The development of nanostrured SiO_2 binders for application in cellular concrete

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Abstract

Nanotechnology can be used to create alternative eco-friendly non-portland cement binders. Using “top-down approach,” nanostructured SiO_2 binders (NB) with polycondensation-polymerization hardening were developed [1]. The proposed NB technology involves a mechano-chemical synthesis of NB in an aqueous environment.

NB is an inorganic multimineral polydisperse system that has predominantly aluminosilicate composition containing a nano-dispersed component (average size of 30 nm) in an amount of 2-10% and is characterized by adjustable rheological properties. Mechanical properties of NB depend on the composition of the dispersion medium, dispersion state of the surface coatings and solid particles (the colloidal component), the packing density, conditions of hardening and, especially, the parameters of nano-dispersed phase. Currently, NB can be manufactured using high-temperature firing (for refractory applications), but also using natural and/or autoclave curing.

The portland cement systems with 50% of nanodispersed NB demonstrated an increase of the compressive strength by 35% vs. reference. The cellular concrete based on NB has a compressive strength of 0.8-1.2 MPa depending on the density. Autoclaving and surface strengthening of NB based cellular concrete leads to the increase of the density and the mechanical strength by 5-20% and 200-400%, respectively. The developed NB concrete has an ultimate fire-resistance and even improves its strength at elevated temperatures.

Keywords: ultra-dense binders, nanostructured binders, silica, nanoparticles, cellular concrete.

1. Introduction

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 as well as that it asserts the enormous pressure on the ecosphere. To reduce the negative impact on the environment the reduction and more efficient use of portland cement in concrete is 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 [2,3]. In addition, the development of alternative to portland cement “green” eco-cements with fundamentally different mechanisms of hardening was proposed [1-4].

It is a challenging task to create a binder that can make a real commercial alternative to portland cement. The possibility of binders using polycondensation-polymerization “contact hardening” mechanism was predicted by Yung: "to manufacture a durable solid material a substance capable of surface hydration, i.e., the formation of a thin film of hydrated gel-like mass on the surface of the grains of powder, then at a sufficient proximity of the grains the possibility of formation of cemented "solid mass" can be realized [1].” However, neither Yung, who studied this matter on a number of different rocks, nor subsequent researchers realize this hypothesis. The polycondensation-polymerization hardening mechanism was realized in the nanostructured binders (NB) based on the technology of Ultra-Dense Binders (UDB) [4]. Fundamental research on a variety of UDBs and related materials (including chemically bonded ceramics and refractory concrete) was performed by Pivinskii and collaborators [4]. They pioneered the new type of high-performance ceramic materials based on quartz glass. Pivinskii formulated the principles of technology UDB such as wet super-fine milling at specific temperatures, liquefaction and subsequent stabilization [4]. The concept of UDB is based on the formation of inorganic polymers from the silicate and aluminosilicate natural rocks. Therefore, the proposed UDB model realizes the self-polymerization and contact hardening ability of these materials. The UDBs are manufactured by wet milling at elevated temperatures (60-80^{o}C) using the optimal range of pH, which tolerates the milling process at very high concentration of solids (i.e. at maximum liquefaction) followed by the rheological stabilization of the suspension using a mechanical gravitational mixing. This process results in a polydisperse grain structure of composite at a very low content of associated liquid, which is critical to achieve the ultra-high density (and so low porosity), high strength and low shrinkage of the binder.

Binding properties of UDB 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 UDB allows realizing different binding mechanisms. For example, the hardening of the most common UDB compositions based on silica and alumosilicates is mainly based on the polycondensation phenomena. In particular, the UDB binder based on silica is characterized by a continuous increase in strength due to crosslinking polycondensation with transition from silanol to siloxane bonding:

$$\equiv \mathrm{Si} - \mathrm{OH} \;+\; \mathrm{HO} - \mathrm{Si} \equiv \xrightarrow{T} \equiv \mathrm{Si} - \mathrm{O} - \mathrm{Si} \equiv \;+\; \mathrm{H_2O}$$

During the process of structure formation water is removed due to polymerization and formation of silanol bonds (Fig. 1). The process of curing or polycondensation of these new types of binders is rather complex and poorly understood. In one of the models the bond is due to the adhesion and attraction of particles and the other - the bond is realized through the formation of Si-O-Si bonds.

