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# STUDY ON THE INFLUENCE OF POLYCARBOXYLATE-TYPE SUPERPLASTICIZERS MASTERGLENIUM ACE 430 AND MasterGlenium ACE 560 ON THE PHYSICAL AND TECHNICAL PROPERTIES OF FINE-GRAINED CONCRETE

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**Abstract.** A study on the influence of polycarboxylate-type superplasticizers on the physical and technical properties of fine-grained concrete was conducted. The proposed concept involves creating high-quality, high-strength concretes based on modified cementing systems characterized by improved construction and technical properties. When using polycarboxylate-type superplasticizers, MasterGlenium ACE 430 and MasterGlenium ACE 560, to reduce the water consumption of concrete mixtures and the water-cement (*W/C*) ratio, an increase in the compressive strength of hardened concrete was observed, which is the result of compaction of the structure.

**Keywords:** cement system, polycarboxylate-type superplasticizer, fine-grained concrete, water-cement ratio, strength.

## 1. Introduction

The widespread use of fine-grained concrete in the production of reinforced concrete structures is constrained by the increased cement consumption compared to concrete with coarse aggregate. It is well known that the strength of fine-grained concrete is influenced by the type and amount of cement, the properties of sand, and the water-cement (*W/C*) ratio. The simplest way to reduce cement consumption in fine-grained concrete is by introducing superplasticizing additives. The use of superplasticizers makes it possible to create mixtures with a lower (*W/C*) ratio, leading to increased concrete strength.

Superplasticizers are indispensable components of modern concrete, which can optimize the plasticity of fresh concrete, as well as influence the mechanical properties, waterproofing, and durability of hardened concrete[1]. The invention of polycarboxylate comb polymers as a new class of concrete superplasticizers became an important milestone for concrete technologies[2]. Polymers of the polycarboxylate ether (PCE), which, perhaps, are the most important invention in concrete technology in recent decades, offer superior water-reducing capacity, superior workability improvement, and lower dosage requirements compared to previous generations of superplasticizers such as polynaphthalene sulfonate (PNS), polymelamine sulfonate (PMS) and acetone formaldehyde sulfonate (AFS) polycondensates[3]. Nowadays, the market offers a wide range of PCE products with different chemical compositions, among which methallyl ether (HPEG) and isoprenol ether (IPEG) PCEs hold the largest market share due to their high economic efficiency[4]. The development and modification of new molecular architectures for PCE have been used to improve the rheology, adhesion, cohesion, and durability of cement paste and concrete[5]. The PCE-type superplasticizer has undoubtedly become one of the most widely used additives in modern concrete formulations due to its high efficiency and tunable molecular structure[6]. PCE is generally used in high-quality concrete production due to its superior properties, such as its strong dispersing ability and water-reducing effect[7]. Superplasticizers based on PCE are today the main components of cured concrete to increase its fluidity while maintaining a low W/C ratio, which promotes its mechanical strength and durability[8].

Dispersing properties of PCE-type superplasticizers are directly related to the molecular structure of PCE, composition, dosage, and mineralogical composition of cement[9]. PCE superplasticizers consist of a combination of negatively charged side chains of carboxylate with linear side chains of poly (ethylene glycol) (PEG), and can be characterized by a large variability of chemical structures, such as diverse molecular weights, functional groups, and chemical architecture, which can be easily adjusted according to application needs[10]. Meanwhile, the

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PCE adsorption behavior can also be altered by introducing different functional groups into the main chain or by adjusting the carboxyl density of the chain[11]. PCEs have a unique chain structure with a high density of anionic groups along the polymer chain and dangling polyoxyethylene side chains. This structure provides a strong ability to deflocculate and disperse cement particles due to the synergy of electrostatic repulsion and steric hindrance[12]. Anionic groups are adsorbed on the surface of cement particles, providing electrostatic forces of repulsion, while side chains extend into the pores of the solution, creating steric hindrance forces[13]. The dispersing ability of polycarboxylate superplasticizers can be considered as the electrostatic and steric stabilizations of cement suspensions. For this, PCEs must be adsorbed on the surface of cement particles to become effective[14]. PCEs reduce the cohesive force between particles and release water captured by agglomerated cement particles, mainly due to the steric hindrance effect created by adsorbed PCE molecules on the surface of the particles[15]. In addition, PCE is widely used in the concrete construction industry because of its high water reduction, good slump retention, and structural designability of comb-shaped molecules[16].

Despite the higher cement consumption compared to heavy concrete with coarse aggregate, the total cost of structures and products made from fine-grained concrete using standard sand in regions with a shortage of coarse aggregate is reduced by 15–20 % due to the lower cost of fine aggregate (sand) as a locally available material. The cost-effectiveness depends on specific regional construction conditions, the size and purity of the fine aggregate, as well as the type of structure or product. The production of reinforced concrete structures using fine-grained concrete significantly reduces the need for coarse aggregate (crushed stone). Given that the transportation distance for crushed stone is 1.5–2 times higher than the national average (300–400 km), this reduction allows for lower railway transportation costs and significant financial savings. Consequently, the cost of structures decreases, and overall, construction projects can be completed more quickly.

A major potential for improving the economic efficiency of manufacturing structures and products from fine-grained concrete lies in reducing cement consumption per cubic meter of concrete mixture. Currently, conditions have been created for significantly reducing additional cement consumption through the use of blended fly ash and superplasticizing additives, as well as modern concrete-forming technologies.

The purpose of this study is to investigate the impact of polycarboxylate-type superplasticizers, MasterGlenium ACE 430 and MasterGlenium ACE 560, on the physico-technical properties of fine-grained concrete made with small aggregates from local raw materials. The authors aimed to study the effect of these superplasticizers on concrete mixtures with a high cement content and fine-grained aggregate (sand), which belong to the class of heavy fine-grained concretes and differ from traditional heavy concretes that contain coarse aggregate (crushed stone).

