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THE INFLUENCE OF MINERAL ADDITIVES ON THE PROPERTIES OF ULTRA-HIGH STRENGTH CONCRETE

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Abstract. The article presents the results of a study of the influence of highly active mineral additives on the physical and mechanical properties of ultra-high strength concrete. Currently, according to the classical concept of making ultra-high strength concrete, a significant amount of ultradispersed microsilica is introduced, which determines the increased cost of its preparation. In order to obtain cost-effective ultra-high-strength concrete, the composition of mixtures was evaluated according to the criteria of strength and economy by replacing microsilica with technologically optimized highly dispersed zeolite (SSA=1200 m^2/kg), which belongs to the class of superzeolite. It is shown that for modified concrete with the addition of microsilica, the compressive strength after 2 days is 88.8 MPa, after 28 days – 161.0 MPa. When microsilica is partially replaced by superzeolite, sufficiently high mechanical parameters are achieved: after 2 days the compressive strength is 75.8 MPa, after 28 days the strength increases by 2.1 times and is 163.2 MPa, in this case a flexural strength of 12.1 MPa is achieved. The microsilica has a positive effect due to increased reactivity, especially at an early age. Similarly, the fine fraction of superzeolite is characterized by the acceleration of the pozzolanic reaction, while the coarser fraction contributes to increasing the degree of hydration of the Portland cement due to the desorption of water molecules from micropores and provides internal care for concrete. The cementitious matrix is compacted by filling the intergranular space due to the formation of nanodispersed C-S-H phases. Thermal analysis showed that the amount of calcium hydroxide in the superzeolite cementitious system is 2.75% or 66 kg/m^3, which meets the requirements for ultra-high strength concrete. The synergistic combination of microsilica and superzeolite with high surface activity and polycarboxylate superplasticizer provides high packing density and the necessary strength characteristics of ultra-high strength concretes, as well as contributes to their cost-efficiency, which opens the prerequisites for a large-scale engineering application of such concrete in construction.

Keywords: ultra-high strength concrete, microsilica, superzeolite, polycarboxylate superplasticizer, strength, structure formation, cost-effective design.

Introduction. One of the most important directions in construction is the development of construction materials of a new generation, in particular, ultra-high strength concretes, which are characterized by improved construction and technical properties and belong to the class of ultra-high performance concretes. Such concretes are attracting increasing interest worldwide due to high mechanical properties and durability [1, 2]. Currently, ultra-high strength concrete is mainly used for the construction of high-rise buildings, bridges, tunnels and other structures that require high bearing capacity and durability. At the same time, ultra-high strength concretes have problems that require attention and solutions, in particular, such as fragility, significant heat generation, low crack resistance, high cost, etc.

Analysis of recent research and publications. Ultra-high strength concretes (UHSC) belong to a special class of cementitious materials, which are formed with an optimized gradation of granular components, a low water-to-binder ratio (W/C = 0.20...0.25), and the addition of mineral and chemical additives [3, 4]. As a result, ultra-high strength concrete has a compressive strength that is approximately 3-5 times higher than traditional concrete. The resulting material is characterized by increased workability (slump flow ≥ 200 mm), high mechanical parameters (after 28 days, compressive strength ≥ 150 MPa, tensile strength ≥ 7 MPa, modulus of elasticity 40...60 GPa) [5, 6]. These characteristics of UHSC are mainly based on the high packing density, which is achieved by calculating the amount of fine particles such as cement, microsilica and quartz sand. Due to the increased specific surface of small particles and low water content, the use of significant amounts of superplasticizers is necessary. Ultra-high strength concrete is obtained by modification with surface-active substances and highly dispersed active mineral additives. However, the high preparation cost of ultra-high strength concrete limits its large-scale engineering application [7, 8].