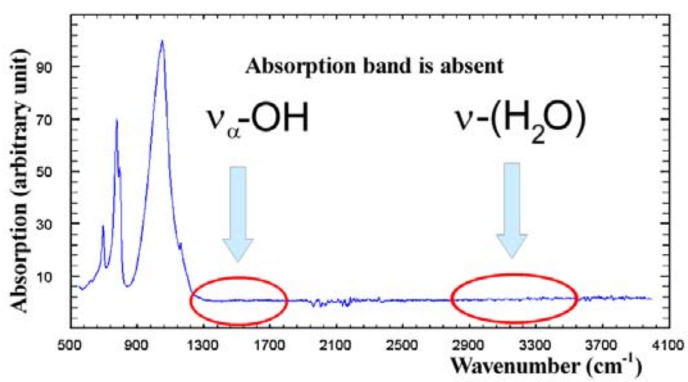


Fig. 1. IR spectrum of hardened UDB:
The absorption bands of occluded water (n-H_2O) and OH-group (n_a-OH) on silica-oxygen tetrahedron peaks are absent (the corresponding zones are marked on the spectrum).

It should be noted that the UDB technology has been used only for the production of refractories. Limited use of these systems is due to their inherent dilatant (shear thickening) properties, which significantly limits the compaction of mixtures based on UDB and, therefore, complicates the manufacturing technology/process. At present, this problem is solved by the complex modification of UDB. This allows controlling the structure of binder at the nanometer level and so adjusting its rheological properties. Maintaining a high concentration of solid phase, resulting nanostructured binder (NB) is highly fluid, stable in time system, which gives it a significant technological advantage. The presence of nanosized particles in the NB has a significant impact on the porosity reduction of the final product due to the effect nano-filler [2,3].

In NB, the nano- and micro-sized particles are located in the vacancies between the relatively large “structure-forming” particles of the matrix system. In the absence of nano-sized particles the gaps between the particles are relatively large resulting in excess volumes of the dispersion medium entrapped within the matrix phase and as a result in a matrix with larger capillary pores. Therefore, the use of nanoparticles helps reducing the viscosity of the NB mixture at equal values of water-solid ratios, or reduces the latter, while maintaining the same viscosity. As a result, the structure of the matrix phase of NB is optimized using three mechanisms: the structural-mechanical, electrostatic, absorptive-solvate (Fig. 2). Structural and mechanical effects on the UDB system are being implemented by introduction of an additional clay component. Specific structure of clay particles contributes to the creation of structural and mechanical barriers, which allows for very high stability of the layer of dispersion medium between the particles of the dispersed phase. Optimization of the structure through the implementation of the electrostatic and absorptive-solvate complexion is carried out using surface active agents [5,6].

The established regularities of NB suspension stability control allows, in the first place, to increase their sedimentation stability, to increase the volume concentration of the solid phase (which is common to all systems under study), and directed to adjust the rheological properties. Modification of the spatial structure of the resulting Nanostructured Binder (NB) by incorporation of nanoparticles of a certain size and shape and complex effects of surface active agents have a positive effect on the microstructure and performance of the material, as well as simplify the technology of NB.

At present, the effect of a nanoscale mineral modifiers such as layered alumosilicate minerals of kaolinite $Al_2Si_2O_5(OH)_4$, montmorillonite $(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)\cdot nH_2O$, talc $Mg_3Si_4O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, antigorite $(Mg,Fe^{2+})_3Si_2O_5(OH)_4$, vermiculite $(Mg,Fe^{3+};Al)_3(Si,Al)_4O_{10}(OH)_2\cdot 4H_2O$, and others, composed of the crystalline structures with packets of the tetrahedral Si-O and octahedral (Al,Mg)-O layers. In addition, the optimal range of compositions and technological regimes for NBs based on the raw materials of different origins which may not show the effect of hetero-coagulation.

