Yang *et al. Int J Concr Struct Mater* (2023) 17:50
https://doi.org/10.1186/s40069-023-00601-8

International Journal of Concrete
Structures and Materials

RESEARCH **Open Access**

Research of Nano-modified Plain Cement Concrete Mixtures and Cement-Based Concrete

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Abstract
The use of complex modifiers for plain cement concrete mixtures and concrete is becoming increasingly popular in modern materials science. The article presents studies of the influence of a polymer additive structured by carbon nanomaterials on physical and mechanical characteristics of plain cement concrete mixtures. IR spectroscopy and thermogravimetry have shown that the use of carbon nanomaterials significantly altered the structure of plain cement concrete mixtures. As a result of the fact that the high-strength nanomaterial is the center of crystallization of cement rock newly formed structures, a denser reinforced microstructure is formed, which significantly increases the strength properties of plain cement concrete mixtures. The inclusion of a polymer complex additive in plain cement concrete mixtures leads to higher and longer plasticizing, which plays an important role in the production of monolithic products. It was determined that, in the presence of a complex modifier (polymer additive structured by carbon nanotubes), the crystalline structure of calcium hydrosilicates is compacted, which causes high physical and mechanical characteristics of modified plain cement concrete mixtures. It has been experimentally shown that the additive Ethacryl HF (France) from the class of polycarboxylates, chosen for research, acts as an accelerator for setting and curing cement paste, and also increases its strength characteristics. In general, in this study, there is a water-reducing effect from the application of the additive for all plain cement concrete mixtures. Water requirements are reduced by 5 mas. %, while the strength is increased by 19%. The formulation of plain cement concrete mixtures modified by polymer additives, structured by carbon nanotubes, with high performance were developed.

Keywords Cement, Concrete, Nanomodification, Polymer additive, Carbon nanotubes

1 Introduction

The development of the construction industry in recent decades has been carried out under the sign of ever-increasing requirements for the optimal and efficient use of raw materials and energy resources. Among the various resource-saving measures that are widely used in the production of cement and concrete, the first place is occupied by the use of multifunctional chemical additives. Among the advantages of using additives, the most important are the saving of raw materials (mainly cement) in the composition of concrete and a significant improvement in their physical and mechanical properties. The main direction in the development of modern concrete technology is to obtain concrete with specified technical and technological properties while minimizing material and energy costs. In order to adjust the properties of concrete, different methods are used. One of the most common is the use of special additives, which for the most part significantly increase the cost of concrete and, improving some properties, worsen others.

Journal information: ISSN 1976-0485 / eISSN 2234-1315.

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For the modification of concrete, the activation of the components of the concrete mix has also found wide application, incl. mixing water. It has been established that water is the only component of cement composites that initiates various reactions in the cement system (Su et al., 2001). It is known that under the directed external action of physical forces, the characteristics of water change (Atynian et al., 2019a, b). The use of activated water for mixing concrete on Portland cement viscous dough has a significant impact on the cement hardening process and leads to an improvement in a number of composite formation properties (Atinyan et al., 2019).

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One of the promising ways is the synthesis of multifunctional chemical additives. To date, the most promising and relevant is the use of carbon nanomaterials as multifunctional additives.

Today and in the long run, the main structural building material remains concrete. It is an artificial mixture of astringent (cement), fillers (sand, slag, ash, zeolites, etc.), water and, if necessary, special additives, which is characterized by structure complexity, has a relatively low cost, low energy intensity, available raw material base and can be used under different operating conditions (Collepardi, 2001).

At the present stage of the construction industry development, according to the low-carbon development strategy, there is an urgent need to increase the production of cements and concretes with a reduced content of high-energy-consuming clinker, and reduce CO_2 emissions during production. The rational solution to the above problem is technologically optimized composite Portland cements, their clinker-efficiency being significantly increased due to favorable combinations of mineral constituents (Collepardi, 2003; Singh et al., 2021). According to the EU strategy, greenhouse gas emissions should be reduced by 50–55% by 2030 compared to 1990. In this regard, a comprehensive set of activities known as Green Deal, was developed, which presupposed the transformation of the EU into a "climate neutral zone" with "zero" emissions of harmful gases by 2050 (Su et al., 2001). This determines the complete restructuring of the European economy, as the climate situation in the world has reached a critical point. Therefore, there is a need to take active measures and apply alternative solutions to improve the environmental condition (Collepardi et al., 2004; Komarinsky et al., 2015). The EU Strategy for Sustainable Development envisages a long-term vision of a modern and low-carbon economy that will reduce CO_2 emissions, while taking into account synergies between strategic links of different values (Bieliatynskyi et al., 2022a). At the same time, the intensive development of nanotechnologies in the construction industry requires the development of new technological methods that make it possible to control the structure formation of composite materials, including concrete, at the nano- and micro-levels. At the same time, the most effective way is to change the very structure of concrete with the help of various kinds of additives that increase the technical-physical and technical-operational qualities of not only the concrete itself, but also the concrete stone. At the same time, the most effective additives that change the structure of the concrete stone itself are additives that work at the nanolevel. Effective methods for obtaining nanomodifying additives currently proposed are technologies that are characterized by high energy consumption and the cost of process equipment, sufficiently high pressure, the use of plasma and arc discharge, as well as highly toxic reagents with multi-stage chemical purification. In addition, there is a problem of uniform distribution of additives in the volume of concrete when using tenths and hundredths of a percent, especially if the additives are in powder form. Therefore, the search for cheap and at the same time effective methods for obtaining nanomodifying additives for concrete is very relevant. But it is also necessary to fill the information gap on changing the structure of the cement matrix itself, which, when mixed with water, will form a new skeleton.

Increasing resistance to dynamic influences, as well as physical and mechanical properties and crack resistance of cement-based building materials is an important and urgent problem in the operation of buildings and structures. Physico-mechanical properties of cement-based concrete with nanofillers have been of interest to scientists for a long time. In particular, the characterization of multifunctional nanotechnical mixed metal oxides for industrial applications is described in the study of Singh et al (2021). The study of the mechanism of modification of workability and mechanical properties of a cement composite reinforced with graphene oxide was considered in the work of Suo et al (2019). Pressure sensitivity of multiscale cement-based composites reinforced with carbon admixtures was investigated in Hong et al (2018). The behavior of cement mortar under compression with the addition of nanometakaolin was investigated by scientists Xiaoyu et al (2018). A low dose of nanosilica modification on lightweight concrete was characterized in the work of Zhang et al (2018). Functionalization of carbon nanotubes was described in Basiuk et al. (2015). The component composition of technical cement composites and its development were presented in their monograph Sydor, (2021).

The development of the construction industry in recent decades has been carried out under the sign of ever-increasing requirements for the optimal and efficient use of raw materials and energy resources. Among the various resource-saving measures that are widely used in the production of cement and concrete, the first place is occupied by the use of multifunctional chemical additives (Bieliatynskyi et al., 2022b). Among the advantages of using additives, the most important are the saving of raw materials (mainly cement) in the composition of concrete and a significant improvement in their physical and mechanical properties. The main direction in the development of modern concrete technology is to obtain concrete with specified technical and technological properties while minimizing material and energy costs. In order to adjust the properties of concrete, different methods are used. One of the most common is the use of special additives, which for the most part significantly increase the cost of concrete and, improving some properties, worsen others.

For the modification of concrete, the activation of the components of the concrete mix has also found wide application, incl. mixing water. It has been established that water is the only component of cement composites that initiates various reactions in the cement system (Su et al., 2001). It is known that under the directed external action of physical forces, the characteristics of water change (Atynian et al., 2019a, b). The use of activated water for mixing concrete on Portland cement viscous dough has a significant impact on the cement hardening process and leads to an improvement in a number of composite formation properties (Atinyan et al., 2019).

One of the promising ways is the synthesis of multifunctional chemical additives. To date, the most promising and relevant is the use of carbon nanomaterials as multifunctional additives.

The aim of the work is to study the composition of the cement matrix, as the main part of the composite plain cement concrete mixture, containing cement, fly ash of power generating enterprises and nano-additives in the form of carbon nanotubes in the paste of a superplasticizer of polycarboxylate type. Nano-additives will allow to synthesize of elongated formations as part of the cement matrix hydration products, which will fill the pore space of artificial stone and will create a dense waterproof structure on the surface. In order to achieve the aim, the following tasks must be accomplished:

- to investigate the mechanical properties of matrices on the basis of various types of cement, including Portland cement slag, fly ash and to identify the possibilities to intensify hardening processes and improving physical and mechanical properties of cements by using polymer additives structured by carbon nanotubes;
- to study the mechanism of physical–chemical hydration and hardening of concrete mixtures modified by polymer additives structured by carbon nanotubes;
- to assess the impact of polymer additives structured by carbon nanotubes on the physical and mechanical properties of concrete mixtures;
- to establish criteria of efficiency and optimum additive concentrations.

