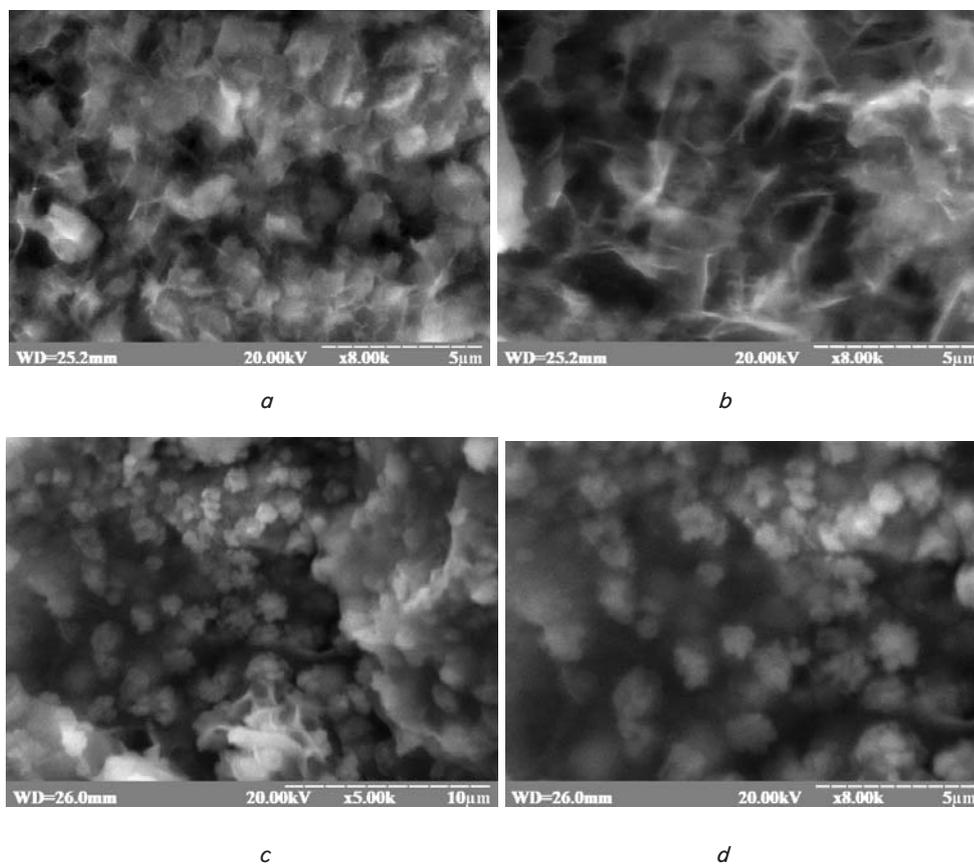


Fig. 5. SEM images of the synthesized aluminum-containing nanocomposite: *a, b* – Ca-Al-NO<sub>3</sub> LDHs; *c, d* – Ca-Al-NO<sub>3</sub> LDHs–PCE

To establish the peculiarities of the structure formation processes, it becomes necessary to study the influence of the synthesized aluminum-containing seeds Ca-Al-NO<sub>3</sub> LDHs and Ca-Al-NO<sub>3</sub> LDHs–PCE on the strength and phase composition of Portland limestone cement.

### 5.3. Determining the strength and establishing the structures of the Portland limestone cement modified with nanocomposite the type of Ca-Al-NO<sub>3</sub> LDHs–PCE

According to DSTU B EN 196-1, the effect of nanocomposite (sample 1 and sample 2) on the physical and mechanical properties of the Portland limestone cement CEM