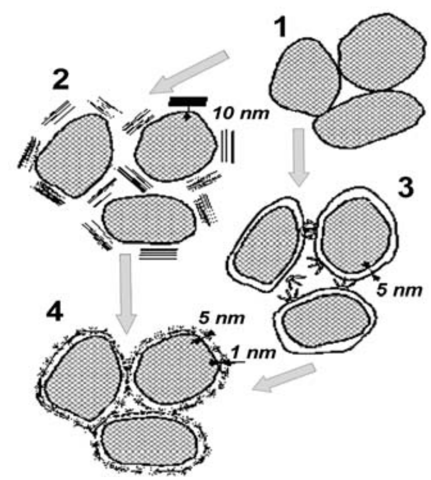


Fig. 2. Scheme of optimization of matrix phase structure of nanostructured binder:
1 – original system; 2 – the formation of structural and mechanical barriers; 3 – the formation of electrostatic and absorptive-solvate layers; 4 – the formation of binder matrix structure.

2. Nano-Dimensional Components in Nanostructured Binder

Investigation of nano-structure of the NB demonstrated the presence of nano-sized silica components (Figs. 3, 4). In order to eliminate the contribution of micron- and submicron- sized fractions of 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. Fig. 3 shows the particle size distribution of centrifuged NB. The main distribution peak corresponds to the particle size of ~ 30 nm. These dimensional parameters are confirmed by the analysis of nano-scale structure of NB using Transmission Electron Microscope (TEM) JEM-2000 FXII, Fig. 4.

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 (Fig. 4).

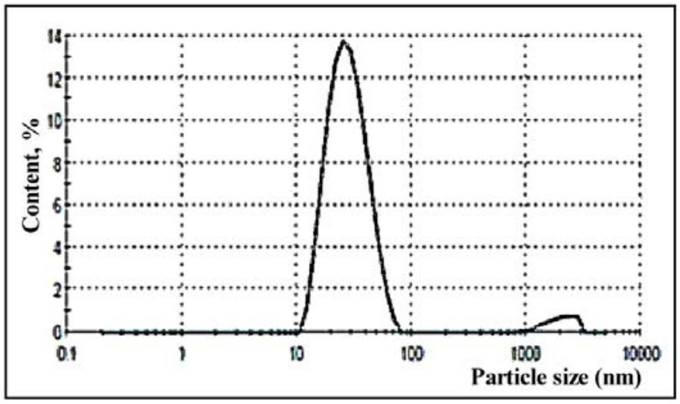


Fig. 3. Particle size distribution of NB centrifugate

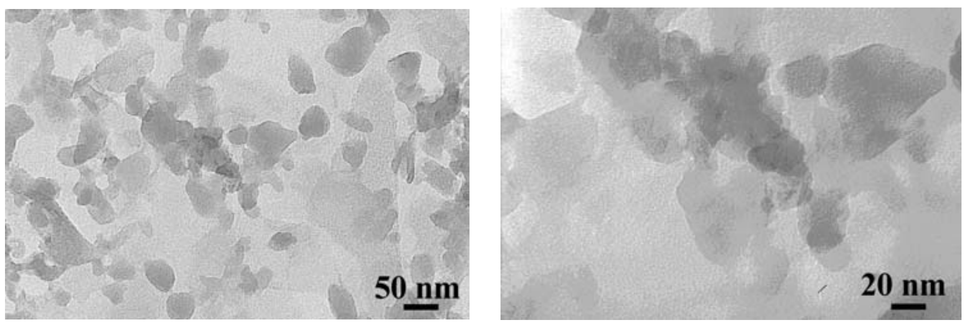


Fig. 4. Morphology of nano-dispersed fraction of NB based on silica sand under TEM

As an independent method for evaluation of dimensional parameters of nano-scale structures of NB, the Small-Angle X-Ray Scattering (SAXS) method was used. SAXS is a fundamental method which to provide structural information on inhomogeneities of the electron density with characteristic dimensions at nanoscale. The intensity of small-angle scattering, I is defined as following:

$$I(s) = (\Delta \rho)^2 \int_{R_{min}}^{R_{max}} D_V(R)\, m^2(R)\, i_0(sR)\, dR$$

here, with the assumption of sphericity of the scattering objects:

R - radius of the sphere;

R_{min} and R_{max} - the minimum and maximum dimensions of the inhomogeneities;

$i_0(x)=\{[\sin(x) - x\cos(x)] / x^3\}^2$ - the form factor of the sphere;

$m(R)=(4\pi/3)R^3$ - the volume of the sphere.