The scientific novelty of the article is that the work provides a useful perspective on the design of the composite material strengthening system and established efficiency criteria and optimal dosages of chemical additives.

2 Materials and Methods

The necessary physical and mechanical indicators of Portland cement compositions are provided by the use of binder, chemical and mineral additives, which meet the requirements of regulatory documents, according to quality indicators. In the research cement, sand, natural gypsum stone, fly ash, chemical additives were used. Portland cement of general construction purpose I-500R of Public Limited Liability Company “Ivano-Frankivsk cement” was used as binder for the development of modern Portland cement compositions. Chemical composition of Portland cement clinker of PLC “Ivano-Frankivsk cement”.

River sand fractionated (0.315–0.900 mm), meeting the requirements of DSTU B.2.7-32-95, was used for the preparation of concrete paste (1:3). These mixtures were used as model systems to assess the impact of chemical additives on the physical–mechanical properties of paste and concrete. Blast furnace slag was used to prepare of Type III/A Portland-blastfurnace cement with a blast furnace granular slag content of 50 mas. % in order to study the effects of chemical additives on hardening processes of cements with active mineral additives. Blast furnace slag was also grinded in a laboratory ball mill with hydrophobic composition to study the influence of chemical additives on the grinding processes of slag and on Portland-blastfurnace cement hardening (Yakovlev et al., 2017; Bednyagin et al., 2017; Atynian et al., 2017; Atynian et al., 2019a,b; Atynian et al., 2020).

The following compounds were investigated as chemical strength modifiers: monoatomic (ethanol, isopropanol), diatomic (ethylene glycol, propylene glycol), triatomic (glycerin) and four atomic alcohols (pentaerythritol), calcium salts of organic and inorganic acids, alkanolamines (mono-, di- and triethanolamine). All the above-mentioned substances were laboratory-derived and used in a chemically pure form. Chemically pure oleic acid was used to modify the hydrophobic properties of cement. Stachement 2597 was used as a comparative commercial superplasticizer.

Alcohols, alkanolamines, and calcium salts, were used as accelerators of setting and hardening to study their effect on the physical–mechanical properties of cements. Stachement 2597 was used as a reference polycarboxylate superplasticizer to study the influence of this type of additive on the physical–mechanical properties of cement and paste. Oleic acid was used as a reference hydrophobic agent and a solvent for experimental additives based on used sunflower oil.

Furthermore, for sake of completeness, considering that carbon nanotubes (CNTs) have attracted much attentions for their numerous technological applications (Singh et al., 2021), their functionalization allowing to address low dispersion and solubilization in many solvents or polymers (Basiuk et al. 2015).

3 Results

In Ukraine carbon nanotubes were used to modify the physical–mechanical and operational characteristics of concrete (Sementsov & Melezhik, 2009). Innovative trend of plain cement concrete mixtures technology is the introduction of nanotechnology (Yanchenko et al., 2006). These methods are based on the directed formation of material structure of a heterogeneous, multiphase system of complex hierarchy from a nano- to macro-structural level by modifying nano-dimensional particles in combination with highly effective polycarboxylate plasticizers (Pushkarova et al., 2014a, b).

Among the nano-modifiers that improve the properties of plain cement concrete mixtures, a lot of attention is paid to carbon nanotubes. The introduction of multilayer carbon nanotubes with a diameter close to the thickness of nano-disperse phase layers C-S-H into cement mixtures may have different effects on cement stone properties (Pushkarova et al., 2011). Koward (2004) determined an increase in strength when a small number of multilayer nanotubes were introduced into high-quality concrete. This means that carbon nanotubes have the potential to increase the strength of concrete, and nanotubes are not perceived as reinforcements in the literal sense, but only as centers that create the conditions for the formation of crystalline neoplasms that proliferate and intertwine, partially splicing and creating a spatial grid that binds cement rock together. However, the number of carbon nanotubes relative to the volume of cement stone is quite small (fraction of percent), which causes some technological difficulties with their uniform distribution in the cement matrix.

The researchers (Bieliatynskyi et al., 2022c, d) show the positive influence of multilayer carbon nanotubes on improving the structure of cement rock, increasing its crack resistance and dynamic viscosity, waterproof, corrosion resistance due to the fact that in the matrix the carbon nanotubes act as “embryos” of elongated crystals, are regulated by increasing the conventionally closed microscopic pores. Carbon nanotubes can accelerate cement hydration, help crystallize calcium hydroxide in cement paste and improve the mechanical properties of cement-based materials.

Thus, the main problem of nano-modification is to control the process of forming the structure of the material “bottom-up” (from nano-levels to cement rock macrostructure) and the kinetics of the entire spectrum of chemical reactions accompanying the hardening process (Collepardi, 2001, 2003; Komarinsky et al., 2015). Thus, the use of nano-disperse modifiers makes it possible to control the interaction kinetics between cement and water and to achieve maximum positive effects in the following stages: the dissolution of cement grains, obtaining the specified rheology; colloidation, ensuring the necessary mobility in time; crystallization, increasing the number of centers of crystallization of neoplasms and thus increasing the strength, water and frost resistance of concrete (Atynian et al., 2019a; Collepardi et al., 2004; Su et al., 2001).

The complex of physico-chemical interactions in the cement stone structure at the nanoscale facilitates the passage of hydration reactions, revealing new patterns for understanding the nature of hydrate phases and the development of high-performance plain cement concrete mixtures (Atynian et al., 2019b; Atynian et al., 2020; Kanchanason & Plank, 2015). Problems of dispersion and homogeneous distribution of carbon nano-modifiers in the cement matrix environment have not been solved due to increased inclination to agglomeration, insufficient adhesion of nanotubes to the matrix (Bieliatynskyi et al., 2022e; Kanchanason & Plank, 2015; Kim et al., 2013). This makes it impossible to fully utilize their high elasticity modulus.

Thus, the development of complex modifiers based on polycarboxylate plasticizers in combination with carbon nanostructures to improve the performance characteristics of plain cement concrete mixtures is an urgent task of modern materials science. Portland cement mark M500 (JSC “Ivano-Frankivsk cement”) was used as a binder, river sand with a module of size Mkr = 1.89 was used as fine aggregate, gravel of river (fraction 5–20 mm) as large aggregate, and the ash of the Thermal power station-5 (hereinafter—TPS-5), Kyiv. Ethacryl HF (France) from the class of polycarboxylates was used as a polymeric additive (Fig. 1).

The complex modifier was obtained by dispersion of carbon nanotubes TU Y 24.1-03291669-009:2009-carbon nanotubes in water medium with the help of ultrasonic disperser (frequency 22 kHz) for 10–20 min. with the gradual addition of the required amount of polymer superplasticizer to ensure uniform distribution of nanoparticles in the paste. The complex modifier was introduced into the mixing water, where it was previously mixed until the moment of injection into the cement. Mixing components were mechanically mixed with a mixer for 120 s. The resultant slurry was then injected into the cement and mixed. As a result, a cement dough with certain concentrations of a polymer additive of 4.5 mass. % and carbon nanotubes 0.1 or 0.5 mass. % relative to the amount of cement was obtained.

Multi-layer carbon nanotubes, synthesized by catalytic CVD synthesis using three-component iron-bearing catalysts, were used to reinforce cement matrices. In Fig. 2 TEM micrographs of the initial carbon nanotubes obtained with a JEM-100CXII transmission electron microscope (accelerating voltage, 100 kV, resolution, 2.04 A) are shown. The outer diameter of the VNT was 10–40 nm, the specific surface area was 200–400 m^2/h, and the bulk density was 20–40 g/dm^3.