Improving the packing density of cementitious materials by mixing with ultrafine supplementary cementitious materials plays an important role in increasing the physical and mechanical properties of concrete caused by minimizing the void content in the cementitious matrix. Ultrafine particles of active mineral additives are characterized by high values of the interphase zone and surface energy, and also provide a more complete synergistic effect of other components, forming a rheological matrix of the concrete mixture with a minimum water content. That in turn contributes to the directed formation of the microstructure of the cementitious matrix and thanks to its compaction and pozzolanic reactions in the non-clinker part [9]. Therefore, very high packing density is the main attribute in achieving low porosity of cementitious matrix, which leads to significant durability of ultra-high strength concrete compared to conventional concrete [10].

The excellent characteristics of ultra-high strength concrete, such as durability and high mechanical parameters, largely depend on the physical properties and kinds of highly active mineral additives used. One of the commonly used amorphous silicon dioxides is microsilica, a by-product of industrial silicon production with a particle size in the submicrometer range. Microsilica in the early period of hydration plays an important role not only as a microfiller, but also as a superpozzolana. At the same time, the high content of microsilica in the composition of ultra-high strength concretes can lead to an increase in the viscosity of the mixture and agglomeration, which leads to a decrease in the mechanical properties of concrete. On the other hand, the size of amorphous SiO_2 particles in submicrometers is effective for filling the voids present among the particles of cement and other constituent materials, that is, it manifests itself as a microfiller effect [11].

Large reserves of natural pozzolana – zeolite tuffs – are concentrated in Europe. At the same time, zeolites increase the water consumption of cement, which slows down the development of their strength [12]. On the other hand, the use of "super zeolite", which is a natural zeolite crushed to a smaller size than cement, opens up significant prospects. Such a "superpozzolana" provides an increase in the density of laying cement mortar with the same ease of workability [13]. It should be noted that in ultra-high strength concrete, which is developed with a low water-to-binder ratio, the hydration of the cement grains can potentially be limited. To solve the problems related to hydration, the possibility of using superzeolite, which has a high porous structure, should be investigated to ensure the internal care of the cementitious system with the age of hardening [14].

In this regard, it is advisable to conduct research on the replacement of microsilica or its part in the composition of the mixture for ultra-high strength concrete with addition of superzeolite, which will contribute to the improvement of the entire hydration process due to its high pozzolanic activity and ability to internal care with the age of concrete hardening. Modification of cementing systems with an organic component makes it possible, by changing the nature of their surface within wide limits, to activate the processes of structure formation of the cementitious matrix and to improve its microstructure. The improvement of the modern concept of creating ultra-high strength concrete is achieved by using highly effective modifiers and introducing highly dispersed active mineral additive such as superzeolite.

The purpose and tasks of the work – research of the influence of highly active mineral additives of microsilica and superzeolite on the processes of structure formation of the cementitious matrix and mechanical properties of modified fine-grained ultra-high strength concretes.

Research materials and methods. Production of high-quality concrete mixtures is ensured by Portland cement CEM I 42.5 R PJSC "Ivano-Frankivskcement", which meets European standards and is made on the basis of Portland cement clinker with a standardized mineralogical composition.

For designing the grain composition of ultra-high performance concrete, fine sand from the Davydivsky deposit (Lviv region, average density ρ_a=1370 kg/m^3, fineness modulus FM=1.16) and sand from the Slavuta deposit (Khmelnytsky region, ρ_a=1502 kg/m^3, FM=2.0) were used.

Highly active microsilica Elkem Microsilica Grade 940-U (SiO_2 content – 92.3 mass.%, SSA = 16 m^2/g) was used as an artificial mineral additive. As a component of pozzolanic action, zeolite tuff from the Sokyrnytskyi deposit (Transcarpathian region) was used, the main mineral of which is clinoptilolite $(Na, K)_4CaAl_6Si_{30}O_{72}\cdot 24H_2O$. Technologically optimized highly dispersed zeolite (SSA =1200 m^2/kg) belongs to the class of superzeolite, which allows to increase the packing density and improve the cohesion of cement paste. Characteristically, the cost of superzeolite is an order of magnitude lower compared to microsilica, which creates broad prospects for its mass use in concrete technology.