II/A-LL 42.5 R ( $R_{c2}=25$  MPa,  $R_{c28}=62.5$  MPa) was investigated. It was found that with the introduction of Ca-Al-NO<sub>3</sub> LDHs–PCE (C-A-N-H-PCE), the flowability of standard cement-sand mortar (C:S=1:3; W/C=0.50) decreases from 190 to 160 mm. At the same time, there is an increase in compressive strength in all terms of hardening (Fig. 6). When introducing in CEM II/A-LL 42.5 R the nanocomposite Ca-Al-NO<sub>3</sub> LDHs–PCE, the flowability (W/C=0.50) increases to 240 mm (plasticizing effect – 26.3 %), the compressive strength limit after 8 and 14 h, 1; 2; and 28 days increases and is 4.8; 14.1; 20.0; 28.9; and 78.1 MPa, respectively. It should be noted that with the introduction of Ca-Al-NO<sub>3</sub> LDHs–PCE, due to the water-reducing effect  $\Delta W/C=30.0$  %, there is an increase in strength after 8 h – by 2.0 times, after 14 h – by 1.7 times; in the period 1...28 days, the increase in strength is 50 %. Thus, after 28 days of hardening, a strength of 90 MPa is achieved; capillary porosity decreases to 8.9 %.

To identify the effect of nanocomposite on the processes of structure formation of Portland limestone cement, a study was conducted using the methods of physicochemical analysis. It was found that for the Portland limestone cement CEM II/A-LL 42.5 R, after 5 min, pH is 12.4; after 24 h – pH=12.7. For a suspension based on CEM II/A-LL 42.5 R with 2.0 wt% Na[Al(OH)<sub>4</sub>], the pH value reaches 13.0 in all terms of the study. With the introduction of PCE, the pH value decreases to 12.3, and after 1 day it increases to 12.8. It should be noted that the introduction of the nanomodifier Ca-Al-NO<sub>3</sub> LDHs–PCE makes it possible to achieve a pH value of 12.80 (after 5 min) and 13.1 (after 24 h), which indicates an increased alkaline environment.

For cement stone based on CEM II/A-LL 42.5 R (paste 1:0, water demand – 0.29), the compressive strength after 12 h is 4.3 MPa; after 1, 2, and 28 days – 21.2; 39.0; and 72.5 MPa, respectively. With the introduction of 3.0 wt% Na[Al(OH)<sub>4</sub>], the water demand of the paste increases to 0.35 while after 12 h the strength increases by 24.0 %, after 1 day – by 44.0 %. With the introduction of Ca-Al-NO<sub>3</sub> LDHs–PCE, water demand decreases to 0.25. At the same time, the strength after 12 h increases by 4.3 times (18.7 MPa), after 1 day – by 3.8 times (42.5 MPa), after 28 days – by 1.6 times (up to 101.5 MPa). This indicates a significant intensification of the hardening processes of the nano-modified cement paste.

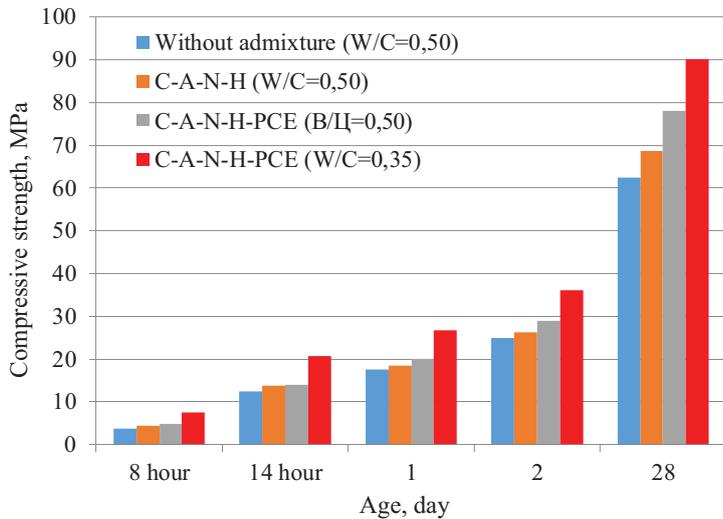


Fig. 6. Compressive strength of nanomodified Portland limestone cement

According to X-ray phase analysis (Fig. 7), for cement stone, after 1 day of hydration, the lines of calcium hydroxide ( $d/n=0.493$ ;  $0.263$  nm) and ettringite ( $d/n=0.973$ ;  $0.561$  nm) are recorded. When the nanocomposite Ca-Al-NO<sub>3</sub> LDHs–PCE is introduced, a decrease in the intensity of the portlandite line with  $d/n=0,493$  nm is observed, by 2.6 times, which indicates an amorphization of the Ca(OH)<sub>2</sub> structure in the nanomodified cement paste.