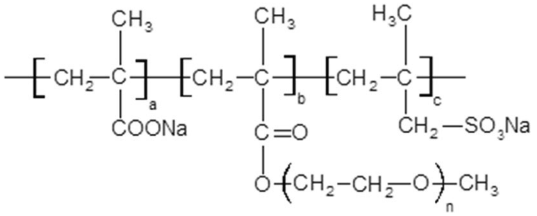

Fig. 1 Structural formula of Ethacryl superplasticizer HF (*a*:*b*:*c* = 6:1:0–5, *n* = 1–100)

The IR spectra of the samples were recorded on a Perkin-Elmer Fourier IR spectrometer, model Spectrum 65, using a Miracle ATR ATR attachment (ZnSe crystal) in the region of 4000–600 cm^{-1}; 20 successive scans were averaged for each spectrum. The background spectrum was recorded and subtracted automatically. Recording and subtraction of the background spectrum were done automatically. The stability of the samples to thermooxide destruction was determined using the method of thermogravimetric analysis (TGA) on the derivative of the company “MOM” brand “Q-1500” (Hungary) in the air in the temperature range from 20 to 1000 °C at a heating rate of 10 °C /x. 100 mg). Physical and mechanical tests of plain cement concrete mixtures were carried out according to DSTU B.V. 2.7-187:2009, DSTU B.V. 2.7-188:2009 and DSTU B.2.7-214:2009, which covered the determination of density, time of cement paste setting, strength limits at compression. The cement concrete mixtures were examined on samples with dimensions 2 × 2 × 2 cm, which were tested for 1.7 and 28 days of curing under normal conditions (temperature 20 ± 3 °C, relative humidity 60 ± 5%).

Sampling of clinker, active mineral additives and cement powders for any of the conducted studies was done by accommodation. Grinding of clinker, active mineral additives, gypsum stone and mixing cement with chemical additives was done in the laboratory ball mill. Ceramic or metal cylpebs were used as mill bodies. Grinding of materials was carried out until the full passage through the sieve 008. Cement and additives were mixed for 7 min. The range of clinker particle dimensions was based on the sieve analysis and microscopic particle size distribution. The dispersity of the active mineral additives was analyzed only by the sieve analysis.

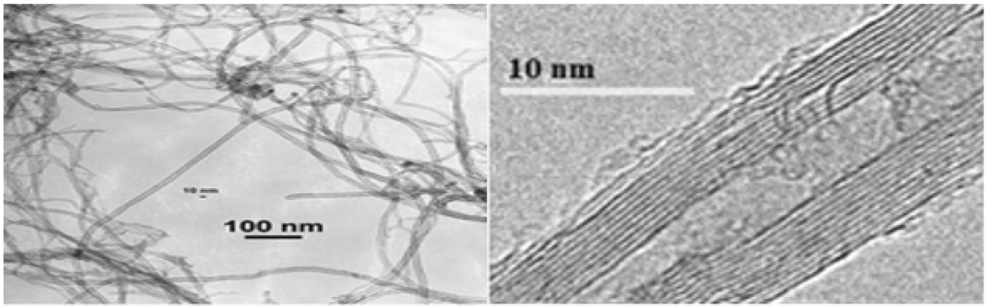

Fig. 2 TEM microphotographs of the original multilayer carbon nanotubes

The sieve analysis was carried out using the method given (Königsbergera et al., 2018) when grinding clinker and active mineral additives. The analysis was carried out using a seiving apparatus of fibro-cement (Bieliatynskyi et al., 2022f). New carbon additives in the required amount were introduced into the laboratory ball mill together with grinding material. PMS-200 silicone oil was used to determine the size distribution of clinker particles using the microscopic method described as an immersion liquid. Normal density and timing were determined by the Vic mini-device using the small sample method. The compression strength was determined for 20 × 20 × 20 × 20 mm cubes using compression strength determination for small samples.

The study of the hydrophobic properties of cements and active mineral additives was carried out according to the following methods: a glass filled with water is gradually poured with a thin layer of 2–3 g powder. Hydrophobic powder must form a film on the water surface; cement is leveled with a thin layer on the glass surface and a few drops of water are applied to it. The water on the hydrophobic powder shall be in the form of a freely moving drop of at least 5 min (Garrault, 2005; Zakharov, 2008). These two techniques together are called "a hydrophobic test". According to the third method, the cement powder is poured into a dry glass and filled with water. After 5–10 min, the water is drained, and the hydrophobic powder should remain dry and loose. The fourth method is based on the study of water sorption kinetics from air. Cement powder was stored in the desiccator for 15 weeks in the environment with humidity of 83–85%.

The study of hydrophobic additives efficiency can be based on the determination of the water absorption of concrete. In this study, water absorption was determined for cement rock samples after 3 and 28 days of hardening. In addition, the hydrophobicity of cement was estimated according to the angular edge of the water droplet wetting applied to the pressed cement tablet (Garrault, 2005) and the surface of the evenly distributed cement layer. The wetting angle was also calculated from the measurement of capillary rise. The plasticity and solvent mixture method was used to determine the effectiveness of plasticizing additives. Fractionated dried sand with sand grains of 0.315–0.900 mm was used in the research. The mechanism of cement hardening with additives was investigated by the following three methods: the determination of the amount of connected water, a derivative analysis method, and an infrared spectroscopic analysis method.

To prepare the samples for the research, 1 g hydrated cements were crudely ground in absolutive isopropanol paste to stop the hydration process. The dispersed and hydrated cements were kept at a temperature of 105–110 °C for 2 h, after that they were crushed in a metal mortar until full passage through the sieve 008.

The derivatographic analysis includes the production of curves of TG, DTG and DTA, the change in temperature and mass are recorded simultaneously. During the analysis, the materials in the analysis process were heated to a temperature of 1000 °C at a rate of 20 °C / min (for dispersed cement) and 10 °C/min (for hydrated cement). The curve removal rate was 2.5 mm/min. IR spectra of dispersed and hydrated cements are recorded on an automatic spectrometer in the wavelength range of 400–4000 cm^{-1}.

Spectra obtained from compressed samples made of a homogeneous mixture of solid solvent and cement under analysis. Carbon nanotubes (CNT) with high mechanical characteristics are regarded an effective means of improving the physical and mechanical properties of composite materials. They have free chemical bonds; therefore, they can provide better adhesion of the concrete mixture and aggregate, thus increasing the material strength. Nanofibers and nanotubes can also play the role of reinforcement material due to their high strength and large elastic modulus. They can also be centers of directional crystallization. However, in order to realize this possibility, it is necessary to have a good connection between the surface of the CNT and the matrix (Li, 2013). This ensures an efficient load transfer from the material to the nanotube and ultimately leads to an increase in the composite strength. Otherwise, nanotubes can worsen the composite strength.

The main properties of cement, including its activity and hardening rate, are determined not only by the chemical and mineralogical composition of clinker, the shape and size of allite and white crystals, the presence of certain additives, but also to a greater extent by the fineness of the grinding product, its particle size composition and the shape of the powder particles. Cement powder is very heterogeneous in its granulometric composition, moreover, the degree of heterogeneity is largely determined by its physical and technical properties, in particular uniformity of hardening, strength at different hardening periods, etc.

A dispersive analysis of Portland cement showed that the weight of the cement fraction was in the range of 7.75–100 µm. From the point of view of the optimal ratio of the amount of energy used to increase the specific surface, methods of additional grinding and dispersion of the cement powder, the obtained values of particle sizes are objectively preferable. In the formation of a high-quality micro-concrete structure of cement–sand products, the granulometric composition of sand is of great importance. The closer the particles to each other, the stronger the contact between them; and the more volume of such strong contacts in a unit the higher the strength of the structure of the monolith.

Based on the granulometric composition of the bulk material, the quantitative distribution of its composite particles by linear sizes was estimated. The analysis showed that the main weight of the sand particles was in the range of 45–300 μm. Thus, research demonstrated that nano-modified concrete samples were more likely to gain strength, average 30–40%, and have a strength of 20–25% more than the non-additive specimens at design age. The addition of a nano-modifier of a 0.0006% cement mass ensures a stable strength growth of 20–25%.

To obtain high-tech self-sealing concrete, it is necessary to focus on the structure formation. In addition to the traditional methods of the regulation of the new generation concrete structure, it is also possible to modify concrete with nanoscale particles, which are structurized when introduced into the mineral matrix of the binder. The result is nano-modified materials with completely new properties. Different types of nanoparticles are now available.

The recipe and percentages of concrete mixtures vary from country to country depending on the materials used and the final use of self-sealing concrete (Table 1).

Self-sealing concrete offers the following advantages:

- high physical and technical performance for strength and durability;
- very high initial strength of concrete, its mobility and plasticity, no stratification, these properties persisting for a long time and do not change during transportation;
- obtained concrete surfaces are of excellent quality and high density;
- self-sealing concrete mixture can be used to fill complex constructions of innovative architecture with thick reinforcement, heavy access or long narrow forms;
- the use of self-sealing concrete makes it possible to dispense with vibration when laying;
- reducing the need for highly skilled labor, that is, reducing labor costs;
- saving time and thus shortening the construction time;
- the use of self-sealing concrete reduces equipment wear and thus saves depreciation costs;
- self-sealing concrete means quiet and safer construction.

