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The role of the crystallo-chemical factor in the evaluation and improvement of the nanomodification efficiency of mortar and concrete

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Abstract. The article presents a new approach to the control of the processes of structure formation of binder systems, taking into account the achievements of nanotechnologies. The possibilities of managing the structure of the material at the nanoscale and the micro-level by introducing primary nanoscale additives or forming nanoscale objects in the bulk of the material are considered. The peculiarities of contact zone formation and microstructure of artificial stone based on nanomodified Portland cement and alkaline binder systems are investigated. The role of the crystallo-chemical factor and its influence on the strength formation of all levels of concrete structure are shown. It is proved that when using micro silica modifying additives, their efficiency at the micro level is higher than at the meso- and macro-levels. At the same time, the modification of the binding systems by artificial zeolites provides a more pronounced effect in concrete at the macro-level – due to the crystallo-chemical similarity of additives, products of hydration and minerals of the aggregate. Taking into account the crystal-chemical similarity of the new formation opens new possibilities for the choice of nano additives, considering not only the principle and nature of their action at the level of nanoscale and microstructure, but also the influence on the peculiarities of the formation of the contact zone at the meso- and macro-levels, which will have a decisive influence not only on the strength, but also on the special properties of concrete.

1. Introduction

The introduction of a nanotechnological concept is a fundamentally new approach to managing the processes of structure formation of binder systems in the direction of solving the problems of synthesis and formation of the specified performance characteristics of concrete and mortar. It should be understood as the application of techniques for managing the structure of a material at the ultramicroscale level of solid phase and pore space construction by introducing primary nanoscale additives or forming nanoscale objects in the bulk of the material [1-7].

Obtaining fast-hardening Portland cement by top-down nanotechnology is achieved by grinding Portland cement in the presence of a polymer modifier with the formation of solid structured nano-shells on the surface of cement grains or the use of ultra-fine Portland cement obtained in high energy mills. However, these technologies require the use of special equipment, which increases the cost of finished material.

The implementation of the "bottom-up" nanotechnological approach ("bottom-up") is to manage the processes of structure formation with the introduction of primary nanosized specially prepared

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components – oxide (SiO_2, TiO_2, Fe_2O_3, etc.), carbon modifiers (fullerenes, single-, multilayer tubes) and nano additives in the form of synthesized embryos of certain hydration phases, such as zeolites or low basic calcium hydrosilicates [2].

This approach opens new opportunities for the creation of a wide range of nanomodified building composites, including: concrete with improved functional properties. These additives not only alter the nature of the formation and composition of the products of hydration of the binder compositions, but also affect the formation of the structure of mortar and concrete, changing the processes of formation of the contact zone "binder substance – aggregate", which also has a significant impact on the performance and durability of artificial stone.

The aim of this work is to establish the role of the crystal-chemical factor in the evaluation of the nanomodification efficiency of mortar and concrete.

2. Materials and methods of research

Two binding compositions were investigated: Portland cement, modified with a complex organo-mineral additive comprising microsilica, and ash-alkaline system, modified with artificial zeolite phases obtained by hydrothermal synthesis using man-made raw materials [8, 9].

The following materials were used as raw material for the first composition: Portland cement PC I-500R-N, Dnieper quartz sand, with M_{kr} = 1.28; claydite gravel of grades 400, 500, 600, nanocrystalline additive – Tripoli earth of the Konoplya field ground to a specific surface (S_{pit} = 21997 cm^2/g); polycarboxylate superplasticizer “SikaPlast 555W”.

The ash of Trypillya DRES is used for the preparation of ash-cement, and the binder compositions also included slag blast-furnace granulated from the Dnipropetrovsk plant named after I.P. Petrovskyi; as alkaline component is soluble sodium silicate with silicate module 2 and density 1300 kg/m^3. The Dnieper quartz sand with modulus of size 1.2 was used as a small aggregate, and crushed granite of different fractions was used as a large aggregate. The ash-slag mixture was prepared by compatible grinding in a ball mill of ash and blast furnace slag for 1.5 h, the specific surface of the resulting mixture was 490 m^2/kg (Blaine).