In calculating the $D_V(R)$ value R_{min} DV (R) Rmin was taken to be zero and the value of R_{max} was chosen individually for each case by the most successful fit. The result of research yielded the following values of average diameter of spherical nano-sized particles for NB -26 nm for the reference UDB - 54 nm.

To polydispersity was estimated by an independent method, based on an analysis of the scattering intensity of the mixture of different types of non-interacting particles (the program/software MIXTURE - IR RAS). The differential particle size distribution curves (normalized to the unity) are shown in Fig. 5. 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 UDB. Maxima of the distributions correspond to the values obtained for the average diameter of spherical nanoparticles.

Thus, the results obtained by SAXS, practically coincide with the dimensional parameters of nano-scale structures determined by TEM and UV-laser analysis.

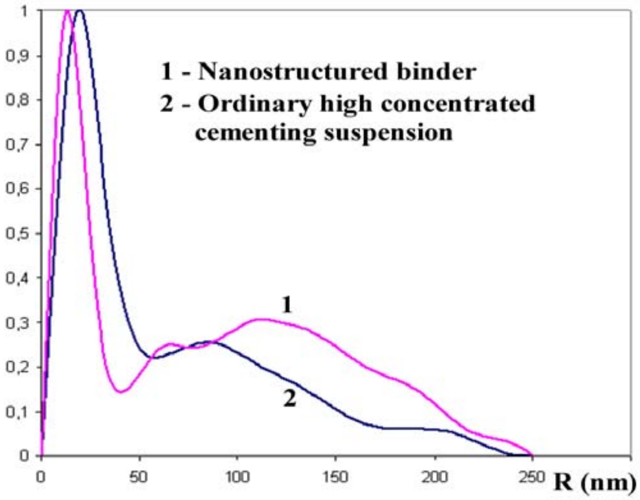


Fig. 5. The Particle Size Distributions of NB and Reference UDB

3. The Application of Nano Binders

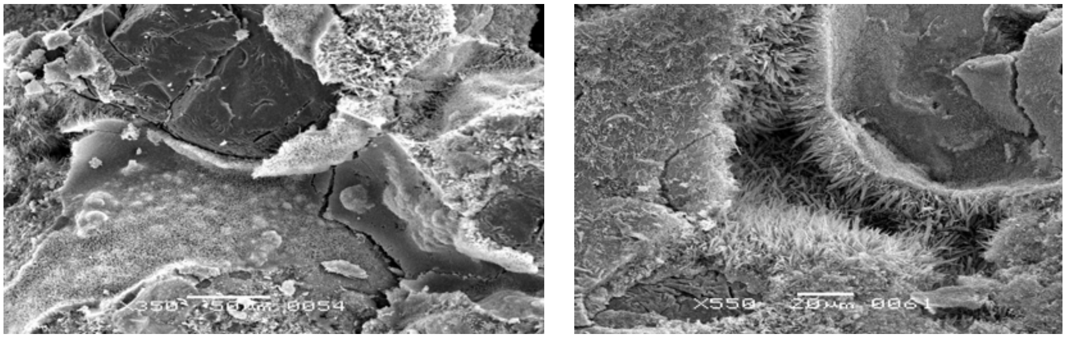
The main advantages of nanostructured binders are their performance characteristics, environmental compatibility, high adaptability, availability of raw materials and low cost. The NBs are characterized by low cost due to the availability and widest distribution of mineral raw materials for its production and, consequently, minimal transportation costs, saving for energy for high temperature processing and an unlimited shelf life. High flexibility of proposed technology is associated with unique performance characteristics at low water demand and a wide temperature range of application or operation.

Green eco-friendly NB may replace the portland cement in a number of applications. Currently, NB can be used as the active component in the refractory materials (which require high-temperature firing), but also in construction materials manufactured using natural and/or autoclave curing. The use of NB technology for the production of refractory materials can reduce the average density by 45%, and the thermal conductivity by 30%. The systems cured at natural conditions the increase of the strength by 20-40% is achieved.