For the nanomodified cement paste with Ca-Al-NO<sub>3</sub> LDHs–PCE after 24 h of hydration ( $W/C=0.40$ ), thin lamellar crystals of calcium hydroaluminates were detected by electron microscopy (Fig. 8, a, b). It was found that the increase in the strength development of nanomodified cement is achieved by increasing the number of heterogeneous contacts due to an increase in the dispersion of the components of the mixture.

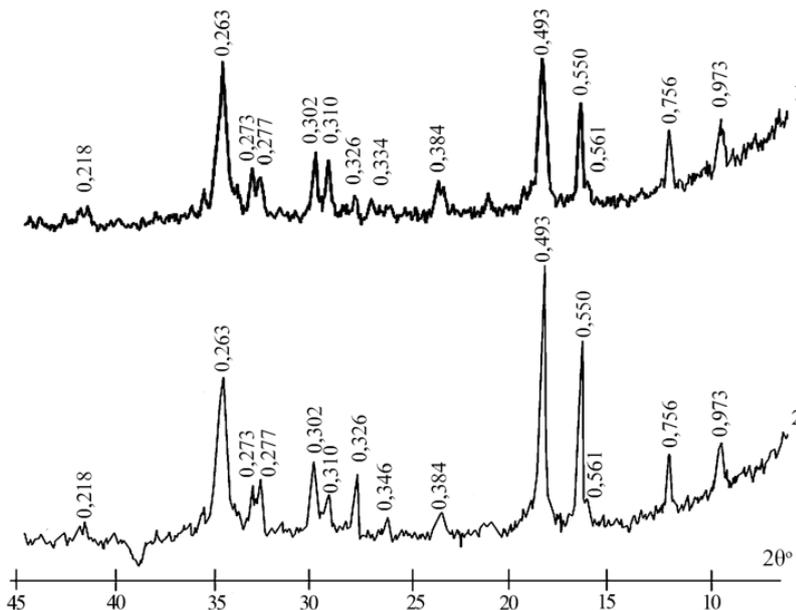
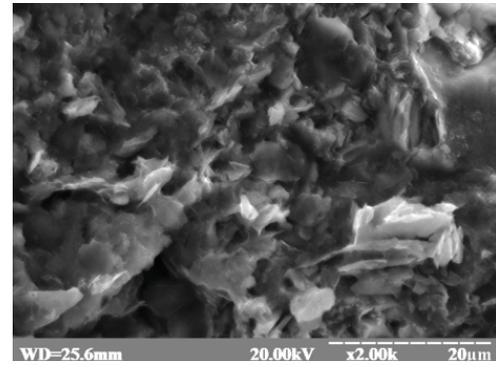
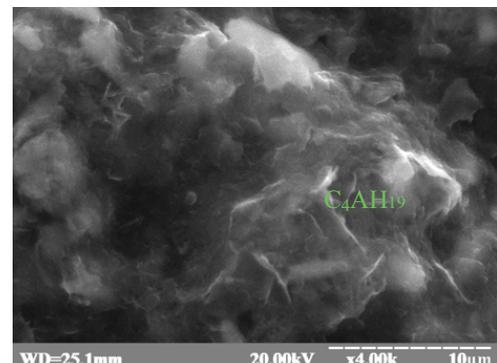


Fig. 7. Diffractogram of cement stone based on CEM II/A-LL: 1 – without admixtures; 2 – with nanocomposite Ca-Al-NO<sub>3</sub> LDHs–PCE



a



b

Fig. 8. SEM images of cement stone based on CEM II/A-LL with nanocomposite Ca-Al-NO<sub>3</sub> LDHs–PCE after 1 day of hydration