Particle size distribution of samples of finely dispersed active mineral additives was determined using a Malvern Mastersizer 3000 laser granulometer in the range from 0.01 to 3000 μm [15]. For Portland cement CEM I 42.5 R (SSA=350 m^2/kg), particles smaller than 1.0 and 5.0 μm make up 3.90 and 18.92%, respectively. Superzeolite has a bimodal distribution of particles by volume, while the amount of fine fraction up to 5.0 μm is 38 vol. %. This fraction makes the main contribution to the specific surface of superzeolite. Average diameters by specific surface area D[3;2] and volume D[4;3] for portland cement, microsilica, and superzeolite are 5.21 and 24.8 μm, respectively; 0.40 and 10.0 μm; 3.81 and 19.6 μm. The increased content of highly dispersed particles in the range of up to 1.0 μm is characteristic of microsilica determines its significant specific surface and high excess surface energy. An increase in the surface activity of small fractions and the packing density of large grains creates the possibility of increasing the early strength of multicomponent cementing systems.

Highly effective superplasticizers based on polycarboxylate ethers with nanosized molecular chains were used as modifiers to increase strength due to a significant water-reducing effect. The special molecular configuration of Master Glenium ACE 430 from the BASF company promotes the acceleration of cement hydration.

X-ray phase analysis of concrete samples after 28 days of hardening was performed using an Aeris Research Benchtop X-Ray Diffractometer from Malvern Panalytical.

Thermal analysis of the samples was carried out on a derivatograph Q-1500 of the Paulik-Paulik-Erdey system in the temperature range of 20-1000°C. The samples were analyzed in dynamic mode with a heating rate of 10 ^oC/min in an air atmosphere. The weight of the sample was 500 mg.

Research results. Research on the mechanical properties of concrete was carried out on the optimized composition of the mixture of components. As a rule, granite aggregate has various defects and microcracks that limit the strength of concrete. Therefore, in the mixture coarse aggregate was replaced by finer aggregate, which has better mechanical properties. Flexural strength was evaluated on 40×40×160 mm prisms, and compressive strength on halves of these prisms in accordance with EN 1015-11. Workability was tested in accordance with EN 1015-3. The composition of the concrete mixture was characterized by the quantitative content of components with a consumption of materials per 1 m^3: C = 800 kg, A = 1165 kg (sand with FM=2.0 – 1000 kg + sand with FM=1.16 – 165 kg), active mineral additives – 200 kg, superplasticizer Master Glenium ACE 430 (2.5%) – 20 kg, water 195...205 kg (W/C=0.25). A high-speed mixer was used for the production of ultra-high strength concrete, while the movement time was optimized to achieve homogeneity and quality of the mixture and was 8-10 minutes. The mobility of the mixture was characterized by the spreading of 300 mm cone. In order to improve the quality indicators of ultra-high strength concrete, the compositions were adjusted by replacing microsilica with the addition of superzeolite by 50% and 100%, respectively.

Tests were carried out for concrete through 2; 7 and 28 days of hardening.

As can be seen from Fig. 1, for concrete with additive of microsilica the compressive strength at an early age is R_{c2} = 88.8 MPa, after 28 days –161.0 MPa and the flexural strength – 12.1 MPa. For concrete with the addition of superzeolite, the compressive strength after 2 days – 57.6 MPa, after 28 days – 163.2 MPa. With the introduction of active mineral additives in the amount of 100 kg of microsilica and 100 kg of superzeolite, slightly higher strength indicators are achieved in the early stages of hardening compared to concrete with superzeolite additive; in this case the flexural strength – 12.3 MPa.