As modifying nanoadditives artificial zeolite phases were used, they were obtained in the system Na_2O-Al_2O_3-SiO_2-H_2O by hydrothermal synthesis. As an aluminosilicate component, the waste ash dump of Trypillia DRES, represented by a fraction of less than 0.16 mm, a specific surface area of 380 m^2/kg according to Blaine, whose phase composition according to the X-ray analysis is represented by an amorphous component with quartz inclusions, was used. Sodium silicate soluble with a silicate modulus of 2.8, density ρ = 1400 kg/m^3, was used as an alkaline component in the synthesis of artificial zeolites. The synthesized artificial zeolites were represented by zeolite Zh, obtained on the basis of reaction mixtures of the composition $3.2Na_2O \times Al_2O_3 \times 5.6SiO_2 \times 13.5H_2O$, the sizes of which vary from several nm to 2… 5 μm according to the electron microscopy data (Figure 1).

The research on the efficiency of using different types of nanomodified binder compositions was performed on concrete cubes of 7.07x7.07x7.07 cm and 10x10x10 cm in size. Curing of the sample cubes occurred under normal conditions (95% humidity, temperature 20±2 ° C).

In order to study the processes of structure formation that occur during the modification of cement systems by an organo-mineral additive and fly ash-alkali system by artificial zeolites, and the products of their hydration by electron microscopy, the structure of the cement paste was investigated on the basis of these binder compositions and the contact zone “binder substance – aggregate”. Microhardness of contact zone – “cement stone – aggregate” for high strength concrete was determined using PMT-3 microhardness meter.

3. Research results

The strength of mortar and concrete, as well as their physical-mechanical and special properties, are explained not only by the properties of the cement stone, but also by the peculiarities of the formation of the contact zone at the boundary of the "cement paste – aggregate", both for small and large aggregates.

To determine the efficiency of using nanomodified binder compositions in obtaining mortars and concretes with improved performance, the kinetics of increasing the strength of cement paste, cement-sand mortars and concretes based on nanomodified cement and fly ash-alkaline compositions were investigated.

The results of the studies are shown in table 1 for Portland cement compositions and in table 2 for fly ash-alkaline binder compositions, micrograph of cement stone and contact zone "cement stone – aggregate" of concrete based on Portland cement – in Figure 2 and Figure 4, respectively, and concrete contact zone based on ash cement systems – in Figure 5.

When studying the kinetics of change in the compressive strength of cement paste, cement-sand mortar and lightweight concrete based on Portland cement, modified with complex organo-siliceous additive, it was noted that the introduction of a complex additive based on polycarboxylate superplasticizer "SikaPlast 555W" in the amount of 1.5% and high dispersion Tripoli earth in the amount of 10% of the composition of binders provides a more uniform set of compressive strength of lightweight concrete in the early stages of hardening and later (table 1).