Thus, the introduction of aluminum-containing nanocomposite Ca-Al-NO<sub>3</sub> LDHs–PCE to Portland limestone cement makes it possible to obtain extra rapid-hardening high-strength binder. At the same time, as a result of the nanomodification of CEM II/A-LL 42.5 R, a significant acceleration of hardening is achieved in the early hydration period and a significant increase in the strength of the binder at the age of 28 days relative to the standard strength  $R_{st_{c28}}=62.6$  MPa ( $R_{c1}/R_{st_{c28}}=42.9\%$ ;  $R_{c2}/R_{st_{c28}}=57.6\%$ ,  $R_{c28}/R_{st_{c28}}=144\%$ ), which determines the possibility of its use in repair mixtures.

### 6. Discussion of results of investigating the effect of layered double hydroxides Ca-Al-NO<sub>3</sub> LDHs and polycarboxylate ethers on the hardening of Portland limestone cement

A new direction for solving the task of obtaining rapid-hardening cements with regulated setting time is the use of highly efficient hardening accelerators based on layered double hydroxides (Layered Double Hydroxides – LDHs) [32]. At the same time, it is expedient to design liquid nanocomposites, which can be the driving force for

the introduction of innovative solutions both in concrete production and during the restoration work of reinforced concrete structures. Designing such complex multicomponent cementing systems requires an interdisciplinary approach using the basic fundamental provisions of the physico-chemistry of cements and concretes, as well as nanotechnology [41, 42].

The study of the chemistry of the action of the alkaline aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$  with the formation of the thin-like phase C-A-H in the early stages of hydration of Portland cement determines the possibility of adjusting the kinetics of the processes of structural formation of rapid-hardening cementitious systems. This makes it possible to advance research into the system “cement-accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$ ”, which coincides with the results reported in [7, 8]. However, the difference in terms of the results from [10] is to identify the processes of formation of hexagonal phases of type  $\text{C}_4\text{AN}_{19}$ , which contribute to the rapid growth of the early strength of cement stone due to the action of this accelerator. This indicates the expediency of further advancement of research into this area. The chemical composition of the alkaline aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$  contains 66.1 wt%  $\text{Al}(\text{OH})_3$ . The increased content of the aluminate component determines the possibility of accelerated formation of various kinds of hydroaluminate phases, which significantly affect the processes of early structure formation in cement paste.

During the study of the processes of early structure formation of cementitious systems, it was revealed that the setting time of cement paste can be adjusted by the type and number of new compounds and the rate of their formation (Fig. 1, *a*). At the same time, the binding of water also plays an important role since during the formation of hydration products, part of the kneading water is absorbed (Fig. 1, *b*). Hydrate new formations have a huge surface area and are formed not only on the surface of cement particles but also in the interspace between cement grains. Deposition of high-water hydroaluminate phases of the  $\text{C}_4\text{AH}_{19}$  type prevents the movement of cement particles in water during the process of setting. The formation of phases of the  $\text{C}_4\text{AH}_{19}$  type contributes to the rapid growth of the early strength of cement paste with alkaline-aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$ . This is consistent with the results reported in [8, 10], where it is shown that in an aqueous solution  $\text{NaOH}$  increases the solubility of  $\text{CaSO}_4$  and reduces the solubility of  $\text{Ca}(\text{OH})_2$  while  $\text{Al}(\text{OH})_4^-$  has a delayed reaction with  $\text{CaSO}_4$  to form ettringite. This increases the pH of the aqueous solution to about 13.8 due to an increase in the concentration of  $\text{Na}^+$  in the liquid phase of Portland cement paste. Therefore, the processes of early structuring of the cement-alkaline-aluminate accelerator system are significantly different from the processes of the Portland cement system without admixtures since the film-like high-water phases of C-A-H are the main products of hydration at the initial stage instead of ettringite. As a result, there is a fast setting and increase in strength in the early stages for the “cement-alkaline accelerator” system. On the other hand, the intensive formation of the C-A-H phases leads to an increase in the water demand of cement. Therefore, there is a need to use an additionally highly effective superplasticizer of the polycarboxylate type PCE. At the same time, there is an increase in the strength of the Portland limestone cement CEM II/A-LL with alkaline aluminate accelerator  $\text{Na}[\text{Al}(\text{OH})_4]$  (Fig. 2, *a, b*).