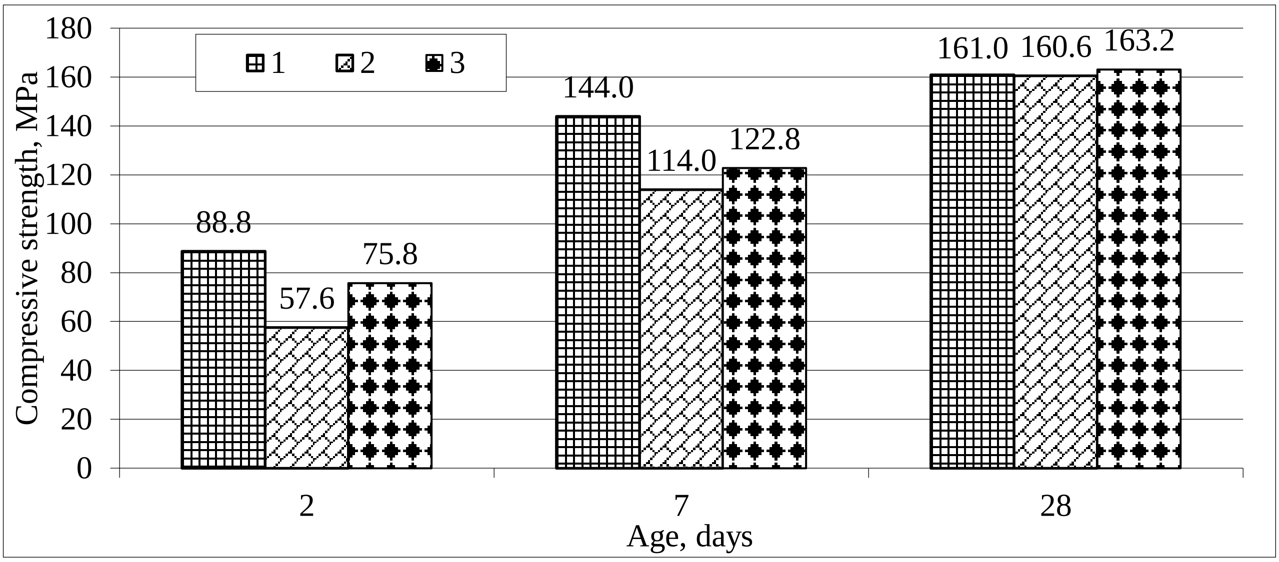


Fig. 1. Compressive strength of concretes with additives of microsilica (1), superzeolite (2) and microsilica + superzeolite in a ratio of 1:1 (3) dditives of microsilica (1), superzeolite (2) and microsilica + superzeolite in a ratio of 1:1 (3)

According to the X-ray analysis data the diffraction patterns of the cementitious matrix with the addition of microsilica show lines of calcite (d/n=0.303; 0.249 nm) and hydrated phase – calcium hydroxide (d/n=0.490; 0.263 nm). The introduction of microsilica with increased reactivity contributes to the acceleration of the pozzolanic reaction with the additional formation of C-S-H gel clusters. After 28 days of hardening of concrete with addition of superzeolite a decrease in the intensity of calcium hydroxide lines is observed (Fig. 2); at the same time, intense lines of quartz appear (d/n=0.334, 0.244, 0.223; 0.212; 0.181 nm) and line of calcite are fixed.

