

## Impact Of Epicrystallization Modifying On Characteristics Of Cement Rock And Concrete

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Abstract- There has been established the set of processes running upon epicrystallization modification of the cement matrix and stages of formation of composites structure by use of artificial aggregate based on granulated reactive silica powders have been considered. Use thereof allows improving the cement matrix structure by means of defect minimization and formation of the closed cell system. Analysis of porosity of separate segments of fine-aggregate concrete on the basis of artificial aggregate based on granulated reactive silica powders allowed ranking them by degree of reduction of nanoporosity. Using the X-ray phase analysis and infrared spectroscopy methods the active chemical and structure-forming effect of the reagent material artificial aggregate based on granulated reactive silica powders on the surface of mineral formations of cement rock have been proved. The described processes determine the fact that upon increase in the total composite porosity as the results of introduction of artificial aggregates based on granulated reactive silica powders to 55–60 % reduction of the composite thermal conductivity by 9–12 times, that of water saturation – by 4 times, increase in concrete strength characteristics by 2 times is observed. The voids being formed instead of artificial aggregate based on granulated reactive silica powders have tightened walls and prevent water migration, thereby increasing the concrete water-proofing and water-resistance of a construction product in general, at that 95 % macro-pores

of the produced composite are closed.

Keywords: cement rock, sodium polysilicates solution, epicrystallization modification, porosity, water saturation (absorption).

### Introduction

Under the influence of environmental factors service life of concrete construction products is reduced significantly. This is particularly so with cellular concretes and concretes based on light-weighted porous aggregates [1–5]. Such materials without additional treatment are characterized by relatively high water absorption, low corrosion resistance. Besides, significant water absorption degrades heat-insulating characteristics of composites during operation. This issue is solved by manufacturers and consumers of concrete products in different ways.

The most common one is introduction in the composition or application to the material surface of hydrophobized agents of different nature. Modification of cement systems by means of active chemical interaction of the composite components between each other is also aimed at increase in water-resistance, strength characteristics and reduction of thermal conductivity of composite. Both in the first and second cases the components used and their action shall not exercise negative effect on other characteristics of

composites. Or it shall be justified by significant improvement of other properties [6–8].

By using water repellent agents in the mixture composition the processes of cement hydration, water diffusion to the cement particles may be disturbed which results in reduction of the composite strength. This is why water repellents proposed by manufacturers are often designed to be applied to the surface. Volumetric hydrophobization is recommended for use for critical structures only. Hydrophobization of concrete products is implemented through two methods: mechanical pore filling or creation of hydrophobic coating of pore walls. In the second case as the result of interaction of water repellents with productions of cement hydration in micropores and capillaries water-, salt- and acid-insoluble hydrophobic films of mosaic structure are deposited.

Design of high-performance construction materials with predetermined properties in this case structural-heat-insulating with reduced water saturation that allow ensuring saving energy costs at all stages of product and structures manufacturing: from extraction of raw materials to operation, integrated approach may be used consisting in establishment and further use of relation between the structural organization of synthesized materials and formation of the finished product properties at all stages of products and structures manufacturing [9–11].

### Experimental procedure

To verify the hypothesis of the possibility of production of structural-heat-insulating concrete with reduced water absorption, increased strength in into composition artificial aggregate based on granulated reactive silica powders was introduced that was obtained in laboratory conditions according to the following procedure. Nodules consisting of the kernel and protective shell were produced from the source raw materials. The kernel is grinded mixture from the silica component (as which silicic acid was used for the model system and gaize of the Korkinsky deposit – as the natural raw material), alkaline metal hydroxide and waterglass in

the specific mass ratio. The obtained mixture was supplied to the standard disk granulator where aggregate kernels of the specified size were produced. After which they were supplied to the rotary drum mixer for formation of protective shell by means of pelletizing in the dry mix consisting of ground lime and sodium fluosilicate.

The obtained aggregate at different amounts was introduced in cement paste and cement-sand mortar to vary porosity of the finished material. To form in the aggregate kernel the reagent material designed for impregnation of the cement (concrete) matrix, the samples were subjected to steam curing at the temperature 85 °C.