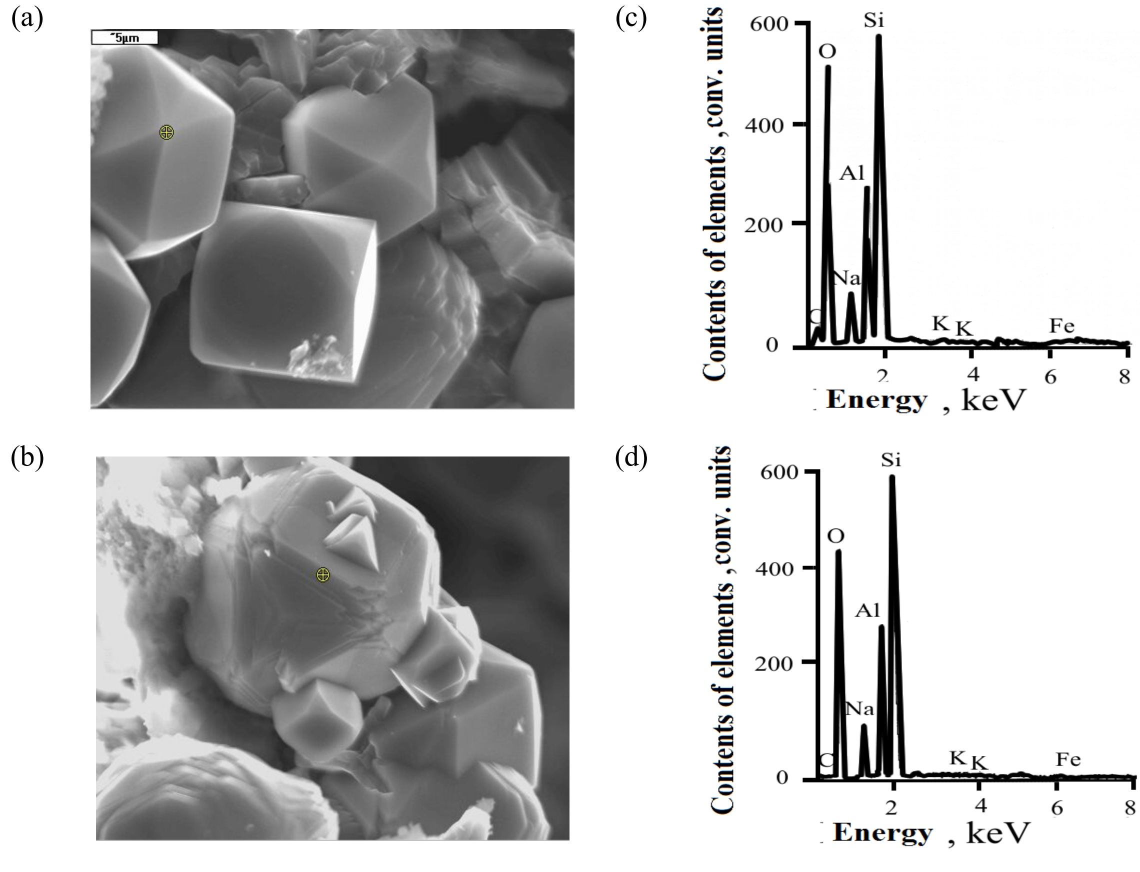


Figure 1. Micrographs (x500) of the surface of the chipped samples based on an alkaline aluminosilicate composition of $3.2Na_2O \times Al_2O_3 \times 5.6SiO_2 \times 13.5H_2O$, which provides synthesis of zeolite Zh, (a, c) and the content of the basic elements according to electron probe analysis (b, d).

In case of gradual complication of the structure, during the transition from cement stone to concrete, there is a decrease in the speed of strength gain over time: for cement stone, the increase of strength by 28 and 365 days is 80 and 53%, respectively; for mortar – 54 and 59%; for concrete – 66.8 and 60% compared to the strength of the control composition.

The significant increase in strength of the cement stone with the introduction of additives in the composition of cement systems can be explained by the direct synthesis of crystal-chemically similar compounds (table 3) and the layer-by-layer reinforcement of the cement matrix by plate and needle-forming on the basis of low-basic calcium silicates CSH (I) and tobermorite 11,3A with plasolite and hydrogarnets, which are capable of splicing and contribute to the formation of a better microstructure of cement stone (Figure 2) [4, 6]. Such a structure is formed by the crystallization of crystals according to the Royer-Friedel scheme, a necessary condition of which is their crystallo-chemical similarity, which is estimated by the magnitude of the difference of the parameters of the crystal lattices and should not exceed 15% [7]. This is confirmed by the electron microscopy data presented in Figure 2.

Analyzing the tendency of changing the strength of artificial stone with different levels of structure, we can conclude that at the macro-level such products of hydration of modified Portland cement systems as CSH (I); tobermorite 11.3Å; plasolite and hydrogarnets are crystal-chemically similar in parameter "a" (Table 3) and can form corresponding splices, which is a prerequisite for the appearance of a considerable number of contacts of splicing between new formation, which contribute to obtaining a sufficiently dense structure with low porosity and having a dominant effect on high physical-mechanical properties of cement stone [9-11].