## 2. Experimental

### 2.1. Materials

High-quality Portland cement CEM I 42.5R from PJSC "Ivano-Frankivskcement" which meets European standards, ensures the production of high-quality concrete mixtures made based on Portland cement clinker with a standardized mineralogical composition. Rapid-hardening Portland cement of the CEM I 42.5R brand is intended for producing concrete of strength class (C25/30) and higher for all construction work types. This cement is recommended for achieving maximum strength in products quickly, especially during cold weather when heat treatment time cannot be reduced.

For the design of the grain composition of fine-grained concretes, fine sand from the Mykolaiv deposit (Lviv region, $\rho_{bulk}$ = 1370 kg/m$^3$) and sand from the Yasinetsky deposit (Lviv region, $\rho_{bulk}$ = 1350 kg/m$^3$) were used. Based on density classification, the natural sand from the Yasinetsky deposit can be attributed to dense class and heavy group sands (more than 1300 to 1800 kg/m$^3$): bulk density – 1350 kg/m$^3$ (according to clause 3.2 DSTU B V.2.7-29-96). The studied sand also meets the requirements for bulk density, clause 4.4.2 of DSTU B B.2.7-32-96. Based on the particle size distribution, the sand can be classified as high-grade sand: the fineness modulus is 1.17, and the residue on sieve N 063 is 0.7 wt. % (according to clause 3.4 DSTU B V.2.7-29-96). According to the content of fine particles less than 0.05 mm in size, it belongs to the group with a low content – 1.1 wt. % (according to clause 3.5 DSTU B V.2.7-29-96).

Based on density classification, the natural sand from the Mykolaiv deposit can be attributed to dense class and heavy group sands (more than 1300 to 1800 kg/m$^3$): bulk density – 1370 kg/m$^3$ (according to clause 3.2 DSTU B V.2.7-29-96). The studied sand also meets the requirements for bulk density, clause 4.4.2 of DSTU B B.2.7-32-96. Based on its grain composition, the sand can be classified as high-grade sand: the fineness modulus is 1.47, and the residue on sieve N 063 is 14.0 wt. % (according to clause 3.4 DSTU B V.2.7-29-96). According to the content of fine particles less than 0.05 mm in size, it belongs to the group with a low content – 4.5 wt. % (according to clause 3.5 DSTU B V.2.7-29-96).

Highly effective superplasticizers based on polycarboxylate ethers with nanosized molecular chains were used as modifiers to increase the strength of cementitious systems due to a significant water-reducing effect. MasterGlenium ACE 430 (liquid with density $\rho = 1.06\pm0.02$ g/cm$^3$, pH = 5.5±1.0) is an additive based on a new-generation PCE. MasterGlenium ACE 560 (liquid with density $\rho = 1.06\pm0.02$ g/cm$^3$, pH = 5.0±1.0) is a highly effective thinning additive based on polycarboxylate ether technology (Master Builders Solutions Polska sp. z o.o.).

## 2.2. Methods

Scanning electron microscopy (SEM; based on the raster microscope of the REMMA-102-02 electron microanalyzer, SELMI, Ukraine) was used to determine and evaluate the microstructure of concrete samples after the age of 7 days hardening. Infrared spectra of both the superplasticizers and modified cement pastes were obtained using an FTIR spectrometer (Cary 630) in the wavelength range of 4000–650 cm$^{-1}$ by 128 scans with a resolution of 4 cm$^{-1}$ to identify functional groups. X-Ray diffraction analysis of cement dough samples with and without additives after 7 days of hardening was carried out using an Aeris Research Benchtop X-Ray Diffractometer from Malvern Panalytical. Decoding of the experimental profile of the diffractogram (by Rietveld) was carried out in the HighScore+ software package using the crystallographic database ICDD PDF 4+ 2022 (64-bit).

The concrete slump tests – measuring the workability of concrete mixture's was evaluated according to Ukrainian national standard DSTU B V.2.7-114-2002 and according to DSTU B V.2.7-176:2008 (EN 206-1:2000, NEQ).

The concrete sample's water absorption (after 28 days of hardening under normal conditions) was determined following DSTU B.V.2.7-170:2008.

The compressive strength class of concrete was determined by DSTU B V.2.7-239:2010 on prism samples with a square section of 40×40×160 mm, obtained after the bending test of prism samples by DSTU B V 2.7-187, manufactured and aged under standard conditions according to DSTU B V.2.7-224, EN 12390-2.

# 3. Results and Discussion

Depending on the purpose and operating conditions of the concrete, the requirements for its composition change, determining its properties, affecting the production technology, and influencing durability. The strength of fine-grained concrete is not influenced by the total number of contacts within a given concrete volume but rather by the packing density of sand grains and the number of contact points that bind each grain into a monolith, depending on their mutual arrangement. Therefore, fine-grained concretes made with fine sands exhibit lower strength than those made with coarser sands. As cement consumption increases and sand grains become more spaced apart, the influence of sand on the structure and strength of fine-grained concrete decreases. In this case, fine sand has a lesser impact on reducing concrete strength. For the production of structures and products from fine-grained concrete using standard sands (with a coarseness modulus of 2.1 and higher), an additional cement consumption of approximately 100 kg per 1 m³ of concrete (for strength grades 200–300) is required compared to conventional concrete made with coarse aggregate (crushed stone) of the same compressive strength grade. For fine-grained concretes made with non-standard fine sands (with a coarseness modulus of 0.8–2.0), the additional cement consumption compared to concrete with crushed stone may be 170–180 kg per 1 m³ or more.

Modification of Portland cement with a polymer component makes it possible, by changing the nature of its surface, to activate the processes of structure formation of the cement matrix in a wide range and improve its microstructure.