However, self-sealing concrete has its drawbacks:

- when working with self-sealing concrete, it should taken into account the temperature, the temperature must be above zero;
- particularly long-term concrete mixtures can still lead to spalling, this factor must be taken into account to avoid breaking the material stability;
- concrete mixture mobility can be reduced by delay in laying works, so it is necessary to organize the work process clearly;
- when designing and installing the formwork, the increased pressure of the mixture compared to the usual concrete should be taken into account, which means that the formwork should be stronger (Collepardi, 2001).

The composition and structure of the fly ash depend on the properties of the coal to be burned and its combustion. The fly ash of thermal power plants for concrete (DSTU B V.2.7-205:2009) has the following composition and physico-chemical properties.

It is advisable to start disposing of the fly ash by extracting rare-earth and other metals in its composition. Furthermore, the fly ash is characterized by large inclusions of underburned coal grains (0.125 mm sieve residue is 15 mass%), which significantly increase water consumption and reduce its efficiency (Tables 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12).

Table 2 demonstrates that it is advisable tostart disposing of the fly ash by extracting rare-earth and other metals in its composition. Furthermore, the fly ash ischaracterized by large inclusions of underburned coal grains (0.125 mm sieve residue is 15 mass%), which significantlyincrease water consumption and reduce its efficiency.The primary study was micrographs of fly ash particles (Table 3). The features of the samples

Table 1 Composition of the concrete mixture for self-sealing concrete manufacturers from different countries

Concrete mixture components	Consumption for 1m^3, kg			
	Japan	EU	USA	India
Water	175	190	180	163
Portland cement with reduced heat generation	530	–	–	–
Portland cement	–	280	375	
Cement	–	–	–	330
Ash	70	–		
High-lime ash	–	–	–	150
Clay filler	–	245	–	–
Slag granulate	–	–	119	–
Fine aggregate	751	865	936	917
Large aggregate	789	750	684	309/455
Superplasticizer additive	9	4.2	2500[b]	2400[b]

[a] The large aggregate of two fractions (10 mm/20 mm) is used only in India

[b] These consumption are presented in ml

Table 2 Chemical composition of fly ash and Portland cement clinker PLC "Ivano-Frankivsk cement"

Material name	Chemical composition, %					
	SiO_2	$Al_2 O_3$	$Fe_2 O_3$	CaO	MgO	SiO
Fly ash	20–40	8–11	10.0–15.0	25–50	2–4	1.0–3.0
Portland cement M500	18–26	4–7	0.3–6.0	62–68	5	1.0–3.5

Table 3 Physical and chemical properties of fly ash

Characteristics	Value
Density g/cm^3:	
Bulk	0.33–0.36
True	0.52–0.65
Disperse composition:	
Diameter, μm	20–600
Mean diameter, μm	76–124
Unconfined compressive strength, MPa	27–32
Chemical resistance, %:	
In a basic solution	2.0–7.1
In an acid solution	1.5–6.5
Water absorption of a filling layer, %	86–100
Fusion point, °C	1000–1400
Heat capacity, $J \cdot m^{-3} \cdot K^{-1}$., at 25 °C	880–1700
Coefficient of thermal conductivity, W/(m K), at 25 °C	0.121–0.232
Freeze–thaw resistance, cycle	> 20
Permitivity, F/m	2.08–2.65
Dielectric loss tangent	0.011–0.268
Specific electrical resistance, Ω·m	$5.1–10^8–5.2–10^{11}$
Specific activity of natural radionuclides, Bq/kg	134–280

Table 4 Impact of mineral additives such as fly ash on the properties of Portland cement PPC I—500 (paste 1:0)

Cement paste sample	Ultimate tensile strength, MPa, time, days			
	1	2	7	28
No additive	29.6	47.9	50.8	52.6
Fly ash	32.7	47.0	53.4	55.0

Table 5 Test results (compressive strength) with the introduction of additive No. 1

Material	Per 1 m^3	Per 7 l
Water	140	0.98
Cement	420	2.94
Sand	580	4.06
Spalls	1260	8.82
Additive	8	0.56

were studied by scanning electron microscopy (SEM) on a JSM-6390LV scanning electron microscope (JEOL, Japan). The studies were carried out in the mode of secondary electrons at an accelerated voltage of 15 kV and low beam currents. This observation mode was chosen to minimize recharging effects. Using electron optical microscopy, the sizes of fly ash microspheres obtained f the diameter of the microspheres varies within (20–100) μm, but the vast majority of them have a size diameter of ≈ 60 μm (Table 4).

The primary study was micrographs of fly ash particles. The features of the samples were studied by scanning electron microscopy (SEM) on a JSM-6390LV scanning electron microscope (JEOL, Japan). The studies were carried out in the mode of secondary electrons at an accelerated voltage of 15 kV and low beam currents. This observation mode was chosen to minimize recharging effects. Using electron optical microscopy, the sizes of fly ash microspheres obtained from CHP-5 in Kyiv were determined (Fig. 3). It can be seen that the diameter of the microspheres varies within (20–100) μm, but the vast majority of them have a size diameter of ≈ 60 μm (Fig. 4).

In this regard, it is advisable to introduce ultradisperse mineral additives into quick-hardening cement systems with a developed surface providing initial density of the system. Due to the specific range of technical properties and commercial attractiveness, ash microspheres are a modern multifunctional material with a perspective of application in many industries (Bartos et al., 2004; Yang et al., 2022).

The modification of physical–mechanical properties of concrete mixtures. The additive was introduced into the concrete on the basis of a polymer admixture structured by hydrocarbon nanotubes. The concrete included such constituents as cement, spalls, sand and water. 39.29 is a number, which determines the brand strength.

The additive No. 1 (Table 5)

The addition of water was larger than the calculated recipe by 85.7 g, as the concrete was at a temperature of 30 °C.

Table 6 Test results (compressive strength) with the introduction of additive No. 2

Day 3	Day 7	Day 28
Cube 1	*Cube 1*	*Cube 1*
2475 g–124 kg/s–38.6 MPa	2450 g-179 kg/s-55.7 MPa	2505 g–189 kg/s–59 MPa
Cube 2	*Cube 2*	*Cube 2*
2440 g–97 kg/s–30.6 MPa	2460 g–171 kg/s–53.2 MPa	2490 g–153 kg/s–47.6 MPa
34.6 MPa/39.29	54.45 MPa/39.29	53.3 MPa/39.29
88%	138.5%	135%

Table 7 Test results (compressive strength) with the introduction of additive No. 3

Day 3	Day 7	Day 28
Cube 1	*Cube* 1	*Cube* 1
2440 g–97 kg/s-30.6 MPa	2455 g–110 kg/s-34.4 MPa	2400 g–149 kg/s-46.3 MPa
Cube 2	*Cube* 2	*Cube* 2
239 g–19 kg/s-41.6 MPa	2400 g–120 kg/s-37.4 MPa	2410 g–67 kg/s-20.7 MPa
35.35 MPa/39.29	35.9 MPa/39.29	33.8 MPa/39.29
98.9%	81.3%	86%

Table 8 Test results (compressive strength) with the introduction of additive No. 1 with the addition of 24 g

Day 3	Day 7	Day 28
***Cube* 1**	***Cube* 1**	***Cube* 1**
2500 g–133 kg/s-41.9 MPa	**2475 g–95 kg/s-30.0 MPa**	**2350 g–134 kg/s-40.7 MPa**
***Cube* 2**	***Cube* 2**	***Cube* 2**
2510 g–170 kg/s-52.9 MPa	2450 g–65 kg/s-20.7 MPa	2450 g–182 kg/s-103.5 MPa
47.1 MPa/39.29	52.35 MPa/39.29	48.6 MPa/39.29
119.8%	64.5%	123.5%

Table 9 Test results (compressive strength) with the introduction of additive No. 1 with the addition of 35.5 g

Day 3	Day 7	Day 28
Cube 1	*Cube* 1	*Cube* 1
2440 g–135 kg/s-41.9 MPa	2420 g–120 kg/s -37.4 MPa	2470 g–139 kg/s-43.2 MPa
Cube 2	*Cube* 2	*Cube* 2
2470 g–108 kg/s-33.8 MPa	2405 g–156 kg/s-48.5 MPa	2450 g–159 kg/s-49.5 MPa
37.8 MPa/39.29	42.9 MPa/39.29	46.3 MPa/39.29
96.3	109.2	117.9

The additive No. 2. (Table 6)

140 ml of water were added to the recipe.

The additive No. 3 (Table 7)

The amount of water was larger by 190 g.

The additive 1 (Table 8)

24 g of the additive were added per 7 l.

The additive 2 (Table 9)

35.5 g per 7 l.

The additive 1 (Table 10, Table 11)

40.5 g per 7 l.