Table 1. Kinetics of change in compressive strength for cement paste, cement-sand mortar and lightweight concrete based on Portland cement modified with a complex organo-silica additive

Kind of artificial stone	The presence of additives in the composition of cement compositions	Compressive strength, MPa, of artificial stone, after curing, days	
		28	365
cement stone	without additives	56.1	79.5
	with complex organo-siliceous additive	101.1	121.9
cement-sand mortar	without additives	52.1	59.3
	with complex organo-siliceous additive	80.4	94.7
lightweight concrete	without additives	22.9	27.6
	with complex organo-siliceous additive	38.2	44.2

The efficiency of modifying Portland cement compositions with a complex organo-silica additive is determined by the nature of the change in the microhardness of the contact zone: "binder substance – aggregate", the results of which are shown in Figure 3.

The analysis of the obtained data shows that the microhardness of the investigated sample of expanded clay concrete based on unmodified Portland cement in the area of 20 μm wide from the conditional grain boundary of the aggregate gradually increases from 1300 MPa (aggregate) to 2100…2300 MPa (cement mortar), which is 20% more than microhardness of the stone of mortar part of concrete (Figure 3, composition No. 1).

Modification of expanded clay concrete with the addition of the superplasticizer "SikaPlast 555W" (Figure 3, composition No. 2) increases the microhardness at the aggregates boundary to 2450 MPa, which is 24% more than the microhardness of the similar zone of the control composition.

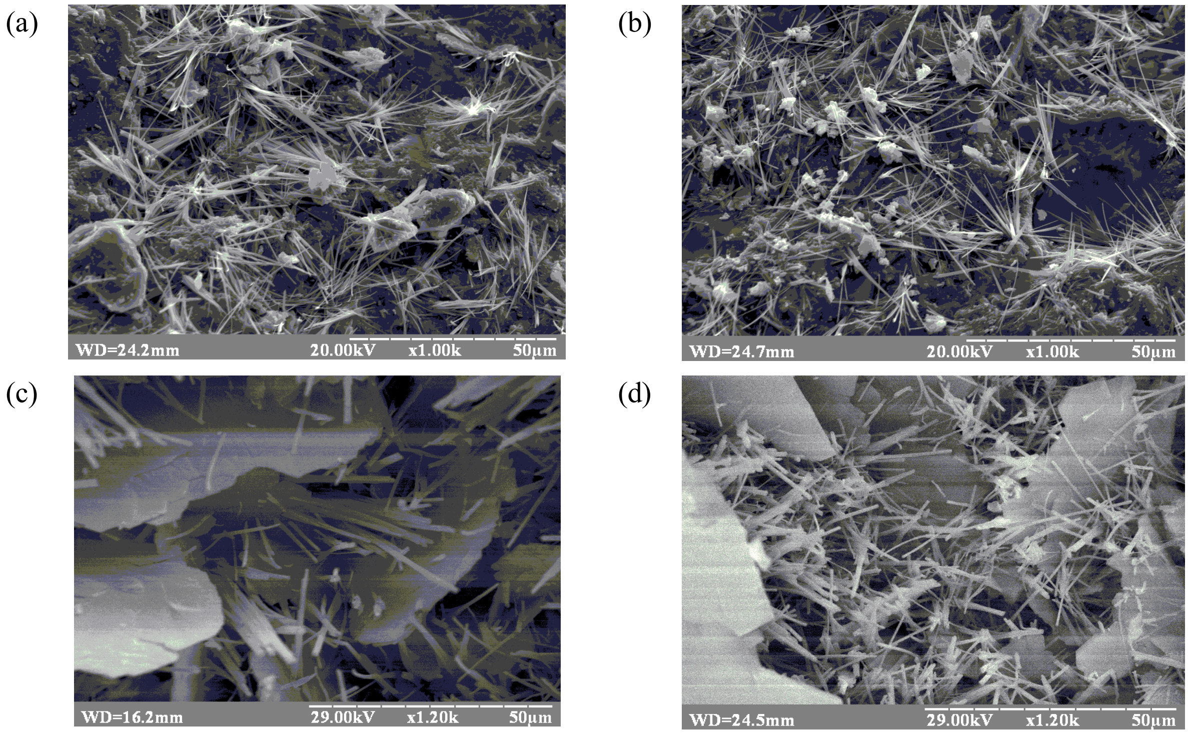


Figure 2. Photographs (×1000…1200) of microstructure for cement stone modified with complex organo-siliceous additive containing polycarboxylate superplasticizer "SikaPlast 555W" and fine-ground tripoli earth of Konoplya deposit after 28 (a, b) and 365 (c, d) days of hardening.