The composition of the concrete mixture based on high-quality Portland cement PC CEM I 42.5R is characterized by the quantitative content of components with the consumption of materials per 1 m$^3$: Cement = 800 kg, Sand1(Mykolaiv) = 1200 kg, Sand2 (Yasnyska) = 200 kg, Superplasticizer = 8 kg (1.0 wt. %), Water = 240 kg, *W/C* = 0.30 (standard composition). The concrete mixture's workability with MasterGlenium ACE 430 (1.0 wt. %) additive is characterized by the concrete slump test of 149.0 mm, whereas with MasterGlenium ACE 560 (1.0 wt. %) additive – 156.0 mm. For concrete of this composition with the MasterGlenium ACE 430 (1.0 wt. %) additive, the value of compressive strength at an early age is $f_{cs}2 = 59.6$ MPa, after 28 days of hardening is 88.4 MPa, and for concrete with the addition of MasterGlenium ACE 560 (1.0 wt. %) $f_{cs}2 = 57.6$ MPa and $f_{cs}28 = 89.4$ MPa, respectively (Fig. 1). The flexural tensile strength of concrete for this composition with the addition of MasterGlenium ACE 430 (1.0 wt. %) at the early age of hardening is $f_{fs}2 = 7.91$ MPa, at the age of 28 days is $f_{fs}28 = 12.5$ MPa, and for concrete with the addition MasterGlenium ACE 560 (1.0 wt. %) – $f_{fs}2 = 8.62$ MPa and $f_{fs}28 = 13.4$ MPa, respectively (Fig. 2). Water absorption of concrete samples by mass after 28 days of hardening under standard conditions with the MasterGlenium ACE 430 (1.0 wt. %) additive is 2.76 %, and for concrete with the MasterGlenium ACE 560 (1.0 wt. %) additive is 2.57 %.

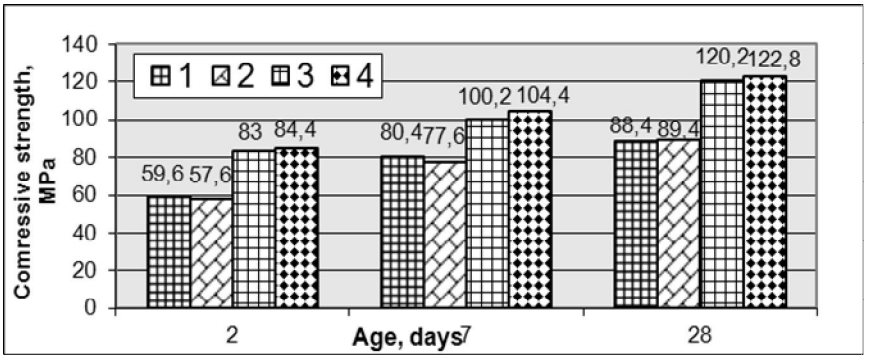


**Fig. 1.** Compressive strength of concretes with additives of MasterGlenium ACE 430 (1.0 wt. %) (1), MasterGlenium ACE 560 (1.0 wt. %) (2), MasterGlenium ACE 430 (2.0 wt. %) (3), MasterGlenium ACE 560 (2.0 wt. %) (4)

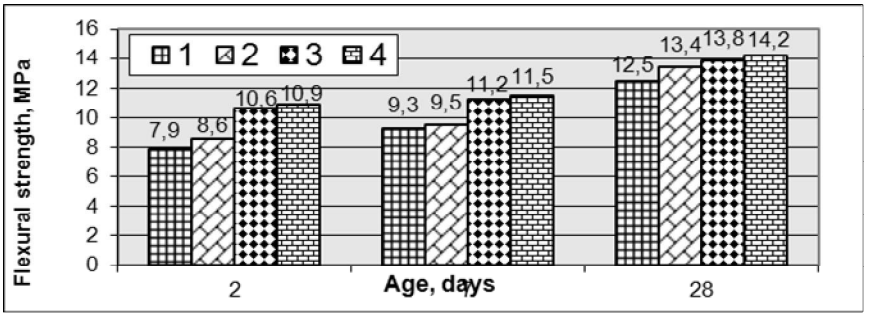


**Fig. 2.** Flexural strength of concretes with additives of MasterGlenium ACE 430 (1.0 wt. %) (1), MasterGlenium ACE 560 (1.0 wt. %) (2), MasterGlenium ACE 430 (2.0 wt. %) (3), MasterGlenium ACE 560 (2.0 wt. %) (4)

One of the main factors for obtaining high-strength concrete capable of providing both mechanical properties and structural durability is a low (within 0.20–0.25) *W/C* ratio. In this case, polycarboxylate-type superplasticizers, characterized by a water-reducing effect of 30–40 %, can be particularly effective. To study the water-reducing effect of the polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560, a control concrete composition without polycarboxylate-type superplasticizers was prepared based on the standard composition. A comparison of the properties of the control composition and the concrete compositions containing the polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560 in an amount of 2.0 mass % of the cement mass at a *W/C* ratio of 0.25 was conducted. Based on the test results, it can be concluded that the polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560 exhibit water-reducing effects of 33.3 % and 39.0 %, respectively.

Polycarboxylate superplasticizers can significantly improve the fresh mix workability and the strength of hardened concrete at low *W/C* ratios[17]. The W/C ratio is one of the main parameters for the preparation of concrete, which can significantly affect its workability, mechanical properties, and durability. Thanks to polycarboxylate-type superplasticizers, it is now possible to produce high-performance or ultra-high-performance concrete(UHPC) with a low *W/C* ratio and high superplasticizer dosage[18]. In dense mixtures with a low *W/C* ratio, most of the water is bound to the surface of cement particles and newly formed compounds. As a result, the release of water only slightly increases the volume of the dispersion medium. Consequently, the adhesion forces between the particles are not fully neutralized, and no significant thinning effect occurs. The plasticizing effect of concrete mixtures increases with increasing mobility and with increasing dosage of superplasticizer[19]. For concrete of this composition, which was prepared from a concrete mixture with a reduced *W/C* ratio ($W/C = 0.25$) and an increased content of superplasticizing additives, the value of compressive strength with the addition of MasterGlenium ACE 430 (2.0 wt. %) at an early age is 83.0 MPa, and after 28 days of hardening 120.2MPa, and for concrete with MasterGlenium ACE 560 (2.0 wt. %) additive – $fcs2 = 84.4$ MPa and $fcs28 = 122.8$ MPa, respectively (Fig. 1). The flexural tensile strength of concrete for this

composition with the addition of MasterGlenium ACE 430 (2.0 wt.%) at the early age of hardening is $f_{fs}2 = 10.66$ MPa, at the age of 28 days діб – $f_{fs}28 = 13.8$ MPa, and for concrete with the addition of MasterGlenium ACE 560 (2.0 wt. %) – $f_{fs}2 = 10.9$ MPa and $f_{fs}28 = 14.2$ MPa, respectively (Fig. 2). The workability of the concrete mixture's with the addition of MasterGlenium ACE 430 (2.0 wt. %) is characterized by concrete slump test of 200.0 mm, and with the addition of MasterGlenium ACE 560 (2.0 wt. %) – 210.0 mm.