Determination of distribution of the material nanopores was performed with the use device SoftSorbi-II Ver. 1.0. IR-spectra of materials were obtained with the use of the IR-Fourier spectrometer VERTEX 70 within the spectral range from 370 to 7500  $\text{cm}^{-1}$ . X-ray phase analysis of the cement rock samples was performed by the diffraction spectra obtained at the X-ray work station WorkStation ARL 9900, with the use of the Co-anode emission. Qualitative X-ray phase analysis of mineral crystalline phases was performed with the use of the diffraction database PDF-2. In order to determine the quantitative ratio of crystalline phases (% wt.) full-profile quantitative X-ray phase analysis was used.

The following raw components were used during the study: cement ИЕМ I 42,5 H produced by the CJSC ‘Belgorod cement’, sand of the Ziborovsky deposit in the Belgorod Region. For production of artificial aggregate gaize of the Korkinsky deposit of Chelyabinsk region, sodium silicofluoride  $\text{Na}_2\text{SiF}_6$ , aqueous solution of sodium silicate, quicklime were used.

### Results and discussion

Implementation of epicrystallization modification of the cement (concrete) matrix is performed with the use of the artificial aggregate based on granulated reactive silica powders (AAGS) designed in the Belgorod State Technological University named after V.G. Shukhov [12, 13]. Epicrystallization (from the Greek *epí* – after)

modification by synthesis of artificial composites (construction materials) on the basis on inorganic binders implies infiltration meta-somatic transformation by activated functional (protogenetic) mineral systems of the material crystalline matrix for the purpose of formation of new alliances or transformation of the mineral individuals surfaces.

Silica raw material of various geneses may be used as the main AAGS component. Previously [12] wide range of both natural and industrial silica materials was investigated. There was designed the express method of estimation of activity of silica components as the raw material for AAGS production as well as ranking of different kinds of the mineral raw material by the degree of efficiency of using it as a AAGS functional component by the activity ratio into: highly-active 51–100 %, active 21–50 %, low-active 5–20 %.

During the concrete steam curing activation of the AAGS kernel takes place. As the result of interaction of the silica component with alkaline one polysilicates solution is produced that penetrates the concrete matrix through the nodule protective shell.

The following mechanism of formation of the AAGS material structure is suggested.

I. Initial stage at which settling of cement rock and strength gain take place. Hardening of the composite proceeds in the natural conditions. During this period AAGS acts as 'inert' system component, i.e., interaction (adhesion) of cement rock with the AAGS surface takes place and the nodule content remains the same. This happens due to encapsulation of the active agent in the insoluble envelope protecting the cement rock and preventing hydration disturbance proceeding during the first three days. By completion of the first stage the composite has a dense non-porous structure.

II. The second stage consists in creation of the monolithic honeycombed composite structure. It proceeds during the steam curing in the curing room at the isothermal holding temperature of 80–90 °C and in the steam curing mode for 3–6–2 h. During this period interaction of the AAGS composition components takes

place. The nodule envelope consisting of ground lime and sodium fluosilicate passes the sodium polysilicates solution produced as the result of interaction of alkaline metals with active silica that penetrates the hardened matrix between the nodules filling the cement composite micro-pores. Thus, monolithization of the composite cement skeleton, on the one hand, and formation of pores in place of the AAGS kernel, on the other hand, takes place.

The volume of voids formed by AAGS may be presented as follows:

$$V_{m.nop} = V_{AAGS} - V_{o\delta} - V_{h.e.},$$

Where  $V_{m.nop}$  – volume of the composite macropores,  $V_{AAGS}$  – AAGS volume,  $V_{o\delta}$  – volume of solid casing of void space AAGS,  $V_{h.e.}$  – volume of unreacted AAGS substance.

According to the data of the quantitative full-profile X-ray phase analysis, the dense, solid, water-proof void space envelope is represented by the mineral composition, % wt.: calcite – 10, amorphous phase – 90. Its thickness is determined by the amount of the protective envelope material.