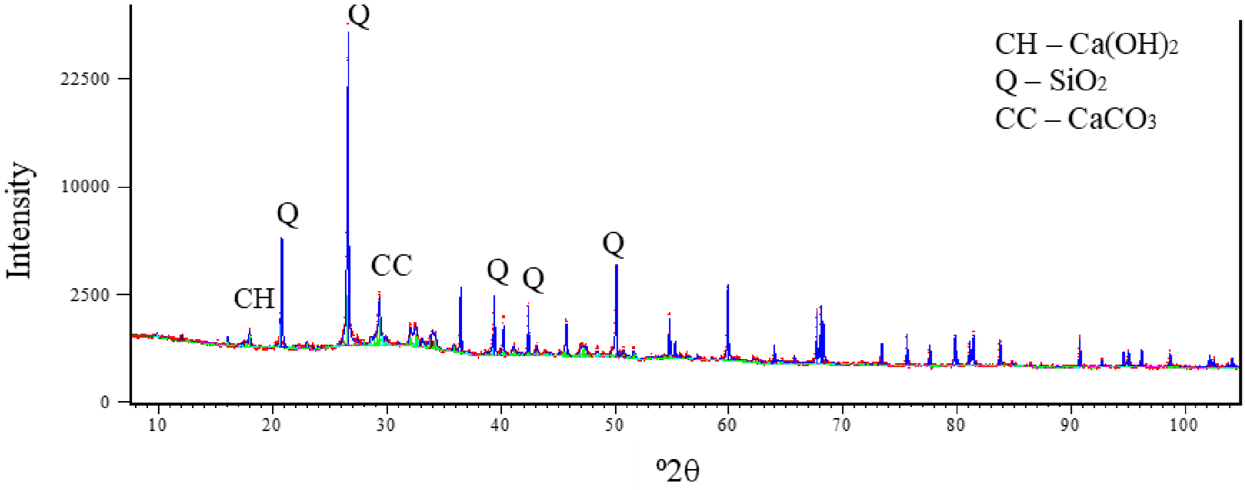
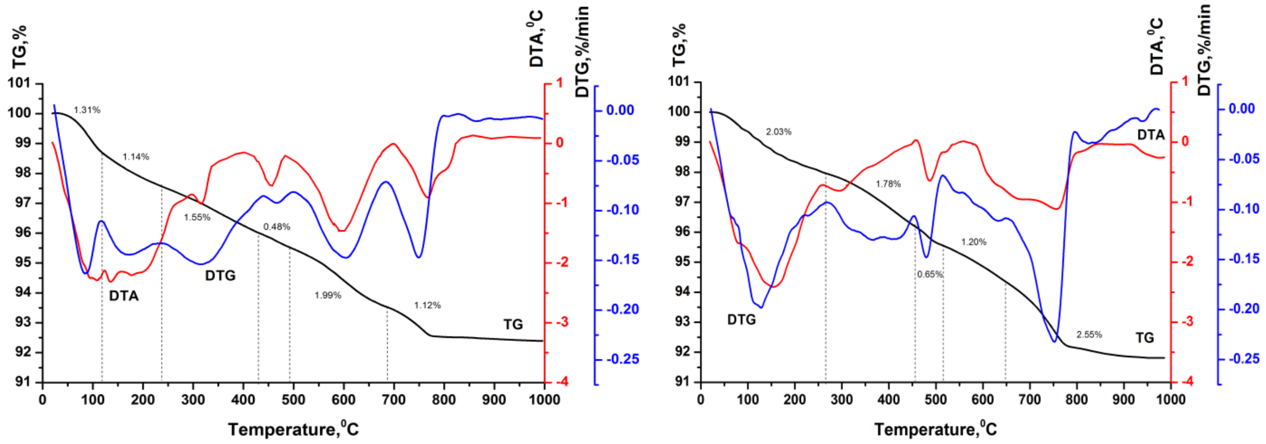


Fig. 2. Diffractogram of cementitious matrix with superzeolite additives after 28 days of hardening

As can be seen from the thermogravimetric analysis data (Fig. 3), the amount of calcium hydroxide in the cementitious matrix with microsilica does not exceed 1.5%, while the amount of $Ca(OH)_2$ in the composite with the addition of superzeolite is 2.75% or 66 kg/m^3, which meets the requirements for ultra-high performance concrete. In this case, the amount of bound water in fine-grained concrete with the addition of superzeolite (4.66 mass. %) is slightly higher than with the addition of microsilica (4.48 mass.%). As a result of the pozzolanic reaction of superzeolite, the cementitious matrix is compacted by filling the intergranular space.



a) b)

Fig. 3. Thermograms of concrete with the addition of microsilica (a) and superzeolite (b) after 28 days of hardening

The results show that microsilica has a positive effect, mainly due to increased reactivity, especially at an early age. The fine fraction of superzeolite is characterized by the acceleration of the pozzolanic reaction, and the coarser fraction helps to increase the degree of hydration of the cementing system due to the desorption of water molecules from micropores, which provides internal care for concrete. The combination of microsilica and superzeolite with a polycarboxylate superplasticizer to a greater extent ensures the maximum density of the cementitious matrix and strength properties of ultra-high-strengh concretes, and also contributes to their cost-effectiveness.