It should be noted that the C-A-H-phases of type  $\text{C}_4\text{AH}_{19}$  are double hydroxides LDHs with a crystallochemical formula  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ . The main elements of LDHs are portlandite-like layers  $[\text{Ca}_2\text{Al}(\text{OH})_6]^+$  between which  $\text{OH}^-$ ,  $[\text{SO}_4]^{2-}$ ,  $[\text{NO}_3]^-$  anions  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{OH})_2 \cdot 12\text{H}_2\text{O}$  [43] can be placed. Such phases refer to the structurally active hexagonal  $\text{AF}_m$ -phases, which are important in the formation of the microstructure of cement paste and largely determine corrosion resistance under the action of chloride aggression. However, in the processes of early structure formation there is a need to stabilize the hydroaluminate phases  $\text{C}_4\text{AH}_{19}$ . In the process of hardening, the conversion of such metastable lamellar phases to cubic granular-shaped  $\text{C}_3\text{AH}_6$  occurs. At the same time, porosity increases due to an increase in the density of  $\text{C}_3\text{AH}_6$ , which is consistent with the results reported in [44]. Stabilization of the structure of layered double hydroxides is achieved by introducing  $[\text{NO}_3]^-$  anions into the interlayer space with the formation of  $\text{AF}_m$ -phase of the Ca-Al- $\text{NO}_3$  LDHs type.

Synthesis of layered double hydroxides of the Ca-Al- $\text{NO}_3$  LDHs type is achieved using the method of sol-gel technology [36, 40]. As can be seen from the data of IR spectroscopy (Fig. 3) and X-ray phase analysis (Fig. 4), due to the reaction of hardening accelerators based on  $\text{Na}[\text{Al}(\text{OH})_4]$  and  $\text{Ca}(\text{NO}_3)_2$ , calcium monohydrated nitroaluminate  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$  is formed with the crystallochemical formula  $[\text{Ca}_2\text{Al}(\text{OH})_6]_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ . With the additional introduction of polycarboxylate ethers, due to the phenomenon of adsorption modification, phase nano-embryos stabilized by PCE are formed. In this sense, of particular interest is the interpretation of the results of electron microscopy, shown in Fig. 5, confirming the establishment of the described fact.

The result of the proposed solutions is to identify the effect of the synthesized nanocomposite based on layered double hydroxides Ca-Al LDHs and polycarboxylate ethers on the strength and structure formation processes of Portland limestone cement. The resulting nanocomposite Ca-Al- $\text{NO}_3$  LDHs-PCE provides a reduction in the water demand of the cement paste to 0.25. With the introduction of the nanocomposite Ca-Al- $\text{NO}_3$  LDHs-PCE to CEM II/A-LL 42.5, high values of early strength (after 8 and 14 h – 7.5 and 20.8 MPa) and standard strength (after 28 days – 90.0 MPa) are achieved, as evidenced by the research results (Fig. 6). The resulting nanomodified Portland limestone cement can be attributed to extra rapid-hardening and high-strength cement. Using the methods of physicochemical analysis, it was established (Fig. 7, 8) that the composition of nanomodified Portland limestone cement is dominated by hexagonal calcium monohydrated nitroalluminates  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 12\text{H}_2\text{O}$ .

This suggests that the synthesized nanoseeding Ca-Al- $\text{NO}_3$  LDHs-PCE belongs to the class of structurally active  $\text{AF}_m$ -phases, which are characterized by increased stability and contribute to a significant intensification of the structure formation of Portland limestone cement in a particularly early period of hardening. As a result of the targeted formation of a dense microstructure in the non-clinker part of the cementitious matrix, strength development is accelerated; the construction and technical properties of cementitious materials are improved.