With the introduction of a complex organo-siliceous additive to the composition of concrete based on expanded clay (Figure 3, composition No. 3), the value of microhardness at the conditional grain boundary of the aggregate reaches 2770 MPa, which is 32% more than the microhardness of the cement stone at the conditional grain boundary and 19% more than the microhardness of cement-sand mortar in the intergranular space compared with the control composition. The compressive strength of such modified concrete based on expanded clay is increased by 25…30%, compared with control light concrete.

The effect of nanomodified additives on the structure formation of alkaline binder systems is different. Comparison of kinetics data of the set of strength of artificial stone obtained using ash-binder systems with different degree of complexity of the structure (paste, mortar and concrete) allows recording the significant influence of the interaction of the aggregate with the modifying additive on the formation of the structure of the artificial stone (Table 2). The nature of the compressive strength of cement-sand samples based on modified ash compositions is characterized by an increase in strength of 8% and 40%, while the increase in the strength of cement paste due to nanomodification of ash binder systems is 14% and 40% after 28 and 90 days respectively.

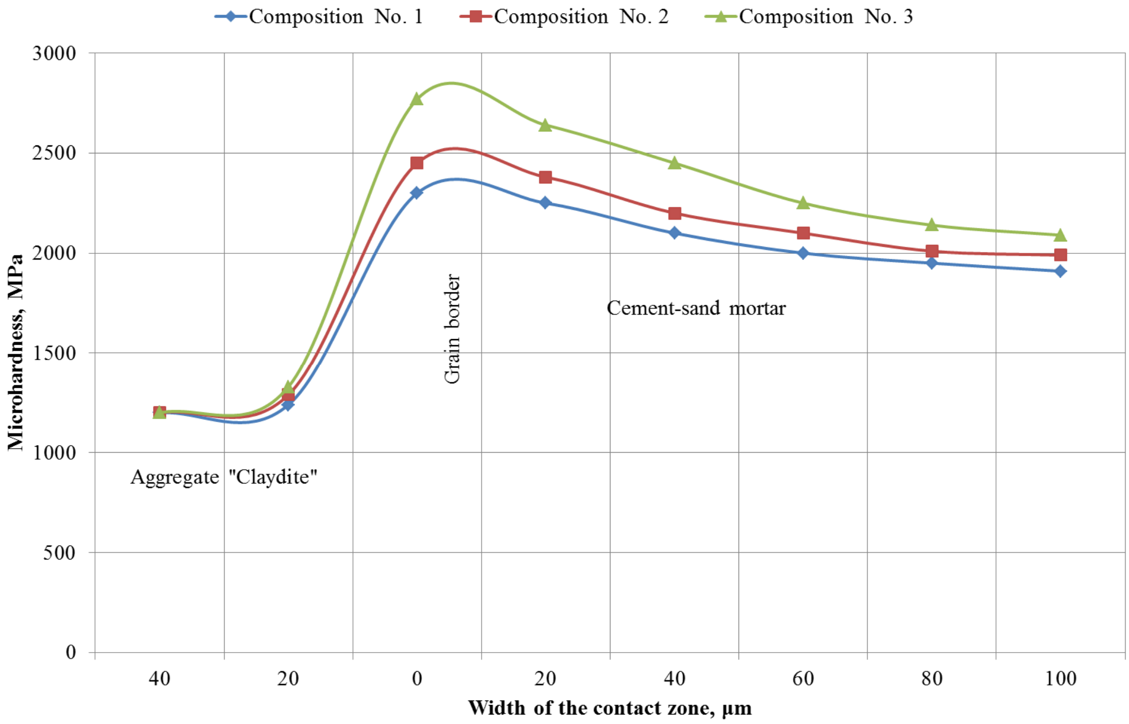


Figure 3. Change of microhardness of the contact zone "binder substance – aggregate" for lightweight concrete: No. 1 – control composition; No. 2 – modified by the SikaPlast 555W superplasticizer; No. 3 – modified organo-siliceous additive based on this superplasticizer and fine milling tripoli earth (microsilica).