The tests showed that the quantity of the additive increased the strength characteristics of the concrete,

Table 10 Test results (compressive strength) with the introduction of additive No. 1 with the addition of 40.5 g

Day 3	Day 7	Day 28
Cube 1	*Cube* 1	*Cube* 1
2490 g–120 kg/s-37.4 MPa	2440 g–158 kg/s-49.3 MPa	2415 g–83 kg/s-26.2 MPa
Cube 2	*Cube* 2	*Cube* 2
2500 g–140 kg/s-43.5 MPa	2460 g–162 kg/s-50.4 MPa	2400 g–102 kg/s-32 MPa
40.45 MPa /39.29	49.8 MPa /39.29	29.1 MPa /39.29
102.9	126.9	74.0

Table 11 Test results for the additive No. 1 with the addition of 40.5 g

Day 3	Day 7	Day 28
Cube 1	*Cube* 1	*Cube* 1
2475 g-80 kg/s-25.3 MPa	2450 g-131 kg/s-40.7 MPa	2500 g-160 kg/s-49.8 MPa
Cube 2	*Cube* 2	*Cube* 2
2450 g–64 kg/s-20.4 MPa	2450 g–102 kg/s-32.0 MPa	2470 g–112 kg/s-35.0 MPa
22.8 MPa/39.29	36.3 MPa/39.29	42.4 MPa/39.29
58.1	92.4	107.8

Table 12 Physical and mechanical properties of concrete with a polymer additive structured by carbon nanotubes

No.	Additive content, %	Normal density, mass. %	Setting time, h.-min		Compressive strength,MPa, time, days		
			Beginning	End	1	3	28
1	0	27.0	0–40	1–35	18.4	28.3	51.1
2	0.1	27.0	0–30	1–40	23.0	36.2	53.1
3	0.5	26.5	0–15	1–20	23.7	32.8	60.8
4	1.0	26.4	0–10	0–40	21.2	30.4	62.9
5	1.5	26.5	0–10	0–40	24.8	36.2	51.6

[a] The determination of the period of concrete setting and curing was carried out at a temperature of 20 °C

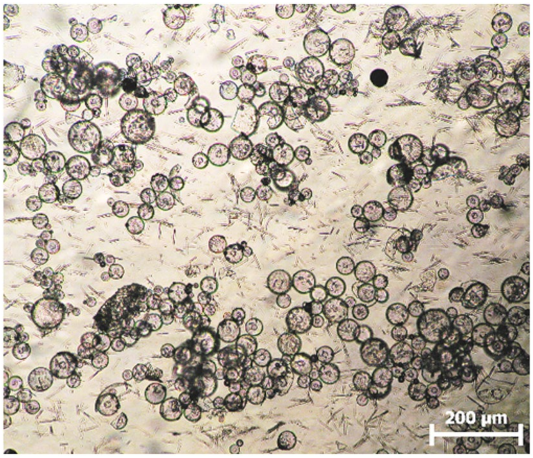

Fig. 3 Micrograph of fly ash microspheres

and the addition of water did not always have a positive effect on its performance.

4 Discussion

The physical and chemical modification of the cement system determines the possibility to regulate its properties, which allows, along with the intensification of hardening, to optimize the structure of the cement matrix. This process ensures an increase in the strength of concrete during compression and especially during bending, thus increasing the concrete durability. The physical and chemical modification of the cement system made it possible to identify additional reserves for improving the rheological and strength properties of the concrete mixture by applying technological effects of a certain intensity, congruent physico-chemical

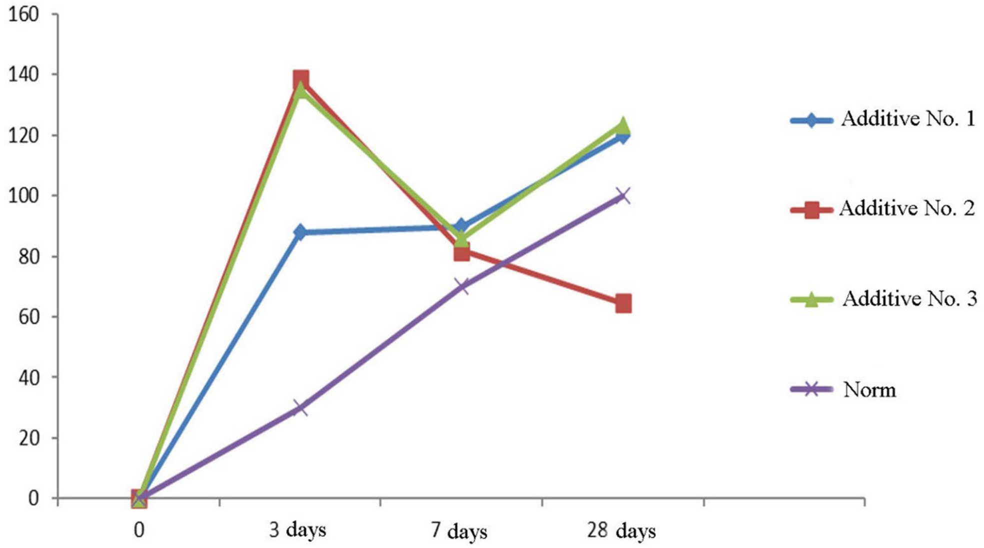

Fig. 4 Concrete cube strength graph

conditions of hydration processes of the cement system. The solution of the given problem is relevant for the monolithic buildings construction technology development in Ukraine. The theory of hydration structuration has not yet become a "dynamic theory" and to a large extent remains a "kinematic scheme", only connecting the parameters of the system, but not determining practically the mechanism of its change and the optimal structure formation.

The studies concluded that there is a reserve for managing these processes. This is especially important when it is necessary to obtain WEC concrete. The process of accelerating the hardening of monolithic concrete reduces the use of formwork per day if, after initial activation, the heat extraction mode continues. The modification of a cement system for the monolithic construction involves the influence on chemical processes that occur during the hydration of clinker minerals and structure formation of the cement matrix. Therefore, modifiers were selected based on their chemical activity relative to clinker minerals, especially calcium aluminates (Ilerisoy & Takva, 2017). Previous studies have shown the feasibility of introducing $Mg_2(OH)3Cl\ 4H_2O$ and $Mg_3(OH)5Cl{\cdot}4H_2O$ into the organo-mineral modifying complex within the cement system, being the main reaction products in the $MgO–MgCl_2–H_2O$ system, under normal hardening conditions. These joints act as the disperse reinforcing component of the cement matrix.

Magnesium chloride hydrate is formed in the form of well-crystallized needles, which are described as spiral tubular filamentous crystals. The mechanical adhesion of these filamentous crystals is seen as the main source of strength creation along with the additional adhesion achieved by the mutual germination of the crystals when they collide. The slow setting and fast hardening of the modified cement system allows to use concrete mixtures for concrete pumping and long-distance transportation of concrete mixtures during the construction of monolithic buildings. Studies of magnesium chloride hydrate phase formation and transformation were performed on samples manufactured with different $MgO/MgCl_2$ ratios and a constant mass ratio of $H_2O/MgO = 2$. Studies demonstrated that the formation and transformation of magnesium chloride hydrate phases was a function of the $MgO/MgCl_2$ ratio, at molar ratio $MgO/MgCl_2$.

The results of the research made it possible to make such a hypothesis of the development of the modified cement system microstructure. This results in mechanical adhesion, which determines the development of initial strength and stiffness. Since there is not enough space for the crystals to grow freely, the crystals are mutually germinated, forming a dense structure that leads to increased strength. The production of needle-like crystals is not considered an absolute requirement for hardening. Strength depends on the formation of reaction products that fill free space, resulting in the formation of a dense microstructure with minimal porosity. Obviously, characteristic growth needle and filamentous crystals contributes to this. Research results indicate that a polymer additive structured with carbon nanotubes accelerates cement setting and hardening and increases strength.

Studies of the influence of a polymer additive structured by carbon nanotubes on the processes of early structuring of a plain cement concrete mixture showed that the additive led to an acceleration of setting time of composite Portland cement by 10–25 min. Strength of cement rock based on nano-modified composite Portland cement with a 0.1 mass.% concentration of carbon nanotubes and 0.5 mass.% in the early period (after 1 day) increases by 29% and 15% compared to the mixture without additives and reaches 23, 7 and 21.2 MPa, respectively; after 28 days, the strength increases by 19% and 23% and constitutes 60.8 and 62.9 MPa.

It was established that the additive acted as an accelerator of concrete setting and hardening at all times and at all concentrations. At the same time, at low concentrations (0.1 mass%), the acceleration of setting takes place in 1–3 days, and at high one (0.5–1.0 mass%), strength is more in 28 days. At all concentrations, the additive may be considered preferable (Table 12).