As a disadvantage, one should note the expediency to supplement the data from the scanning electron microscopy of layered double hydroxides of the Ca-Al- $\text{NO}_3$  LDHs-PCE

type with the data of transmission electron microscopy. The presence of such images at high resolution would make it possible to establish more clearly the sizes of individual nanocomposite particles.

Restrictions on the use of layered double hydroxides may be caused by the temperature factor. Complications can occur under dry hot conditions of hardening. In that case, the conversion processes of hexagonal  $AF_m$ -phases into cubic hydroaluminates  $C_3AN_6$  can be accelerated. Such circumstances cause a reducing in the strength of cementitious matrix. In order to prevent this kind of problem and to provide the necessary kinetics for increasing the strength development of Portland limestone cement, internal care of cementitious materials should be provided.

The resulting rapid-hardening Portland limestone cement is characterized by extra high early and standard strength. This shows prospects for its use in repair mixtures for quick restoration of concrete surfaces, anchoring of building elements, in the repair of premises with high humidity.

However, a diverse assessment of the effectiveness of the obtained extra rapid-hardening Portland cements modified by nanocomposites of the Ca-Al- $NO_3$  LDHs – PCE type is necessary. At the same time, it is advisable to establish their influence on the mechanical and operational properties of cementitious materials, including under different temperature conditions of hardening and under the action of aggressive media. This determines the further area to advance this study.

## 7. Conclusions

1. It has been found that the introduction of 3.0–5.0 wt%  $Na[Al(OH)_4]$  to the Portland limestone cement CEM II/A-LL 42.5 R leads, on the one hand, to a significant acceleration of the setting time (initial – 30–20 min), a decrease in the workability of cement-sand mortar (flowability decreases from 200 to 130 mm), and, on the other hand, to an increase in particularly early strength (after 14 h – by 25–30 %). At the same time, in Portland cement paste with the admixture of  $Na[Al(OH)_4]$ , due to increased water demand, too rapid acceleration of the processes of early structuring and conversion of hexagonal  $AF_m$ -phases to cubic  $C_3AH_6$ , there is a decrease in compressive strength after 7 and 28 days of hardening, by 1.9–2.3 times, while porosity increases by 20.1–22.3 %.

2. It is shown that using the sol-gel technology method, due to reactions  $Ca(NO_3)_2$  and  $Na[Al(OH)_4]$  in the aqueous solution, calcium hydronitroaluminate was synthesized  $[Ca_2Al(OH)_6]_2(NO_3)_2 \cdot 6H_2O$ , belonging to the class of double calcium-aluminate hydroxides of the (Ca-Al- $NO_3$  LDHs) type. These LDHs can be a substrate for polycarboxylate ether molecules and contribute to the formation of nanoseeding based on organic additives and materials of layered structure, which is confirmed by IR spectroscopy, X-ray phase analysis, and scanning electron microscopy.

3. It has been found that the introduction of alkaline-aluminate nanomodifier Ca-Al- $NO_3$  LDHs – PCE to the Portland limestone cement CEM II/A-LL leads to a significant increase in the rate of hardening (after 8 and 14 h – by 2–1.7 times); after 28 days, the strength reaches  $R_{c28}=90.0$  MPa. In terms of early compressive strength after 1 and 2 days relative to the standard strength of CEM II/A-LL, the nanomodified Portland limestone cement is extra rapid-hardening ( $R_{c1}/R_{stc28}=42.9\%$ ;  $R_{c2}/R_{stc28}=57.6\%$ ). It was shown that the nanocomposite Ca-Al- $NO_3$  LDHs-PCE based on layered double hydroxides and polycarboxylate ethers provides regulated setting time, accelerates the processes of early structural formation and the formation of dense microstructure of cement paste, which determines the possibility of creating effective mixtures for quick repair and restoration of reinforced concrete structures.

## Conflict of interests

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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