At the same time, it is noted that the introduction of artificial zeolite additive in the amount of 10% in the composition of binders provides a more uniform set of strengths of concrete based on both of them in the early curing period (up to 28 days) and later: the increase in concrete strength after 28 and 90 days it is 61% and 55% respectively.

The effect of nanomodification of the ash and alkaline binding systems, which is more pronounced on concrete samples, considering the known composition of neoplasms of fly-ash alkali binder compositions and the mineralogical composition of the aggregates, can be explained by the crystallo-chemical similarity between the crystals of the granite rock, which is included in the composition and products of hydration of fly-ash alkaline binding cements modified by the addition of artificial zeolites, which contributes to the formation of stronger contact zone at the level of the macrostructure compared to the zone formed at the level of the mesostructure (Table. 2).

Table 2. Kinetics of change in compressive strength of cement paste, cement-sand mortar and concrete based on fly-ash alkaline binder, modified by 10% artificial zeolite additive

Kind of artificial stone	Binding composition	Compressive strength, MPa, of artificial stone, aged, days	
		28	90
cement paste	without additives	40.17	45.8
	with the addition of artificial zeolites	45.83	64.25
cement-sand mortar	without additives	21.26	24.6
	with the addition of artificial zeolites	23.16	34.48
concrete	without additives	28.73	35.76
	with the addition of artificial zeolites	46.33	55.52

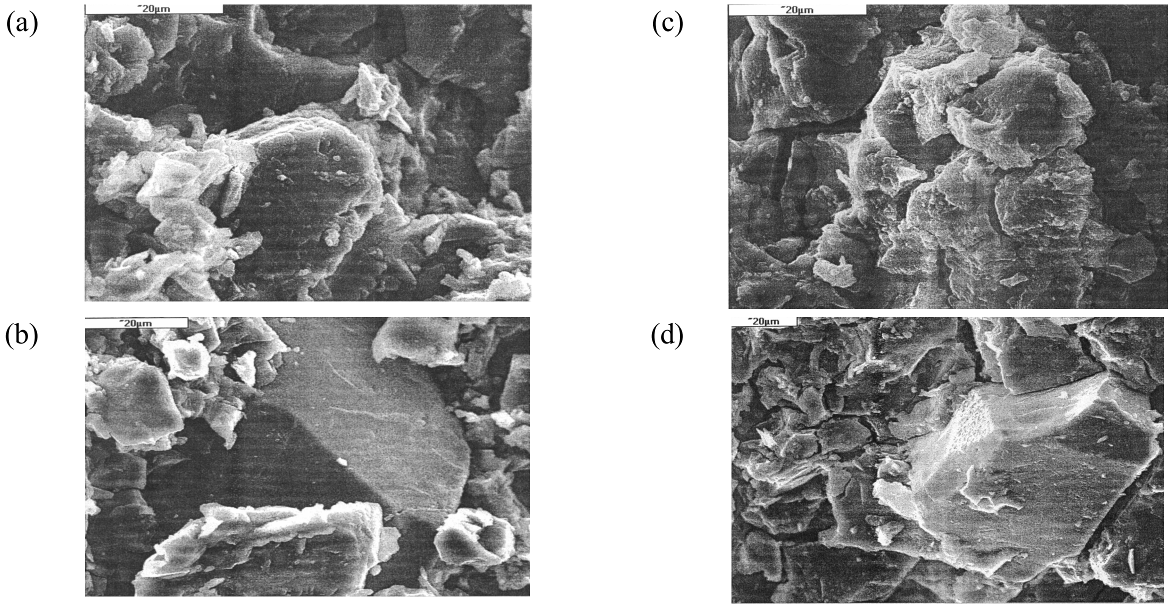


Figure 4. Micrographs (x500) of the surface of the cement chips based on the non-additive fly-ash alkaline binder (a, b) and system modified with the addition of artificial zeolites (c, d)