The acceleration of hydration of the composite plain cement concrete mixtures and the increase in their strength point to the interaction of a polymer additive structured by carbon nanotubes with a plain cement concrete mixture providing a pozzolan reaction (binding of free lime released during cement hardening) (Kropyvnytska, 2020; Rudenko, 2013). In general, for the plain cement concrete mixture, the study shows a decrease in the normal density of the cement paste, indicating a reducing effect from the application of the additive. Water consumption is reduced to 8 mas. % max.

Experimental studies confirmed that the polymer additive structured by carbon nanotubes was a setting and hardening accelerator and a strength-enhancing additive. Moreover, the manifestation of the main technological effects and their degree depends on the method of introduction of the additive in cement systems, and depends significantly on the mineralogical composition of cement and the presence and type of active mineral additives.

It can be concluded that the first sample gains great strength within 28 days and the thickest supplement is 1, which proved to be the most resistant. This is the first and the third sample, gaining more strength, which is also good. It is possible to say that carbon nanotubes can be added to concrete products because they give good strength. It was proven that at normal and low temperatures the addition of a polymer additive structured by carbon nanotubes contributes to accelerating the concrete mixture setting and hardening.

The graph (Fig. 5) shows the strength for our experience. Based on the results obtained for various concrete mixtures, it can be concluded that depending on the type of mixture, a polymer additive structured with carbon nanotubes accelerates cement hardening at all times. It accelerates cement hardening in the morning (1–3 days) and does not affect 28-day strength or affect (slow down) concrete mixture hardening in early time, but contributes to an increase in its strength by 28 days (on average 25%). At the same time, in almost all cases, a polymeric additive structured with carbon nanotubes also acts as a setting accelerator and a water reducer (Fig. 6).

It was experimentally confirmed that the additive accelerates the cement hardening processes, and theoretically it can be assumed that this is due to the formation of a bulk mesh, which is formed due to the presence of carbon

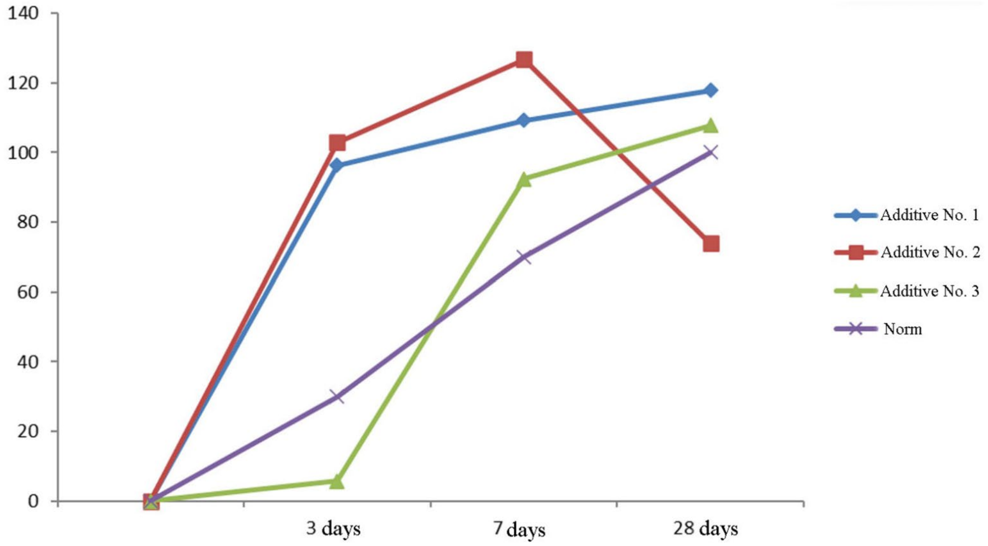

Fig. 5 Concrete cube strength graph

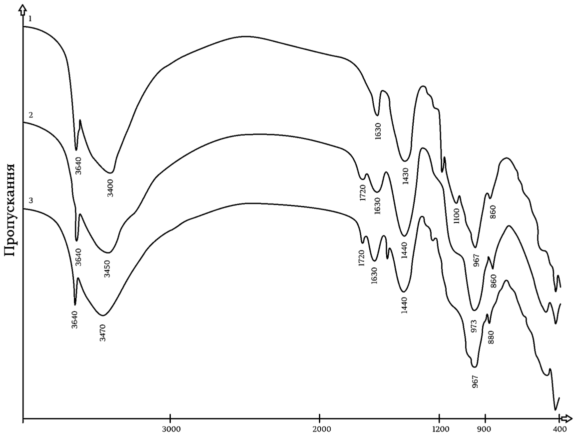

Fig. 6 The IR spectra of M 500 cement of JSC "Ivano-Frankivsk cement"

nanotubes. This process leads to the binding of calcium ions into insoluble compounds in a pore solution and, as a result, the hydrolytic dissociation of clinker minerals is accelerated. In order to study the influence of the complex modifier on the properties of cement rock, studies have been carried out using the method of the infrared spectroscopy and the derivatographic analysis.

Samples of cement rock with a polymer additive structured with carbon nanotubes were investigated. The research results are presented in Fig. 3. The infrared spectra of non-hydrated and hydrated cement show the following absorption bands in the regions (Lerisoy & Takva, 2017; Middendorf & Singh, 2006):

- 900–950 (valence oscillations Si–O), 820, 400–500 cm-1 (deformation) oscillations Si–O)—oscillations of insulated silicate tetrahedra indicating the presence of silicates in cement; the hydration of the silicate phase causes displacement of the band by 900–950 1 cm to the area of large wave numbers; after several days of hydration, the silicate absorption band is applied to the sulphate absorption band;
- 650–800 cm^{-1} corresponds to the oscillations of isolated groups $[AlO_4]$;
- 700–870 cm^{-1}—variation of condensed groups $[AlO_4]$;
- region 400–500 cm^{-1} identifies oscillations of isolated and condensed groups $[AlO_6]$.

According to some sources (Bartos et al., 2004; Garrault, 2005; Ielerisoy & Takva, 2017; Kim et al., 2013; Königsbergera et al., 2018; Kropyvnytska, 2020; Rudenko, 2013; Zakharov, 2008), individual clinker minerals can be identified by spectrogram as follows:

- o C3S—935 and 521 cm^{-1}, C2S—991, 879, 847 and 509, C3A—900, 865, 820, 780, 720,705, 520, 510, 460 и 404, C4AF;
- o 1150, 980, 610 and 450 cm^{-1}—vibrations of the [SO4]2 group, the bands of these regions indicate the presence of gypsum stone in the cement; early formation of ettringite at hydration is identified by the change of sulfate absorption band—a singlet appears at 1120 cm-1, and the subsequent substitution of ettringite with monosulfoaluminate is identified by changing the absorption bands of 1100 and 1170 cm^{1};
- o 1420–1510, 1080, 860–880, 700–720 cm^{-1}—bands indicating the presence of calcium carbonate, and these relate to oscillations of the $[CO_3]^2$-group; in addition to this area (1450–1580 cm^{-1}), there are absorption bands identifying the presence of portlandite and high-core calcium hydrosilicates;
- o hydroxyl groups have narrow absorption bands in the area of 3750–3650 and 1600–1580 cm^{-1};
- o water molecules have a wide band in the area of 3600–3000 cm^{-1} and 1680–1600 cm^{-1}, and the formation of hydrogen bonds between single water molecules may affect their intensity and location, but this entails the emergence of new bands in the area of 800 cm^{-1}.

The study of the hydration mechanism was carried out with the use of of M 500 cement of JSC "Ivano-Frankivsk cement", mixed with water and two pastes with a polymer additive, structured by carbon nanotubes, 0.1 and 0.5 mass. %. Accordingly, the IR spectrogram of non-hydrated cement was taken for comparison.

The IR spectra identifies valence oscillations of isolated silica-hydrous tetrahedra with a absorption band of 900 cm^{-1}. The absorption band with a maximum of 1100 cm^{-1} corresponds to the valence oscillations of the SO4-2 group and indicates the presence of gypsum stone in the cement. The triplet with highs 530, 590, and 650 cm^{-1} indicates the deformation of isolated silica- and alumino-oxide tetrahedra and SO42-group. The absorption band with a maximum of 1450 cm^{-1} indicates the formation of three compounds at once such as portlandite, calcium hydrosilicate and calcium carbonate. Therefore, it can be assumed that during the storage of cement, its partial surface hydration occurred.