Conclusions:

1. Cost-effective ultra-high strength concrete is developed using a multi-level particle packing approach to maximize the density of mixture of multi-fraction fine aggregates and polymineral cementing systems. It was established that modified concrete with additives of microsilica and superzeolite is characterized by increased mechanical properties: at an early age the compressive strength is R_{c2} = 75.8 MPa, and after 28 days increases by 2.1 times and is 163.2 MPa, while the flexural strength R_{f28} =12.3 MPa is achieved.

2. It is shown that superzeolite allows to reduce bleeding, sedimentation, increase the water-holding capacity of the mixture, as well as to provide internal care, as a result of which the strength of concrete increases with the age of hardening. The amount of calcium hydroxide in the cementitious matrix with the addition of superzeolite is 2.75% or 66 kg/m^3, which meets the requirements for ultra-high strength concrete. The replacement of microsilica with superzeolite provides a reduction in the production cost of ultra-high-strength concrete, which largely determines the practical feasibility of its large-scale engineering application in construction.

Prospects for further research. To increase the efficiency and durability of ultra-high strength concrete, it is advisable to continue research in the direction of developing compositions with additives of nanosilica and various types of reinforcing fiber materials.

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ВПЛИВ АКТИВНИХ МІНЕРАЛЬНИХ ДОБАВОК НА ВЛАСТИВОСТІ НАДВИСОКОМІЦНОГО БЕТОНУ

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Анотація. У статті наведено результати дослідження впливу високоактивних мінеральних добавок на фізико-механічні властивості надвисокоміцних бетонів. На даний час, згідно з класичною концепцією виготовлення надвисокоміцного бетону, вводиться значна кількість ультрадисперсного мікрокремнезему, що зумовлює підвищену вартість його приготування. Для отримання рентабельних надвисокоміцних бетонів проведено оцінку складу сумішей за критеріями міцності та економічності шляхом заміни мікрокремнезему на технологічно оптимізований високодисперсний цеоліт (SSA=1200 м2/кг), який належить до клас суперцеоліту. Показано, що для модифікованого бетону з додаванням мікрокремнезему міцність на стиск через 2 доби становить 88,8 МПа, через 28 діб - 161,0 МПа. Встановлено, що при частковій заміні мікрокремнезему суперцеолітом досягаються достатньо високі механічні показники: через 2 доби міцність при стиску становить 75,8 МПа, через 28 діб міцність зростає в 2,1 рази і складає 163,2 МПа, при цьому досягається міцність на вигин 12,1 МПа. Мікрокремнезем вносить позитивний ефект завдяки підвищеній реакційній здатності, особливо в ранньому віці. Аналогічно дрібна фракція суперцеоліту характеризується прискоренням реакції пуцоланізації, тоді як грубша фракція сприяє підвищенню ступеня гідратації цементної системи за рахунок десорбції молекул води з мікропор, тобто забезпечує внутрішній догляд за бетоном. В результаті пуцоланової реакції мікрокремнезему та суперцеоліту відбувається ущільнення цементуючої матриці шляхом заповнення міжзернового простору за рахунок утворення нанодисперсних C-S-H фаз. Термічний аналіз свідчить, що кількість кальцію гідроксиду в цементуючій системі з суперцеолітом становить 2,75% або 66 кг/м^3, що відповідає вимогам для надвисокогоміцного бетону. Представлені результати свідчать про те, що синергетичне поєднання мікрокремнезему та суперцеоліту з високою поверхневою активністю та полікарбоксилатного суперпластифікатора забезпечує підвищену щільність упаковки зерен цементуючої матриці, необхідні міцнісні характеристики надвисокоміцного бетону, а також сприяє зниженню вартості його приготування, що відкриває передумови для більш широкомасштабного застосування такого бетону в будівництві.

Ключові слова: бетон надвисокої міцності, мікрокремнезем, суперцеоліт, полікарбоксилатний суперпластифікатор, міцність, структуроутворення, економічне проектування.

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