Cellular Composites with Ambient and Autoclaved Type of Hardening with Application of Nanostructured Binder

V Nelyubova\textsuperscript{1,2}, N Pavlenko\textsuperscript{1} and D Netsvet\textsuperscript{1}
\textsuperscript{1}Department of Materials Science and Technology, Belgorod State Technological University named after V.G. Shoukhov, Russia, Belgorod, Kostyukov Str., 46

E-mail: vvnelubova@gmail.com

Abstract. The research presents the dimensional and structural characteristics of nonhydrational hardening binders – nanostructured binders. Rational areas of their use in composites for construction purposes are given. The paper presents the results of the development of natural hardening foam concrete and aerated autoclaved concrete for thermal insulating and construction and thermal insulating purposes. Thus nanostructured binder (NB) in the composites was used as a primary binder and a high reactive modifier.

1. Introduction
Due to the accumulated more detailed knowledge of the structure and performance of natural objects at molecular scale, there is a visible tendency in development of basic approaches to producing and application of synthetic materials with nanosized structure.

In spite of the domination of Portland cement as a highly efficient hydraulic binder, it is recognized that its production process is based on the substantial consumption of raw materials and energy and that it asserts enormous pressure on the ecosphere. To reduce the negative impact on the environment, decrease of consumption and more efficient use of Portland cement in concrete are realized. These measures include the use of finely ground cement (FGC), low water demand binders (LWDB), blended cements based on fly ash, granulated blast-furnace slag, microsilica, metakaolin \cite{1–5 and other}. In addition, the development of an alternative to Portland cement “green” eco-cements with fundamentally different mechanisms of hardening was proposed \cite{6–9}.

An actual trend, however, is the development of physical-chemical and technological principles to design new nonmetallic materials on the basis of nanotechnologies by oriented structure formation, optimization of physical and chemical principles in manufacture. The principle of structure formation of materials obtained with high concentrated binder system (HCBS) technology underlies the
conception of design of such a technology. In the given system it is nearly 10% of nanosized particles form as a result of mechanochemical activation of raw materials.

The binders studied in this work are produced by wet milling process at temperature 60–80°C at optimal pH level. All these conditions provide the milling process with critical concentration (max dilution) followed by suspension stabilization on the rheological principle, which is mechanical gravitation mixing. At these conditions, polydispersed granular composition as well as a low amount of bonded liquid is achieved. It is a determining factor if we speak about density (porosity), strength and shrinkage of the binder. Binding properties of the nanostructured binders (NB) are demonstrated when the dispersion medium is represented by inorganic acids, chlorides or sols. The latter are formed directly during the binder production process due to the interaction of the phases. In this case the system is usually modified by surface active agents and catalysts dissolved in the dispersion medium. Tweaking the acid-base characteristics of the solid phase of NB allows realizing different binding mechanisms. As a result, NB can be applied in the maximally wide range of building materials [10, 11 and other].

2. Experimental procedure

Particle size distribution in the materials was analyzed using the methods of laser granulometry. The microstructure of the samples was examined by means of scanning and transmission electron microscopy. Analysis of physical and mechanical characteristics of the finished materials was conducted using standard procedures described in the Russian normative literature.

In order to confirm the mechanism of hardening of the binder, chemisorption analyzer «Chemisorb 2750» connected to the gas quadrupole mass spectrometer «QMS-300» was used. The experiment aimed to compare the spectra of water after the temperature-programmed desorption (TPD) from the surface of the examined material.

The samples were preliminary burned in the muffle furnace at 500 °C for 3 hours in order to remove contaminants from the surface of the samples and water. Then, the samples were cleaned in the device «Chemisorb 2750» in TBD mode under the inert atmosphere (He as a carrier gas, flow rate – 20 ml/min) to a temperature of 500 °C at a heating rate of 10 °C/min. The samples were cleaned two times without cooling to the temperature below 100 °C in order to prevent adsorption of residual water from the carrier gas. For comparison, sand-based samples obtained by three different methods were taken: 1 – dry grinding of sand; 2 – sand ground in water and 3 – nanostructured binder (NB).

All studies were conducted using laboratory and analytical base of the Center of High Technologies of Belgorod State Technological University named after V.G. Shoukhov.

3. Features of nanostructured binder

It is known that hardening of binders is based on transition of silanol bonds to silaksan. However, conformation of these processes was impossible up to the present moment. To confirm the obtained data, the samples of binder were examined for formation of bonds on the surface of the comminuted materials using hemisorption analyzer.
There are 2 forms of desorbed water: lightly bound – with desorption peak 90-360 °C and tightly bound – with peaks in the region of 370 °C. Presence of lightly bound – physically sorbed water – is due to sorption of water by the surface functional groups, tightly bound water is formed by condensation of these functional groups. The intensity of two peaks is stronger for NB, and that indicates a higher content of functional silanol groups on the surface of the sample. Formation of functional groups on the surface of the samples leads to reactivity not only with water but also with other chemical compounds.

Investigation of nano-structure of the NB demonstrated the presence of nano-sized silica components (figures 2, 3). In order to eliminate the contribution of micron- and submicron-sized fractions of the polydisperse binder, the suspension of NB was centrifuged to exclude particles larger than 200 nm.