Water absorption of concrete samples by mass after 28 days of hardening under standard conditions with the addition of MasterGlenium ACE 430 (2.0 wt. %) is 1.27 %, and for concrete with the addition of MasterGlenium ACE 560 (2.0 wt. %) is 1.15 %.

As can be seen from Fig. 1, modified concrete with the addition of polycarboxylate-type superplasticizer MasterGlenium ACE 560 in the amount of 2.0 mass % of the cement mass is characterized by increased mechanical properties at an early age – after 2 days of hardening, the compressive strength reaches $fcs2 = 84.4$ MPa. After 28 days of hardening, the strength of concrete modified with polycarboxylate superplasticizers increases by 1.4 times and is 122.8 MPa, and the tensile strength during bending is $f_{fs}28 = 14.2$ MPa. Reducing the water consumption during the preparation of the concrete mixture leads to an increase in the strength characteristics of concrete and, in some cases, to the possibility of obtaining high-strength, ultra-high-performance concrete with high physico-technical characteristics.

The most promising direction of technical progress in concrete technology is the favorable structure of cement stone formation, which allows for a significant increase in the stability of concrete and improves the complexity of its physical-technical properties. With the help of poly-carboxylate-type superplasticizers, which significantly affect the physico-chemical processes of the Portland cement hardening process, and, as a result, the tech-nological properties of the concrete mixture and the physical-technical properties of the concrete, this task can be solved successfully.

On the diffractogram of cement stone without additives (Fig. 3) after 7 days of hardening, the lines of calcite ($d/n$ = 0.303; 0.249 nm) and hydrated phases – portlandite ($d/n = 0.490$; 0.263 nm) and ettringite ($d/n = 0.973$; 0.561 nm)[20, 21]. According to the data of X-ray diffractometry (Fig. 4, 5), on the diffractograms of cement stone with the addition of MasterGlenium ACE 430 (2.0 wt. %) and with MasterGlenium ACE 560 (2.0 wt. %) after 7 days of hardening, a decrease in the intensity of the hydrate phases lines is observed – portlandite ($d/n = 0.490$; 0.263 nm) and ettringite ($d/n = 0.973$; 0.561 nm). Diffractograms of cement stone based on CEM I 42.5R with the addition of MasterGlenium ACE 430 (2.0 wt. %) and MasterGlenium ACE 560 (2.0 wt. %) after 7 days of hardening (Fig. 4, 5) are characterized by a decrease in the intensity of calcium hydroxide lines, which is due to the possible binding of polycarboxylate superplasticizer with calcium hydroxide with the formation of poorly soluble compounds. It has been confirmed in many studies that the presence of PCE in the aqueous phase significantly affects the precipitation of hydration products in hydrated cement paste. The deposition processes of ettringite and C-S-H are significantly altered when a large amount of polymers is present in the aqueous phase, probably due to the complexation of the polymers with $Ca^{2+}$. This complexation effect can cause strong adsorption of polymers on the initially formed AFt crystals or C-S-H nuclei, and the adsorbed polymers stabilize the initially formed AFt and C-S-H particles and prevent their further growth[22]. Recent studies have proven that the polymer's adsorption causes inhibition of silicate dissolution by blocking their reactive surfaces[23]. Silicate phases can affect the adsorption of superplasticizers due to the formation of C-S-H phases, which add a significant surface area to the system but cannot promote PCE adsorption due to their negative surface charge[24, 25]. C-S-H is formed as a result of the hydration of tricalcium silicate ($C_3S$) and dicalcium silicate ($C_2S$). C-S-H exhibits a disordered layered structure consisting of linear silicate chains[26].

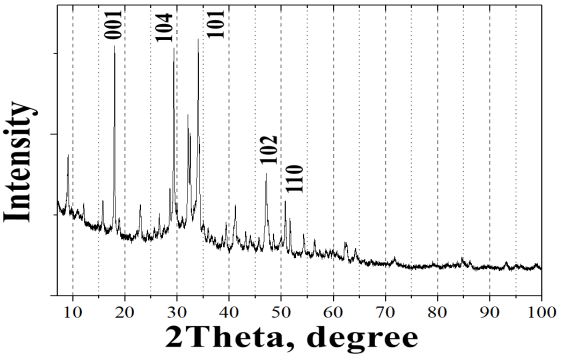


**Fig. 3.** XRD pattern of cementitious matrix after 7 days of hardening

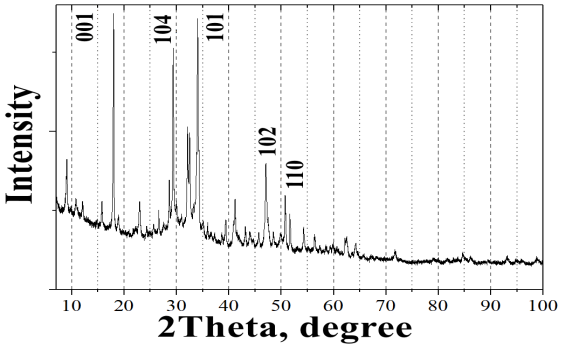


**Fig. 4.** XRD pattern of cementitious matrix with additive of MasterGlenium ACE 430(2.0 mass %) after 7 days of hardening