At the crystallo-chemical level, this can be explained by the fact that the difference in the value of the parameter "b" of the crystal lattices of analcime, which is the product of hydration of the modified alkaline compositions according to [8], and albite and anorthite does not exceed 6...7% (Table 3). This satisfies the above conditions of crystallization and causes the formation of a contact zone with high density and microhardness, which reaches 4600MPa, in the composition of heavy concrete with granite aggregate.

The formation of joint structures of analcime and calcium hydrosilicates with quartz is complicated by a large difference in crystal sizes (more than 50%), which is reflected in the processes of structure formation of the contact zone of cement-sand mortars and explains the uneven kinetics of the set strength of the studied samples (Table 2, 3).

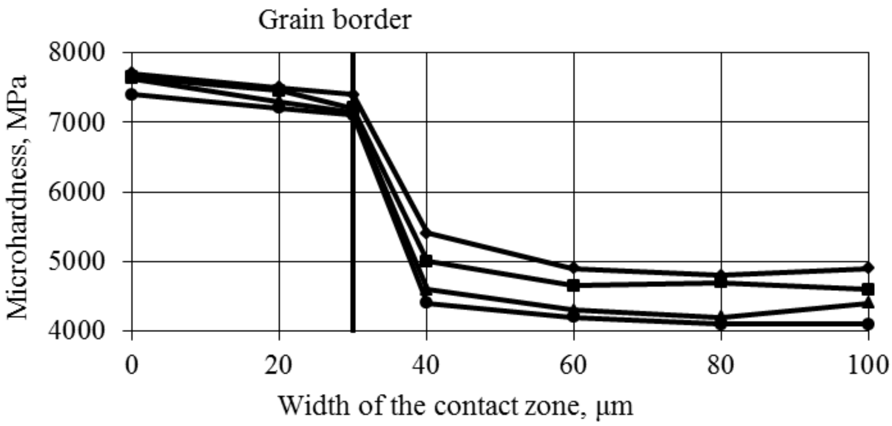


Figure 5. Microhardness of the contact zone of the aggregate and the fly-ash alkaline binder composition without additives (1) and with the addition of 5% (2), 10% (3) and 15% (4) of artificial zeolite Zh

Table 3. Comparison of the parameters of elemental crystal lattices of new formation of artificial stone obtained on the basis of different types of nanomodified binder compositions

Name of minerals	Singonia	Elementary options crystal lattice		
		a	b	c
Products of hydration of Portland cement binder compositions				
Low-base hydrosilicates calcium CHS (I)	orthorhombic	11.2	7.3	9 to 14
Low-base hydrosilicates calcium CSH (II)	orthorhombic	11.2	7.3	10
Tobermorite 11.3Å $5CaO{\cdot}6SiO_2{\cdot}5H_2O$	rhombic	11.24	7.3	18 to 29
Plosolite $3CaO{\cdot}Al_2O_3{\cdot}2(SiO_2{\cdot}CO_2){\cdot}2H_2O$	rhombic	12.14	-	-
Hydrogarnets $3CaO{\cdot}Al_2O_3{\cdot}2{\cdot}SiO_2{\cdot}2H_2O$	rhombic	12	-	-
Hydration products of ash-alkaline binder compositions				
Analcime	Cubic	1.371	1.371	1.371
Low-base hydrosilicates calcium CSH(I)	orthorhombic rhombic	1.12	0.73	0.9-1.4
Calcite		0.495	0.796	0.573
Minerals of aggregates				
Albite	Triclinna	0.823	1.30	0.725
Anorthite	Triclinna	0.821	1.295	1.446
Quartz	trigonal	0.491	-	0.540