The composition of the unreacted substance and its amount are determined by the composition and reactive capacity of the raw material used for AAGS production. As the results of experimental studies showed, by use of the 100 % reaction silica component as which silicic acid was used by model systems design the volume of unreacted AAGS substance equals to 0. Then the formula (1) will appear as follows:

$$V_{nop} = V_{AAGS} - V_{o\delta},$$

By using as the silica component of rocks or industrial wastes meeting the requirements to mineralogical composition set to the raw material for AAGS production  $V_{h.e.}$  will be determined by impurities kind and amount.

Thus, the unreacted substance volume by use of gaize from the Korkinsky coal deposit makes no more

than 30 % of the total AAGS volume. Due to the presence of dense water-proof void space envelope this rest does not exercise significant impact on the composite strength and water absorption in general.

According to BET-analysis of porosity of separate

segment of fine-grain concrete based on AAGS (Fig. 1), the zones of heteroporous composite have been ranked by the degree of reduction of nano-porosity as follows: cement rock → zones of cement rock impregnation with nodule content → void space envelope.

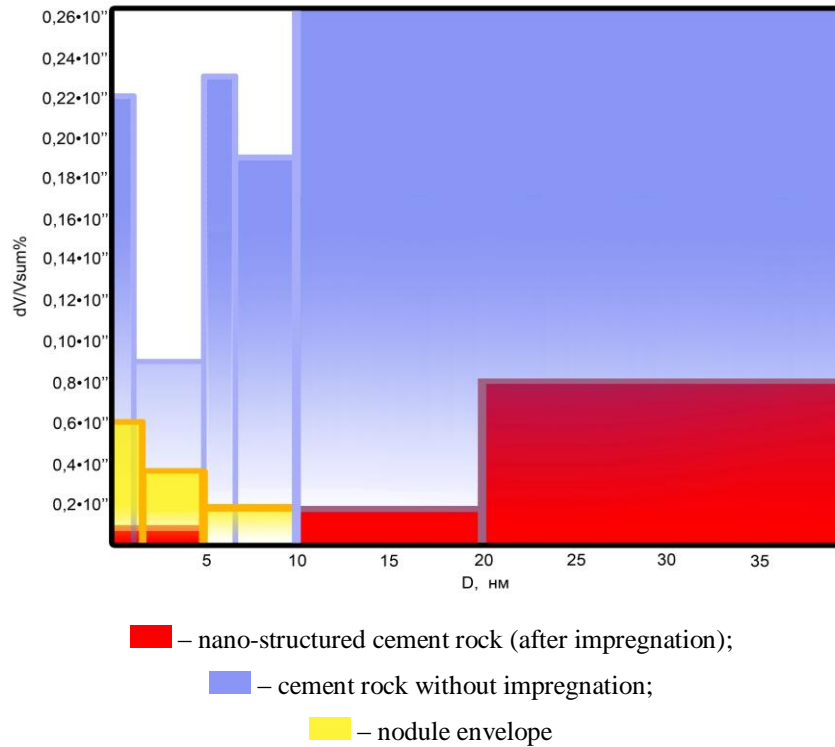


Fig. 1. Nature of nano-porosity distribution across different composite segments

Comparison of IR-spectra of cement rock impregnated with nodule content with the reference one (not subjected to exposure) (Fig. 2) showed

absence of absorption bands in  $870\text{ cm}^{-1}$  and  $3640\text{ cm}^{-1}$  at the spectrum of the sample with AAGS.

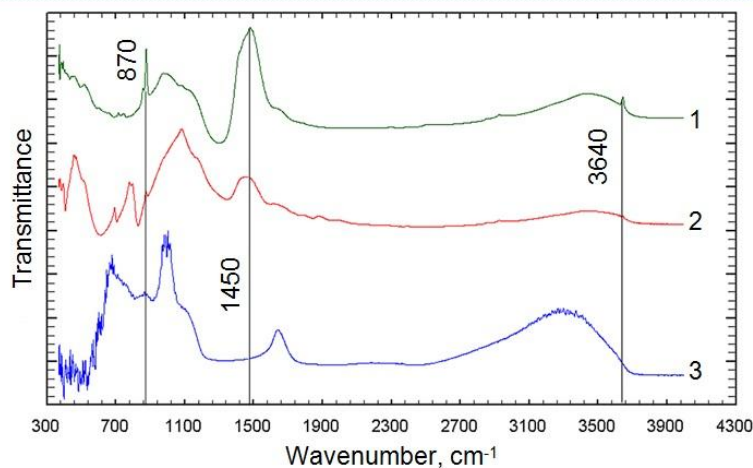


Fig. 2. Change of nature of IR-spectrum of cement matrix with AAGS: 1 – ordinary CS,  
2 – CS with AAGS, 3 –  $\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$