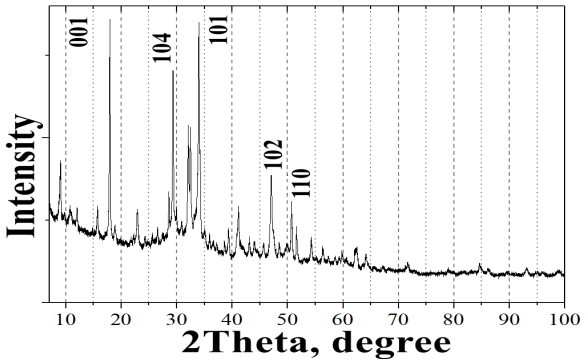


**Fig. 5.** XRD pattern of cementitious matrix with additive of MasterGlenium ACE 560 (2.0 mass %) after 7 days of hardening

In general, the physical-technical properties of concrete are determined by the composition of the solid phase and the volume of pores. The solid phase, in turn, consists of cement stone, which includes hydrated and unhydrated minerals of cement clinker of different morphology and structure, permeated by a system of pores and capillaries, as well as aggregate, the mineralogical composition and surface shape of which determines the strength of the contact zone with cement stone. The introduction of polycarboxylate-type superplasticizers makes it possible to control the kinetics of structure formation of cement dough and concrete mixture in a targeted manner, which, in turn, makes it possible to regulate the main physical-technical parameters of hardened concrete.

As can be seen from the image (Fig. 6, *a*), the concrete matrix without plasticizing additives is characterized by a porous structure with evenly distributed large and small pores. The concrete matrix with additives of polycarboxylate-type superplasticizers MasterGlenium ACE 430 (2.0 wt. %) and MasterGlenium ACE 560 (2.0 wt. %) is characterized by a dense structure without pores and noticeable defects (Figs. 6, *b*, *c*). The PCE addition reduces the formation of large pores in the cement paste, especially in the region around large cement particles, which helps prevent further cracking due to moisture loss[27].

To identify the functional groups of chemical bonds in polycarboxylate-type superplasticizers, FTIR spectra (Figs. 7, 8) were used. As can be seen from the images of the spectrum (Fig. 7, 8), polycarboxylate superplasticizers contain various functional groups 3448 $cm^{-1}$ (O-H; N-H); 2879 $cm^{-1}$ (C–H); 1560 $cm^{-1}$, 1719 $cm^{-1}$ (C=O); 1098 $cm^{-1}$ (C–O–C); 1465 $cm^{-1}$ (-$CH_2$-); 948 $cm^{-1}$ (C–O) and 840 $cm^{-1}$ (C–C). There are two stretching peaks at 2949 $cm^{-1}$ and 1465 $cm^{-1}$, which confirms the existence of -CH and -$CH_2$, respectively[28]. It is noticeable that the peak, which appears at approximately 1144$cm^{-1}$, corresponds to the complex-ethereal group, which is typical for polycarboxylate superplasticizers. Peaks at 1719 $cm^{-1}$ are typical for C=O valence vibrations.

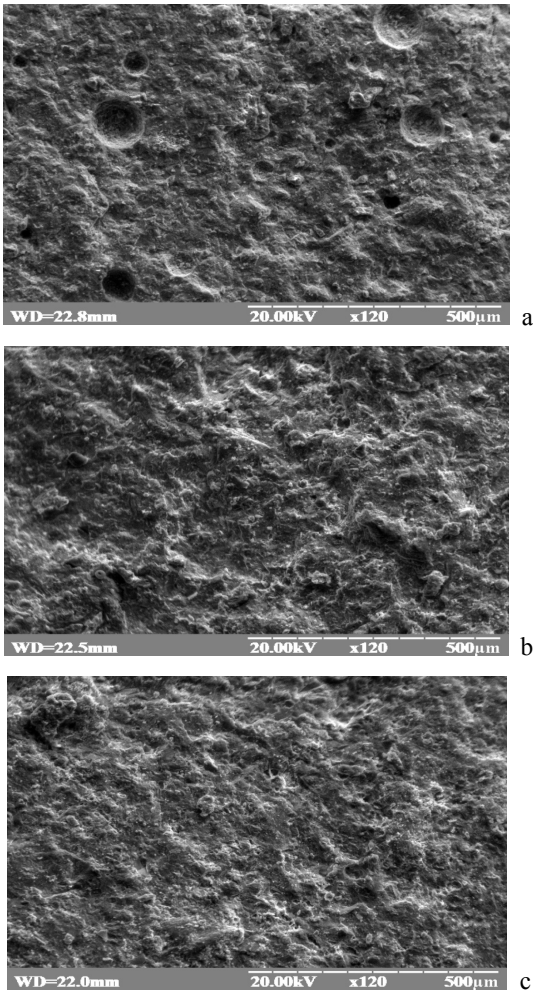


**Fig. 6**. SEM image of control composition concrete matrix after 7 days of hardening (a), matrix with additives of MasterGlenium ACE 430 (2.0 wt. %) (b), with additives of MasterGlenium ACE 560(2.0 wt. %) (c)

Peaks at 1278 and 1098 $cm^{-1}$ correspond to C–O valence vibrations. The peaks at 1059 $cm^{-1}$ are the stretching vibrations of the C–O–C ether group, while the peaks at 1413 $cm^{-1}$ are associated with the O–H deformation vibrations. Considering the absence of the C=C absorption peak at 1620–1680 $cm^{-1}$, this indicates that the monomer was successfully polymerized and PCE was obtained. The peaks at 2949 $cm^{-1}$ and 2879 $cm^{-1}$ are the C–H valence vibration absorption peaks, 2914 $cm^{-1}$ is the $–CH_3$ absorption peak, 2879 $cm^{-1}$ is the –C–H absorption peak in $–CH_2$, and 1719 $cm^{-1}$ and 1098 $cm^{-1}$ can be attributed to the characteristic valence vibration of C=O and the absorption peak of the C–O–C ether bond in the molecular structure[29]. The absorption peaks at 1465 $cm^{-1}$

and 1359 $cm^{-1}$ are associated with bending vibrations of $–CH_2$ near the O atom and vibrations in the plane of $–CH_2$.