After the first day of hardening of the hydrated cement, there is a shift of the band of valence oscillations of the Si–O alite and belite towards large wave numbers (946 cm^{-1}), which indicates the hydration reaction of these minerals. The cement absorption band with 0.1 mass. % is more intensive than other cements (without additive—80%, with 0.1 mass%—90%, with 0.5 mass. %–79%), which, at the same time, along with the shift of maximum, indicates partial polymerization of silica tetrahedra with the formation of dimers.

Cement hydration of 0.1 mass. % is faster, and the share of dimer tetrahedra is greater. If for non-hydrated cement the 500–600 cm^{-1} area is sufficiently clearly divided into three bands, only the peak hydrated samples at 520 cm^{-1} remains on the spectrograms. This fact indicates fairly complete hydration of the aluminate and aluminopherytic phases, and the peak of 520 cm^{-1}, which corresponds to the deformation oscillations of the Si–O and Al–O bonds, identifies still unhydrated silicate and aluminate clinker minerals.

The intensity of absorption bands at 1450 cm^{-1} varies unevenly, for example, in cement without additive—60%, with 0.1 mass. %—62%, with 0.5 mass. %—53%. Since this area confirms the existence of three compounds at once, it is difficult to identify what is formed. However, in the region of 700–720 cm^{-1} for control cement and 0.1 mass cement. % of DOR 1 appears a small absorption band, responding to the deformative oscillations of the $[CO_3]$2-group, while in the area 870 cm^{-1}, the increase of the chemical additive is accompanied by a small absorption band (for cement with 0.5 mass%) indicating the formation of crystalline hydrosilicates. Thus, it can be concluded that as the content of the polymer additive structured by carbon nanotubes increases, the hydration of silicate clinker minerals and the crystallization of hydrosilicates accelerates.

This process is more common for 0.1 mass.% cement of the polymer additive structured by carbon nanotubes, while the absorption band intensity at a maximum of 1100 cm^{-1} is reduced, and the gypsum is consumed much faster in cement with a 0.1 mass. % additive (band intensity 28%), slower in control cement (37.5%) and slower in sample of 0.5 mass. % additive (40%).

The appearance of a wide absorption band with a maximum of 3450 cm^{-1} indicates additionally accelerated hydration of clinker minerals (both silicate and aluminate). The band with a maximum of 3400 cm^{-1} confirms the presence of molecular water in the composition of crystalline and amorphous neoplasms and indicates the presence of CSH-gel and crystalline hydrosilicates, ettringite hydroaluminate. The nature of the change in the intensity of bands is extreme, for example, for the control cement—59%, with 0.1 mass. %—67%, with 0.5 mass. %—55%.

In this way, the acceleration of the hydration reactions of cement constituents of 0.1 mass.% of a polymer additive structured with carbon nanotubes is confirmed. The same is true for the absorption bands in the 3640–3650 and 1630–1650 cm^{-1} regions, which indicate the presence of hydroxyl groups in the composition of portlandite, ettringite, aluminum hydroxide and calcium hydroaluminates.

Hence, the mechanism for accelerating cement setting and hardening when a polymer additive structured with carbon nanotubes is introduced into cements based on IR spectroscopy data of cements hydrated within 1 day, is to accelerate the hydration of silicate and aluminate minerals, resulting in the formation of more crystalline neoplasms as well as the acceleration of crystallization of silicate hydration products. Moreover, the acceleration of processes occurs to a greater extent when cement is hardened from 0.1 mass. % of a polymer additive structured with carbon nanotubes.

There is an absorption band shift corresponding to the valence oscillations of the Si–O bonds into the longer wave region after 28 days of hardening. The maximum band for control cement is 967 cm^{-1}, the cement of 0.1 mass. % SOG 1—973, with 0.5 mass. %—967 cm^{-1}. This phenomenon confirms the continuation of polymerization of silica-acid tetrahedra with the formation of dimers, and this process is more likely to occur in hydrated cement of 0.1 mass. % of the additive, as evidenced by the intensity of the bands—56, 66 and 59%, respectively.

The bands in the area of 1430 cm^{-1} have intensities of 32, 40 and 33%, respectively. In the 870 cm^{-1} region, the bands become more visible (compared to the 1 day spectra) and their intensity increases with the increase in the amount of chemical additive (11, 15 and 13%, respectively). This band indicates the continued formation of crystalline hydrosilicates and increased hydrogen bonds between water molecules. Hydrogen bonds can be formed between water molecules in calcium hydrosilicates, including in fibrous hydrosilicates, which leads to their adhesion by chemical forces (Bolshakov et al., 2014) and additional strengthening of the crystallization carcass already formed. In addition, carbon nanotubes also significantly enhance interaction.

Absorption bands in the 3640 cm^{-1} range (46%, 52% and 47%, respectively) vary dramatically with an increase in additive content, while in 1630 cm^{-1} bands (13%, 13% and 15%, respectively) are approximately equal, indicating a large share of clinker mineral hydration products in 0.1 mass.% cement. There is also an extreme variation in the absorption band intensity with a maximum of 3400 cm^{-1} (46, 52 and 47%, respectively), confirming a greater molecular water content of 0.1 mass. % of the additive in cement hydration products. These events indicate more complete hydration of clinker minerals in the presence of a 0.1 mass.% of a chemical additive when concentrations increase.

Thus, the IR spectroscopic analysis of cement hydrated within 28 days confirms that the polymer additive structured by carbon nanotubes accelerates the hydration of silicate minerals of cement and the formation of crystalline hydrosilicates.

The obtained results of the research into the processes of concrete mixtures hardening after 1 and 28 days allows to conclude that the polymer additive, structured with carbon nanotubes, affects the course of hydration reactions of silicate and aluminate cement minerals, as well as the calcium hydrosilicate crystallization processes. The results obtained by the IR spectroscopic method are confirmed by the water binding kinetics determination and derivative analysis. The results of non-hydrated cement DTG reveal the following phases: at 145 and 165 °C effects identify gypsum stone, at 485 °C a small amount of portlandite formed during storage is possible through partial hydration of free lime or clinker minerals (Collepardi et al., 2004).

Thermal treatment of cement rock is accompanied by several processes as follows: at 100–110 °C, water and organic solvent used in sample preparation are removed; within 100 °C adsorbed moisture is removed; a peak at 125–140 °C appears during the first 15 min of hydration and corresponds to ettringite, its intensity passes through a maximum of 16–24 h of hydration; at 115–125 °C a peak corresponds to cement gel; at 150–220 °C it corresponds to the removal of interlayer water from hydrosilicates of calcium type C–S–N(I) and S–S–N(II); at 215 °C a peak corresponds to the removal of water from the low sulfate form of calcium hydrosulfonate $3CaO*Al2O_3*CaSO_4*12H_2O$.

At 150–200 and 200–280 °C, endothermic effects correspond to the decomposition of hexagonal hydroaluminates, while at 325–400 °C they correspond to cubic calcium hydroaluminate Ca_3A16. At 450–550 0C, calcium hydroxide decomposes, and at 700–900 °C, the crystalline calcium hydrosilicates dehydrate and convert CSH(I) to wollastonite (800–860 °C), and CSH(II) to bellite (600-7000S). In the 610–800 °C range, the secondary calcium carbonate produced by atmospheric carbonization of Ca(OH)2 is decarbonized.

Since the temperature decomposition intervals of the cement hydration products are superimposed on each other, it is advisable to estimate the water binding kinetics by the mass at certain intervals. Based on the mass reduction in the 110–250 °C interval, it is possible to estimate the amount of the formed gel phase consisting of hydrosilicate gels and crystalline hydrosilicates.

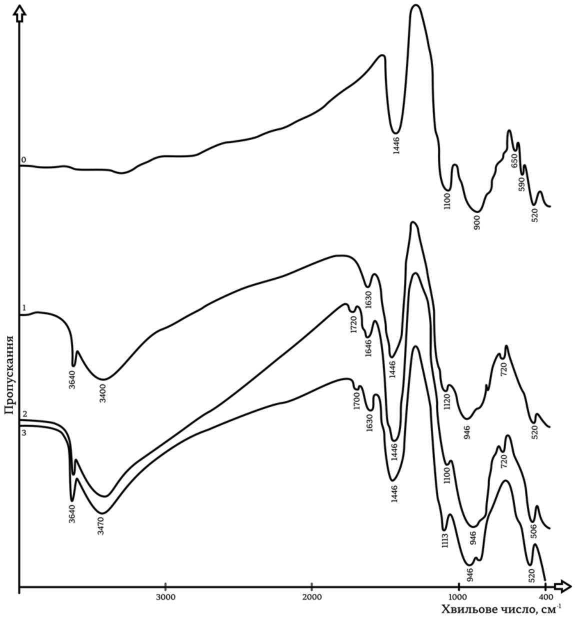

Fig. 7 IR spectra of hydrated cement after 28 days of hardening: 1—control hydrated cement; 2—hydrated cement of 0.1 mass.% additives, 3—hydrated cement of 0.5 mass. % additives

The derivatographic analysis suggests that, first of all, the acceleration of cement hardening is caused by the fact that the additive accelerates the reaction of the aluminum phase hydration, which then crystallizing facilitate the crystalline growth of cement rock. Secondly, the additive accelerates the formation of crystalline calcium hydrosilicates and the conversion of high-base hydrosilicates into low-core ones Cwirzen et al. (2008). The main confirmation of the proposed mechanism of action of the chemical additive is the reduction of mass loss in the temperature interval of calcium hydroxide degradation (especially the period of 1–3 days), which indicates the chemical binding of calcium ions in hydroxide to other soluble compounds.