This fact indicates significant reduction of  $\text{OH}^{-1}$  groups concentration on the surface of the на поверхности Portlandite crystals and, as a result, reduction of its reactive capacity. Significant reduction of intensity of the absorption band  $1450 \text{ cm}^{-1}$  is observed that corresponds to deformation vibrations of the  $\text{OH}^{-1}$  groups at the apexes of silicon-oxygen tetrahedrons which may be interpreted as ‘neutralization’ thereof by alkaline AAGS components. Also, ‘sharpening’ of the profile of wide absorption band  $800\text{--}1200 \text{ cm}^{-1}$  (symmetric and asymmetric deformation vibrations of Si–O-bonds) is observed along with appearance of the clear  $1080 \text{ cm}^{-1}$  which may be explained by nano-structuring of the silica skeleton on the surface of C–S–H-phases.

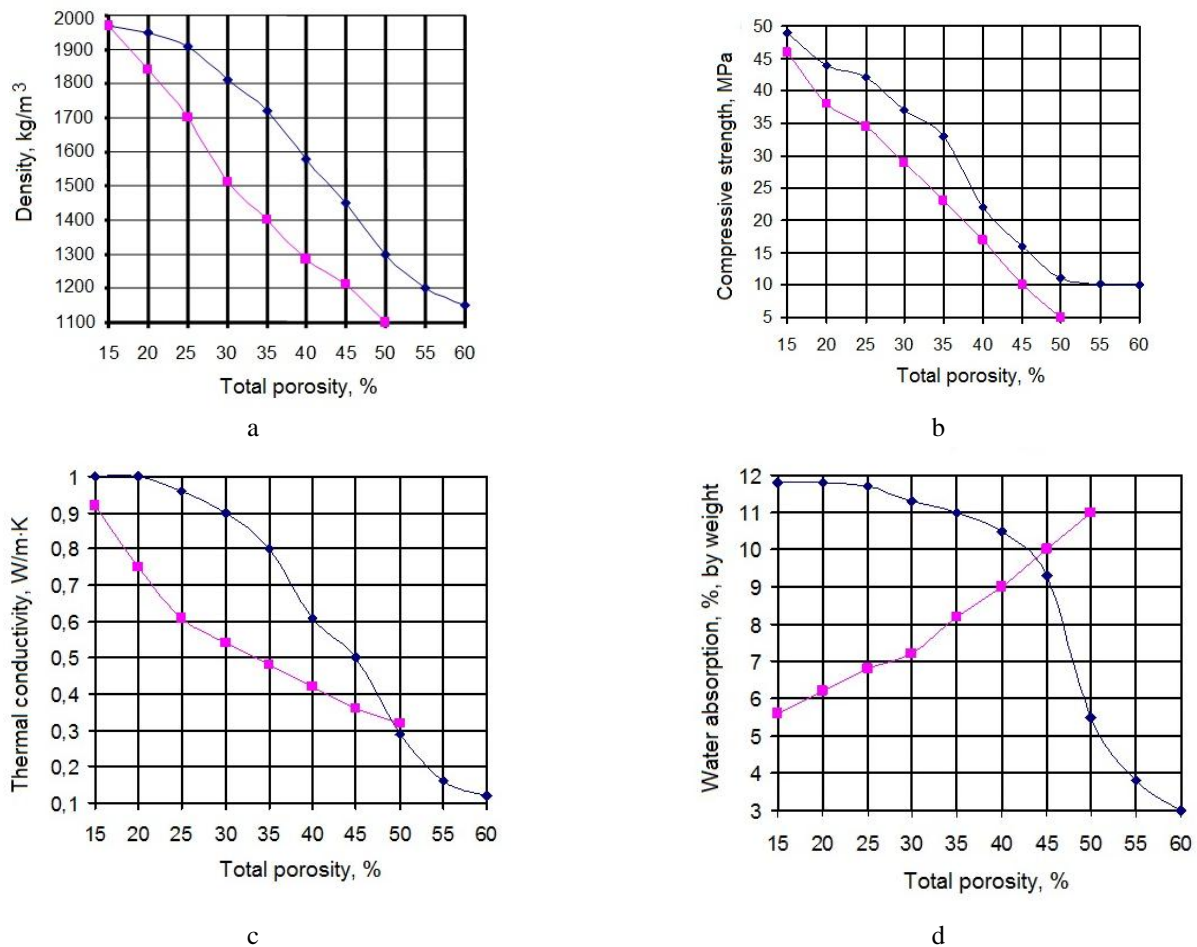
The peculiarities of the IR-spectra observed are interpreted as the result of ‘encapsulation’ by fluid glass in the thin-film form (2D-nanosystems) of cement rock mineral formations. The conclusion may be drawn as to active chemical and structure-forming action of the reagent AAGS material on the surface of cement rock mineral formations.