The absorption peaks at approximately 1241 $cm^{-1}$ and 1098 $cm^{-1}$ were attributed to CO valence vibrations in the complex-ester group and C–O–C valence vibrations, respectively. The absorption peaks at 949 $cm^{-1}$ and 845 $cm^{-1}$ are associated with vibrations in the $–CH_3$ plane beside the C and the O atoms, respectively. The absorption peak observed at 2877 $cm^{-1}$ is due to the valence vibrations of C–H bonds. The absorption peak at 1719 $cm^{-1}$ is a symmetrical stretching absorption peak of the C=O bond in the COOH carboxyl group. The characteristic absorption peaks of CO in the complex-ester group are approximately at 1719 $cm^{-1}$ and 1241 $cm^{-1}$, and the characteristic absorption peaks of C–O–C of long-chain poly(ethylene oxide) are approximately at 1098 $cm^{-1}$ in the PCE spectra (Figs. 7, 8), which indicates the formation of a PCE comb copolymer. The absorption peak at 1359 $cm^{-1}$ is a characteristic absorption peak of the side chain of polyethylene glycol $(CH_2CH_2O)n$. The most intense absorption peak at 1098 $cm^{-1}$ is caused by the asymmetric stretching vibration of the C–O–C ether bond. As can be observed from the infrared spectrum, all polymers had carboxyl and polyethylene glycol groups, so it can be concluded that the samples were binary copolymers of acrylic acid and PEG monomer[30].

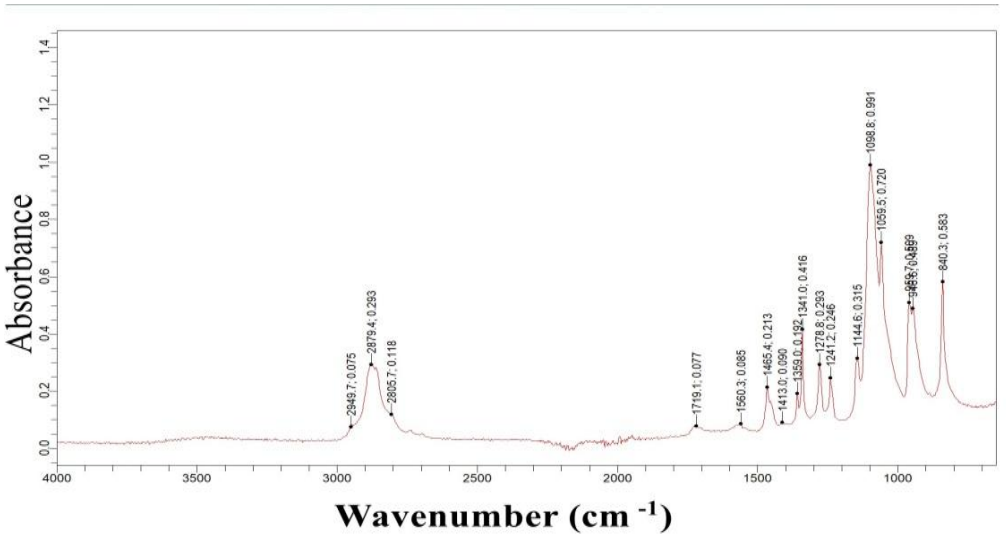


**Fig. 7.** FTIR spectra for superplasticizer MasterGlenium ACE 430

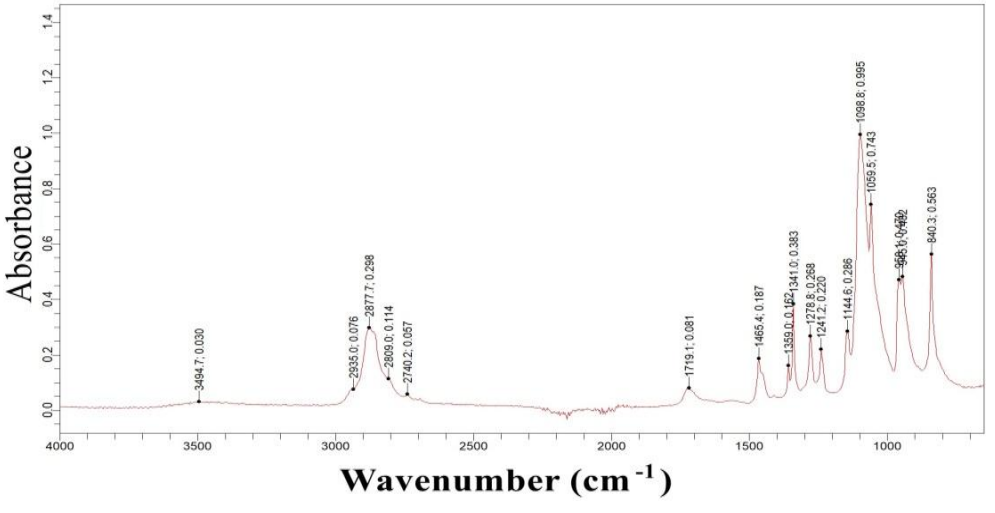


**Fig. 8.** FTIR spectra for superplasticizer MasterGlenium ACE 560

The infrared spectra of the starting materials, such as MasterGlenium ACE 430 and MasterGlenium ACE 560, confirm the structure of polycarboxylate superplasticizers. The authors aimed to identify possible differences in the structure of these superplasticizers using infrared spectroscopy and the possible difference in their

influence on the physico-technical properties of fine-grained concrete. As seen from the infrared spectroscopy data (Figs. 7, 8), differences in the spectral characteristics of the polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560 can be observed based on the presence or absence of absorption bands at frequencies 3494 $cm^{-1}$, 2740 $cm^{-1}$, and 1560 $cm^{-1}$, respectively. The differences in the spectral characteristics of polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560 are confirmed by variations in the results of the physical and mechanical property tests of concretes containing these superplasticizing additives in amounts of 1.0 and 2.0 wt. % of the cement mass (Figs. 1 and 2) and by the water absorption values of the concrete samples after 28 days of curing.