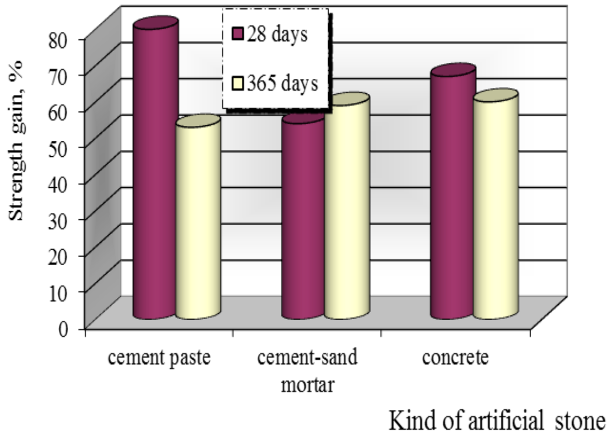
In addition to electron microscopy data, an important characteristic is the microhardness estimation of the "binder substance – aggregate" contact zone. The efficiency of modification of fly-ash alkaline binding compositions modified by artificial zeolites is determined not only by the composition of the new formation, but also by the change in microhardness, the results of which are given in Figure 5.

Analysis of the data obtained shows that the microhardness of the specimen in the 20 to 30 µm wide area from the conditional grain boundary of the aggregate is gradually reduced from 7000-8000 MPa (aggregate) to 4200-4300 MPa (stone of the binder without additives). Modification of the fly-ash alkaline composition of 5% additive of artificial zeolite increases the microhardness up to 4500-4600 MPa, and with the introduction of 10-15% of the additive the value of the microhardness of the contact zone reaches 4600-4700 MPa (see Figure 5), i.e. the modification allows increasing the microhardness by 10 to 12%, which increases the strength of concrete.

It is likely that one of the factors that determine the efficiency of modification of the binder systems is the crystallo-chemical similarity of the new formation to each other and the modifying additive, and in case of complication of the structure, the crystal-chemical similarity between the products of hydration and minerals of the main constituent components of mortar and concrete. The results obtained indicate that when using modifying additives in the form of silica their efficiency at the micro level is higher than at the meso- and macro-levels (Figure 6a).

At the same time, the modification of the alkaline system by artificial zeolites provides a more pronounced effect in the concrete at the macro level, which may be due to the crystallo-chemical similarity of nanoadditives, hydration products and aggregate minerals (Figure 6b).

(a)



(b)

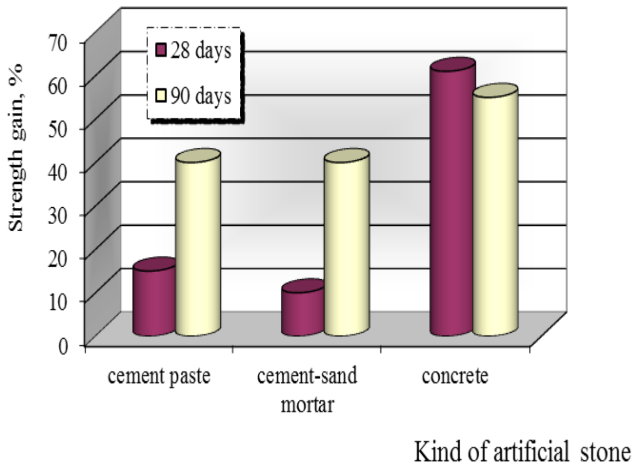


Figure 6. The influence of modifying additives on the change of strength of artificial stone with different complexity of structure: a – the effect of organo-mineral additive on the increase of the strength of artificial stone based on Portland cement, b – the influence of the addition of artificial zeolite on the increase in the strength of artificial stone on the basis of alkaline system

4. Conclusion

Taking into account the crystallo-chemical similarity of new formation at different levels of the artificial stone structure opens up new possibilities for the selection of nanoscales, considering not only the principles and nature of their action in the composition of cement matrices, but also their influence on the peculiarities of the contact zone formation, especially when it comes to the formation of meso- and macro levels of concrete structure.

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