Analysis of performance characteristics of fine-aggregate concrete with different AAGS content showed (Fig. 3) that upon increase in the total composite porosity due to introduction of up to 55–60 % of AAGS its thermal conductivity is reduced by 9–12 times; in LWA concrete at the same porosity characteristics the reduction of thermal conductivity makes no more than 4–5 times; at that the concrete strength properties are increased by a factor of 2. This is explained by the fact that instead of the silica-containing AAGS voids with thickened walls and poly-textured surface are formed

that reduce intensity of heat current within the total composite volume.

Dependence of density on the total concrete voidage by AAGS us differs from the concrete incorporating traditional light-weighted aggregates. In particular, in LWA concrete this dependence features linear nature. This is explained by the fact that by introduction of expanded-clay aggregate porosity of the material obtained is nearly the additive sum of porosity of its constituent components. Increase in macro-porosity of the concrete incorporating AAGS takes place due to solving of the components constituting the nodule kernel. At that the concrete matrix enveloping the nodule loses its porosity. This proceeds the faster the more actively the nodule kernel substance is dissolved. The reaction running most intensively reduces porosity of the concrete matrix this is why in this case dependence of density on the total concrete voidage features flattened nature.

Nature of decrease in water absorption by concrete samples with AAGS totally differs from that by concretes with traditional lightweight aggregates. In particular, water absorption by LWA concrete upon increase in the total porosity up to 55–60 % is increased up to 23–27 % wt. Upon reduction of the density values and increase in the total porosity of designed concrete its water absorption is reduced by 4 times as compared to the reference fine-aggregate concrete.



— LWA concrete, — concrete on the basis of artificial aggregates based on granulated reactive silica powders

Fig. 3. Performance characteristics of concrete depending on total porosity: a – average density, b – compressive strength, c – thermal conductivity, d – water absorption

### Summary

The differences in properties observed between concrete with AAGS and traditional LWA concrete are determined by the fact that voids formed instead of AAGS of the silica raw material have thickened walls and prevent water migration, reducing the material water absorption and thermal conductivity and increasing strength. It shall also be noted that 95 % of macro-pores of the composite produced are closed and waterproof.

### Conclusion

Use of artificial aggregate based on granulated reactive silica powders allows ensuring reduction of water absorption by lightweight aggregate concretes. The mechanism of action of artificial aggregate based on granulated reactive silica powders includes the following

stages: initial stage at which settling of cement rock and strength gain take place; the second stage consists in forming the reagent material in the kernel of artificial aggregate based on granulated reactive silica powders during steam curing; further migration of reagent material in the cement (concrete) matrix ensures creation of the monolithic honeycombed composite structure. As the result of encapsulation of cement rock mineral formations by the reagent material of the artificial aggregate based on granulated reactive silica powders hydrophobic properties of the material are developed and its structure becomes more monolithic due to filling of the matrix micro-pores and micro-cracks. As the result, strength is increased and water absorption by concrete is reduced.

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