The study of the spectral characteristics of cement stone with and without additives in the hydration interval of 1–7 days was carried out using the FTIR spectrum. The spectra of hydrated cement (Figs. 9–11) show peaks at 946 $cm^{-1}$ and 969 $cm^{-1}$, that correspond to asymmetric vibrations of stretching the Si–O bond along the line connecting the oxygen atom of the $[SiO_4]$-tetrahedron with the central Si atom, and indicates limited polymerization into the C-S-H phase with asymmetric stretching at a lower degree of polymerization at 970 $cm^{-1}$. Such phases are at the formation stage of nanostructured level nuclei, since PCE molecules, due to the phenomenon of adsorption modification, prevent their recrystallization processes[31]. It is widely known that the calcium silicate hydrate (C-S-H) phase is stronger and more stable than portlandite or hydrated calcium aluminate due to their lamellar structure. In all three spectra, there are weak bands at 1109 $cm^{-1}$, which correspond to $(SO_4)^{2-}$ groups vibration in sulfates within 1100–1165 $cm^{-1}$ range. Peaks observed at 1082 $cm^{-1}$, 1101 $cm^{-1}$, 1109 $cm^{-1}$ and 1121 $cm^{-1}$ are characteristic of ettringite, indicating its early formation. The peaks of the water band located at 1630 $cm^{-1}$ indicate the H–O–H vibrations of the adsorbed water molecule. Several additional weaker bands between 3000 and 2000 $cm^{-1}$ are overtone modes. In addition, the peaks at 3392 $cm^{-1}$, which fall into the range of 3100–3400 $cm^{-1}$, correspond to valence vibrations of O–H in water molecules. The asymmetric valence vibration of the $C–O(CO_3)^{2-}$bond belongs to the wave range 1420–1427$cm^{-1}$ [32].The oscillations observed at 872 and 713 $cm^{-1}$ are the primary bands of calcite. The presence of these absorption bands confirms the calcite phase ($CaCO_3$) formation[33].

According to spectral data, during cement hydration with polycarboxylate-type superplasticizer additives, adsorption shells form on the surface of clinker grains and their hydration products. With the introduction of the superplasticizer additive, the hydration, as well as cement structure formation, slow down a little due to adsorption layer formation on the surface of hydrating cement particles.

This process is characteristic of the initial stage of cement hydration. At the subsequent stages of cement hydration, superplasticizing additives function according to the well-known mechanism described above. The impossibility of significantly slowing down hydration processes in the presence of MasterGlenium ACE 430 and MasterGlenium ACE 560 polycarboxylate superplasticizers is evidenced by the obtained data on the physical-mechanical characteristics of concrete after 2, 7, and 28 days of hardening, namely the strength values of concrete samples containing these superplasticizing additives in amounts of 1.0 and 2.0 mass % of the cement mass, respectively (Fig. 1 and Fig. 2).