Centrifugation was carried out for 20 minutes at a speed of 5000 rpm. Next, the resulting centrifugate was analyzed by the dynamic light scattering using a UV-laser analyzer Malvern Zetasizer ZS. The parameters of the colloidal solution were selected from the manufacturer’s database for the silica and water as a solvent. The calculation of the distribution of colloidal particles was performed using the manufacturer’s software. Figure 2 shows particle size distribution of the centrifuged NB. The main distribution peak corresponds to the particle size of ~ 30 nm (figure 2).

**Figure 1.** Mass spectra of thermoprogrammed desorption of water obtained from the samples of sand ground by dry (1) and wet method (2), NB (3).

**Figure 2.** Particle size distribution of NB centrifugate.
The microstructure of NB is characterized by pseudo-uniform distribution of polydisperse particles of a size range from 10 nm to 100 nm of polyhedral morphology within the dispersion medium (figure 3).

![Figure 3. Morphology of nano-dispersed fraction of NB based on silica sand under SEM.](image)

Polydispersity was estimated by an independent method, based on the analysis of the scattering intensity of the mixture of different types of non-interacting particles (the software MIXTURE - IR RAS). The differential particle size distribution curves (normalized to the unity) are shown in figure 4. These binders are characterized by their bimodal distributions with a pronounced peak in the nano-scale region. The NB curve is shifted towards smaller sizes when compared to conventional high concentrated cementing suspension. Maxima of the distributions correspond to the values obtained for the average diameter of spherical nanoparticles.

![Figure 4. Particle Size Distributions of NB and Reference UDB.](image)
4. The application of nano-binders in cellular concrete

It became possible to use nanostructured binder as an active silica modifier and the main binder component for production of varying construction materials (figure 5).

The specificity of NB technology allows using a wide range of natural and industrial silica and aluminosilicate rocks as a base raw component. The choice of any given material can be made in view of the regional location of the minerals used, where the binder production is planned. That would allow organization of construction materials production on the NB base in remote regions relative to cement factories.

The main advantages of the nanostructured binder are low cost and high workability. The low cost is conditioned by availability and widespread distribution of raw materials for its manufacturing and, as a result, by reduced transportation costs, no energy costs are incurred for high temperature treatment of raw materials during binder production, it is also characterized by unlimited stock life. High workability occurs due to unique binder properties at low water demand and wide range of exploitation temperatures.

It was established that the application of the nanostructured binder as a modifying agent for autoclaved gas concretes results in improvement of macro- and microstructure of gas concrete before the autoclave treatment and intensification of phase formation under hydrothermal conditions. NB optimizes rheotechnological properties of cellular concrete mix, which provides a smooth intense process of gas evolution by increase of the mixture volume, reduction of swelling time, decrease of the thickness of interporous partitions while maintaining the required strength characteristics of the finished products. As a result of research compositions of autoclaved gas concrete for thermal insulating and construction and thermal insulating purposes with density brands D350-D500 and classes for strength B0.75, B2.5 – B5.5 were proposed.

![Figure 5. Applications of nanostructured binder.](attachment:image)
The specificity of the nanostructured binders allows recommending them as a basic binder for the production of thermal insulating and construction and thermal insulating cellular nonautoclaved concretes obtained by foaming. Foam concrete on the basis of NB has density of 300–900 kg/m³, compressive strength of 3–12 MPa, coefficient of thermal conductivity of 0.008–0.012 W/(m·K), coefficient of water vapor permeability of 0.23–0.14 mg/(m·h·Pa), moisture sorption of 6–10 mass.%, respectively. The use of NB in the manufacture of foam concrete allows improving technological and economic efficiency of the process due to a significant reduction of manufacturing time of foam concrete products with improved technical performance and thermal characteristics.

Application of NB allows obtaining materials with optimum cellular structure, which is characterized by evenly distributed, polydispersed, locked, deformed in the correct polyhedrons porous, with a glossy surface of the near-porous layer, divided with thin dense interporous partitions-walls. Reduction of porosity of an interporous partition-wall is proved by existence of nanodispersed particles in NB and in moulding systems on its basis. When using NB, the particles of the minimum sizes are located in the gaps between relatively large particles of the matrix system, and that promotes creation of a thin film of the binder on the surface of an air bubble.

5. Conclusion

Taking into consideration the development and rapid growth of monolithic and low cottage construction, cellular concretes are a perspective material for creation of effective walling. It has been revealed that the optimum grain structure, high polydispersion of a solid phase, rheological properties of the NB have a positive effect on formation of a rational cellular structure of heat-insulating concrete and its technical and operational characteristics.

Usage of a nanostructured binder when producing lightweight heat-insulating cellular composites allows carrying out the directed formation of the structure of cellular concrete. Obtaining a rational porous structure of heat-insulating materials is a fundamental task in production of cellular concrete. It influences functional indicators of the product quality, provides decrease in heat conductivity of the final material without considerable reduction of its strength characteristics.

Thus, with regard to the development and application of the new type of nanostructured binder and manufacturing technology in construction materials production, it is possible to reduce energy consumption for production of synthetic composites significantly, i.e. to produce raw mixes with qualitatively new energy requirements, which will provide objective conditions for the introduction of nanomaterials in industrial and civil engineering.

6. References

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