Thus, the research results indicate that a polymeric additive structured with carbon nanotubes accelerates the cement paste setting and hardening and increases the plain cement concrete mixture strength. Theoretically, it can be assumed that this is due to the formation of a volumetric mesh in the cement rock due to the presence of carbon nanotubes, which are the centers of the crystallization of the cement rock hydrosilicates, being reinforced and compacted throughout (Fig. 7).

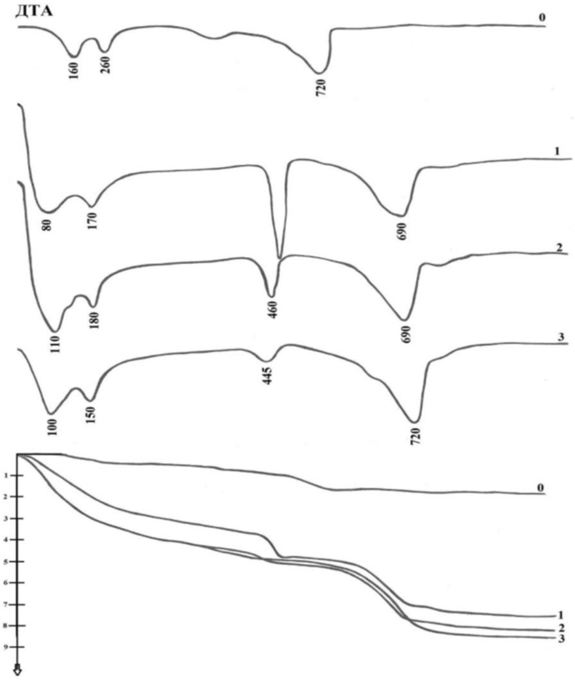

Fig. 8 Thermogram of dispersed and hydrated cement after 1 day of solidification: 0—dispersed cement, 1—control hydrated cement, 2—hydrated cement of 0.1 mass. % polymer additive structured by carbon nanotubes, 3—hydrated cement with 0.5 mass. % polymer additive structured by carbon nanotubes

Such conclusions are confirmed by experimental results in the works (Bernal et al., 2017; Horgnies et al., 2013; Mazurak, 2017). Ultrasonic treatment of carbon nanotubes in acrylic acid solutions was carried out in the cement matrix to obtain a high dispersion of CNT and a subsequent uniform distribution. The results of Raman Spectroscopy (RS) and Transmission Electron Microscopy (TEM) showed that polyacrylic chains were covalently bound to carbon nanotubes rather than adsorbed. Fig. 8 shows the interaction of cement hydration products (Ca(OH)2 and C–S–H) with carboxylic groups on the surface of carbon nanotubes.

Based on the results obtained, the resulting modified nanomixture can be used in various areas—from the restoration and strengthening of structures to the production of reinforced concrete and high-strength seamless monolithic floors. Also where so-called self-compacting concrete is used. The main characteristic of self-compacting concrete is the ability to completely fill the working space even with very dense reinforcement and harden, compacting under its own weight. This ability allows you to abandon vibration technologies for compacting the concrete mass, which means that the work process is characterized by low noise level and low time and energy consumption (Fig. 9).

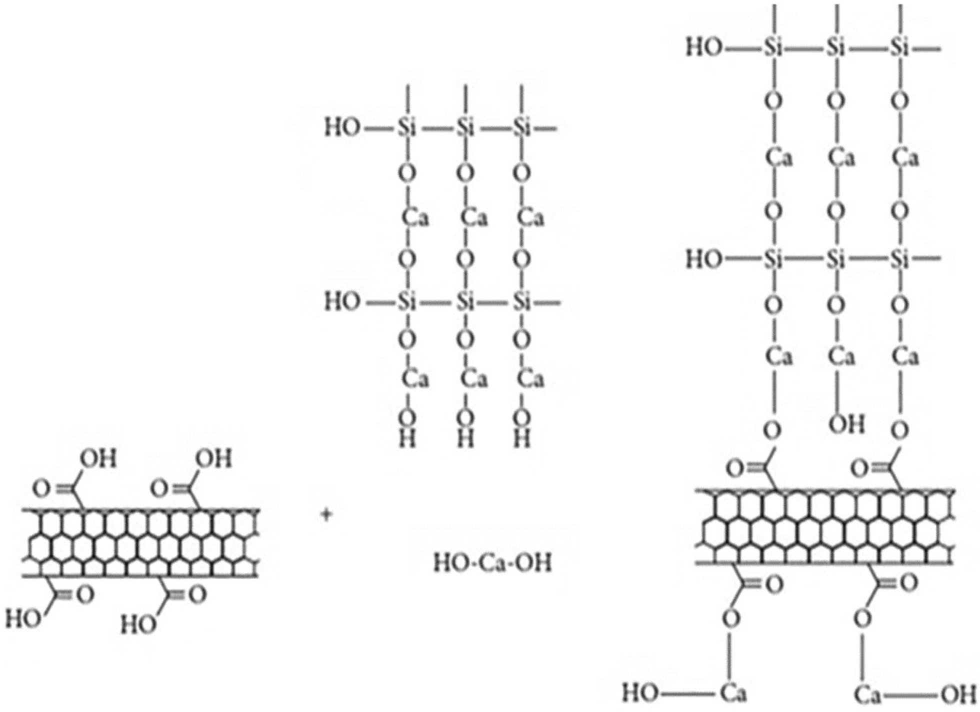

Fig. 9 Reaction scheme between carboxylated nanotubes and cement hydration products (Ca(OH)2 and C-S-H)

5 Conclusions

The following conclusions were made during the study:

1. The dispersion of carbon nanotubes by ultrasonic treatment, stable and homogeneous aqueous dispersions of carbon nanotubes with grafted links were obtained. This ensures more even distribution of CNT in the cement matrix and a chemical bond between them, which significantly improves the performance of such a plain cement concrete mixture.
2. It is shown that it is possible to effectively modify a cement concrete mixture with carbon nanotubes dispersed in a polycarboxylate polymer additive solution.
3. It was established that the dispersion of carbon nanotubes with a content of 0.1 mass.% in relation to cement had the best effect on the compressive strength of the plain cement concrete mixture.
4. When plain cement concrete mixtures were modified by a complex modifier, hydration products were increased. It was established that in the presence of a polymer additive structured by carbon nanotubes, a higher degree of crystallization of calcium hydrosilicates was observed, which results in high physical and mechanical characteristics of the modified plain cement concrete mixture.

The work provides a useful view of designing a composite material strengthening system.

The materials of the article will be of interest to anyone interested in research on the use of MWCNT, modified superplasticizer Ethacryl HF in concrete and research on nano-modified simple cement concrete mixtures and on cement-based concrete.

Acknowledgements

The authors gratefully acknowledge the financial support from the Science and Technology Department of Ningxia, the Scientific Research Fund of North Minzu University (No. 2020KYQD40) and China Scholarship Council under Grant (No. 202008100027, No. 202108100024).

Author contributions

SY: writing—original draft, methodology. AB: writing—original draft, conceptualization. VT: writing—review and editing, data curation, MS: writing—original draft, software. MT: writing—review and editing, supervision. All authors read and approved the final manuscript.

Funding

This research project was supported by funding from the Science and Technology Department of Ningxia, the Scientific Research Fun of North Minzu University (No. 2020KYQD40) and China Scholarship Council (no. 202008100027, no. 202108100024).

Availability of data and materials

Data will be available on request.

Declarations

Ethics approval and consent to participate

All procedures performed in studies involving human participants were in accordance with the ethical standards of the institutional and national research committee and with the 1964 Helsinki declaration and its later amendments or comparable ethical standards. Informed consent was obtained from all individual participants included in the study.

Consent for publication

All individual participants agreed to be included in the study.

Competing interests

The authors declare they have no financial and competing interests.

Received: 7 December 2022 Accepted: 2 April 2023

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