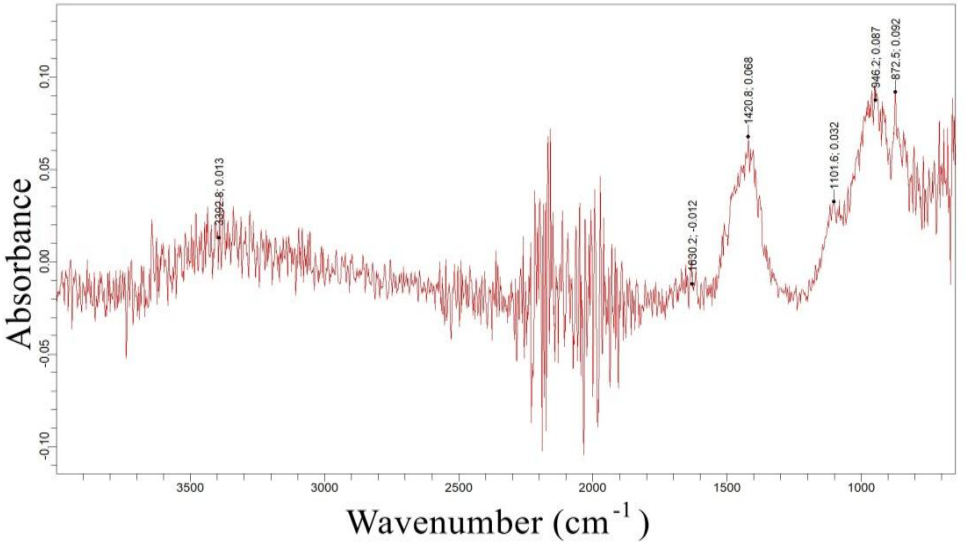


**Fig. 9.** FTIR spectra for cementitious matrix after 7 days of hardening

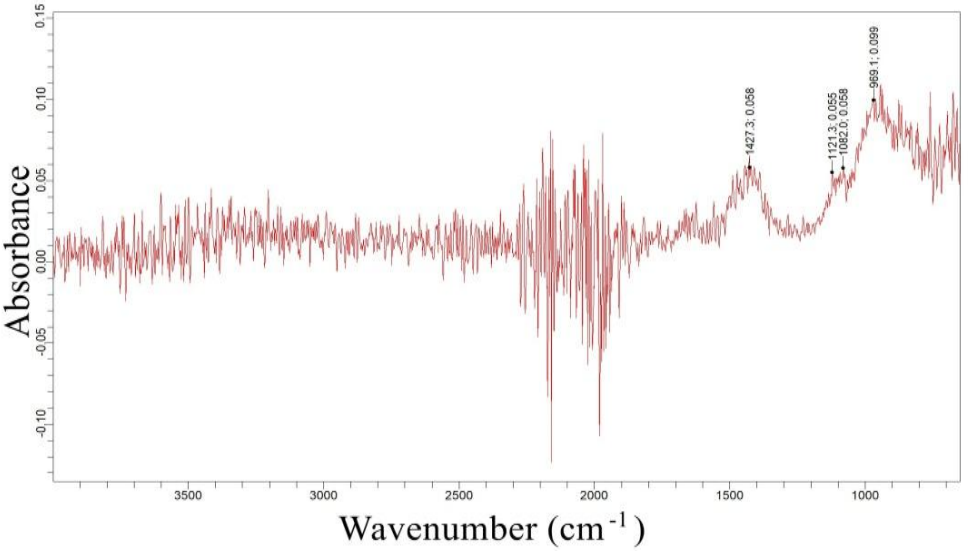


**Fig. 10.** FTIR spectra for cementitious matrix with additives of MasterGlenium ACE 430 after 7 days of hardening

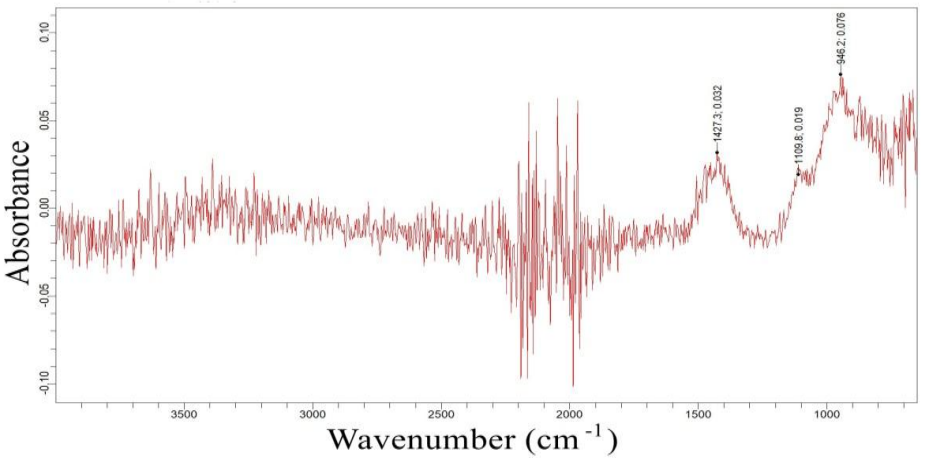


**Fig. 11.** FTIR spectra for cementitious matrix with additives of MasterGlenium ACE 560 after 7 days of hardening

Using cementing systems modified with polycarboxylate superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560, we can produce high-quality ultra-high-strength concretes. These concretes exhibit enhanced construction and technical properties, making them suitable for creating highly functional cement composites with improved physical and mechanical characteristics[34–38].

High-strength stone deposits are virtually absent across a significant part of Ukraine. Therefore, the implementation of structures and products made from fine-grained concrete can be considered appropriate for approximately 50 % of its territory. Fine-grained concrete is hardly used for manufacturing a wide range of concrete and reinforced concrete structures and products. Primarily, the application of fine-grained concrete should be expanded to prefabricated and monolithic foundations, foundation slabs, concrete wall blocks (including basement walls), ventilation blocks, sanitary cabins, balcony slabs, floor and roof slabs with spans up to 6 meters, non-pressure pipes, trays, monolithic road pavements, hydraulic engineering structures, paving slabs, and curbstones.

## 4. Conclusions

The relationship between the hydration processes and structuring of cement systems and the composition and structure of introduced polycarboxylate superplasticizers, MasterGlenium ACE 430 and MasterGlenium ACE 560, was established, which made it possible to reveal the patterns of directed regulation of the technological properties of the concrete mixture and the physical-technical properties of concrete.

During the use of polycarboxylate-type superplasticizers MasterGlenium ACE 430 and MasterGlenium ACE 560, to reduce the water consumption of concrete mixtures and the *W/C* ratio, an increase in the compressive strength of hardened concrete was observed, which is the result of compaction of the structure. The increase in compressive strength reaches its highest value at the age of 2–7 days, and by the 28th day of hardening, reaches values of 120.2 and 122.8 MPa. The tensile strength of concrete during bending for this composition with the addition of MasterGlenium ACE 430 (2 wt. %) at the early age of hardening is 10.66MPa, and at the age of 28 days – 13.8 MPa, and for concrete with the addition of MasterGlenium ACE 560 (2.0 wt. %) – 10.9 MPa and 14.2 MPa, respectively. The compressive strength of concrete increases with increasing dosage of superplasticizers and decreasing *W/C* ratio.

Based on cementing systems modified with polycarboxylate-type superplasticizers, high-quality high-strength concretes are created, which are characterized by improved construction-technical properties. Water absorption of concrete samples by mass after 28 days of hardening under normal conditions with the addition of MasterGlenium ACE 430 (2.0 wt. %) is 1.27 %, and for concrete with the addition of MasterGlenium ACE 560 (2.0 wt. %) – 1.15 %.

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## ДОСЛІДЖЕННЯ ВПЛИВУ СУПЕРПЛАСТИФІКАТОРІВ ПОЛІКАРБОКСИЛАТНОГО ТИПУ MasterGlenium ACE 430 ТА MasterGlenium ACE 560 НА ФІЗИКО-ТЕХНІЧНІ ВЛАСТИВОСТІ ДРІБНОЗЕРНИСТОГО БЕТОНУ

***Анотація.*** *Досліджено вплив суперпластифікаторів полікарбоксилатного типу MasterGlenium ACE 430 та MasterGlenium ACE 560 на фізико-технічні властивості дрібнозернистого бетону. Запропоновано концепцію створення високоміцних бетонів на основі модифікованих цементуючих систем, які характеризуються покращеними будівельно-технічними властивостями та належать до класу високоефективних бетонів. Під час застосування суперпластифікаторів полікарбоксилатного типу MasterGlenium ACE 430 та MasterGlenium ACE 560 для зменшення водопотреби бетонних сумішей та водоцементного відношення (В/Ц) спостерігалося підвищення міцності бетону, що затвердів, на стискання, що є результатом ущільнення структури.*

***Ключові слова:*** *цементна система, полікарбоксилатний суперпластифікатор, дрібнозернистий бетон, водоцементне відношення, міцність.*