The developed NB concrete has an ultimate fire-resistance and even improves its strength at elevated temperatures. At elevated temperatures, similar materials based on cement and autoclave silicate materials are destroyed, and the NB materials increase their strength by 8-10 times.
It is known that in spite of strong competition from modern construction materials (precast panels, aerated blocks, etc.) clay, silica or concrete brick materials are still in demand for the housing construction, especially in low-rise structures. Thus, despite the advantages of silica brick, the problem of obtaining a durable wall material based on autoclaved lime-silica mixtures remains relevant. One solution to this problem is the introduction into the matrix a certain amounts of nanoparticles obtained with NB technology.

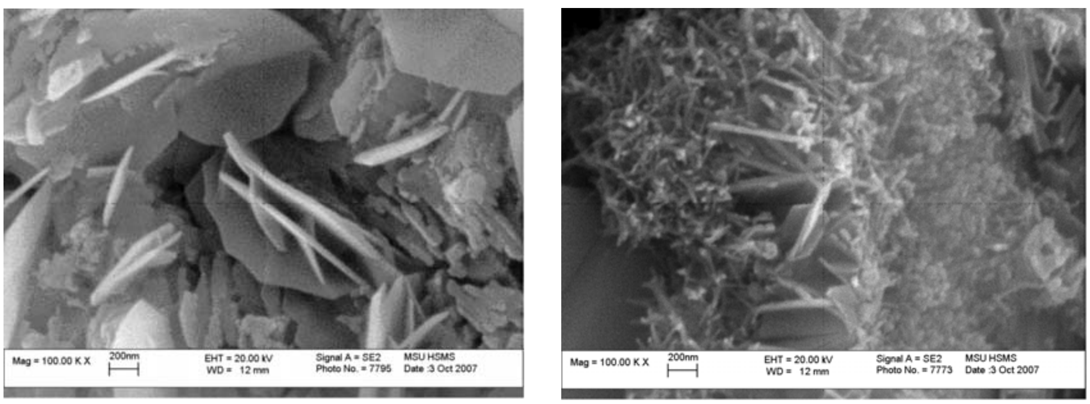
The analysis of the microstructure of autoclaved composites revealed that the experimental composition with the optimum dosage of NB has resulted in a denser cementitious matrix, while the standard samples are characterized by a loose and defective structure (as revealed by high-resolution SEM Supra 50, Fig. 6). This is explained by the high pozzolanic reactivity of NB which binds the portlandit and forms a dense portland-polymineral composite. In this case, the most of the newly-formed products are presented by fibrous aggregates of calcium hydro-silicates - the main carriers of the strength properties of autoclaved silicate materials.

The addition of NB into the portland cement system increases the strength up to 35%, while saving cement component by 50%. The increase in strength is due to the formation of a denser structure of cement paste (Fig. 7) [8]. The structure of cement paste with NB is characterized by a significantly smaller number of microcracks. Further investigation of the interaction of the NB with cement is a subject for further research.



a *b*

Fig. 6. Microstructural Features of Autoclaved Silica-Lime Composites:
a — standard composition; *b* — experimental composition with addition of nanodisperced binder (NB)



a *b*

Fig. 7. The new phases observed under SEM:
a) reference cement paste; *b)* cement paste with optimal content of NB

At the present time it is a very urgent task to reduce the thermal losses of buildings and reduction of material consumption. Addressing energy efficiency in construction calls for the intensification of research and design activities oriented on the creation and production of mainstream materials and structures with improved thermal properties.

As one of the options for practical implementation is a recently developed technology of cellular insulation material (foamed concrete) based on NB. Cellular concrete based on NB can be used as conventional insulating foam, and foam concretes for special purposes - heat-resistant insulating foam concretes.

The cellular concrete based on NB has a compressive strength of 0.8-1.2 MPa depending on the density. Autoclaving and surface strengthening of NB based cellular concrete leads to the increase of the density and the mechanical strength by 5-20% and 200-400%, respectively [9].

4. Conclusions

Production of thermal insulation, heat-insulating structural and fire-resistant materials based on NB was found to be economically sound and environmentally friendly. Thus, through the development and application of a new type of NB and incorporation of this novel material into conventional technology of construction/building materials it is possible to significantly reduce the energy consumption required for the production of artificial composites. New composites with qualitatively reduced energy consumption create the sound conditions for the incorporation of nanomaterials in industrial and civil construction.

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