THE APPLICATION OF NANOSTRUCTURED ZERO-CEMENT BINDERS IN FIRE-RESISTANT CELLULAR CONCRETES

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Abstract

Nanotechnology approach can be used to design zero-cement binders using “top-down” approach. The nanostructured SiO_2 zero-cement binders (NB) can be manufactured from SiO_2-based materials using mechano-chemical activation. The NB is an inorganic multi-mineral polydisperse system containing up to 10 % of nano-sized component (with an average size of 30 nm). The mechanical performance of NB depends on the composition of the dispersion medium, dispersion state of solid particles (the colloidal component), the packing density, conditions of hardening, and the concentration of nano-dispersed phase.

Normally, NB based composites are manufactured by high-temperature firing and used in refractory applications; however, this work introduces the NB composites cured at room temperatures (normal) and in autoclaves. The portland cement systems with addition of 50 % of 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 only slight increase of the density (by 5–20 %) and significant improvement of mechanical strength. The developed NB concrete has an ultimate fire-resistance and also improves the strength when exposed to elevated temperatures.

Keywords: cement binders, nanostructured binders, silica, zero-cement, contact hardening, cellular concrete

1. INTRODUCTION

The portland cement is a highly efficient hydraulic binder, however its production process is based on the substantial consumption of natural resources, such as raw materials and energy. To reduce the negative impact on the environment, the more efficient use of portland cement in concrete is required. Application of finely ground cements (FGC), low water demand binders (LWDB), Vicon cement [3,4], blended cements based on fly ash, granulated blast-furnace slag, microsilica, metakaolin is a clear movement towards ecologically friendly green cements [2-5]. In addition to these, the development of green eco-cement alternative to portland cement based on different hardening mechanisms was proposed [1–6].

It is a challenging task to create a binder that can make an alternative to portland cement. New type of binders with 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” [7]. However, neither Yung, who studied this matter on a number of different rocks, nor subsequent researchers were successful to realize this hypothesis. The polycondensation-polymerization hardening mechanism was realized in the nanostructured binders (NB) based on the technology of Ultra-Dense Binders (UDB) [5]. The study of variety of UDBs and related materials (including chemically bonded ceramics, CBC and refractory concrete) was performed by Pivinskii and collaborators [5]. They pioneered a new type of high-performance ceramic materials based on quartz glass. Pivinskii formulated the principles of technology UDB/CBC such as wet super-fine milling of SiO_2 based materials at specific temperatures, liquefaction and subsequent stabilization [5]. The concept of UDB is based on the formulation of inorganic polymers from the silicate and alumosilicate natural rocks. The proposed UDB model realizes the self-polymerization and contact hardening ability of these materials. The UDBs are manufactured by wet milling process at elevated temperatures (60–80 ^{o}C) using the optimal range of pH, which tolerates the milling process at a very high concentration of solids followed by the rheological stabilization of the suspension using gravitational mixing. This process results in a polydisperse grain structure of composite at a very low content of dispersion medium, which is critical to achieve the ultra-high density (and so a low porosity), high strength and low shrinkage of the binder.

Binding properties of UDB are demonstrated when the dispersion medium is represented by solutions of 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 the surface active agents and catalysts dissolved in the dispersion medium. Tweaking the acid-base characteristics of the solid phase allows different binding mechanisms to occur. 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:

$$\equiv Si — OH + HO — Si \equiv \rightarrow \equiv Si — O — Si \equiv + H_2O$$

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 binder is rather complex and poorly understood. In one of the models, the bond is provided by the adhesion and attraction of particles while the other model proposed that the bond is realized through the formation of Si-O-Si bonds.

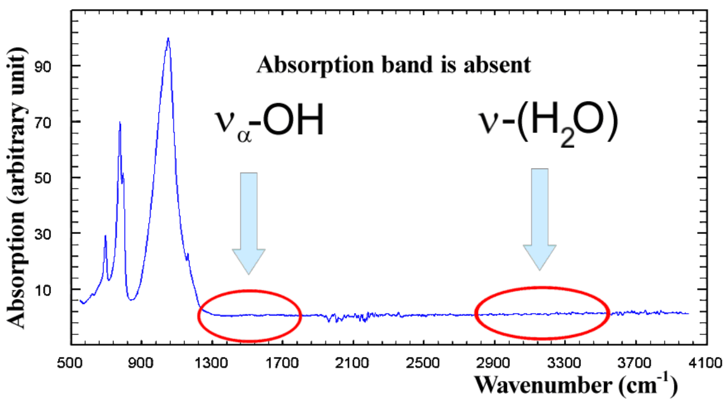

Fig. 1 IR spectrum of hardened UDB

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 previously 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 mixture based on UDB/CBC and, therefore, complicates the manufacturing process. At present, this problem is solved by the complex modification [8-10]. This allows controlling the structure of binder at the nanometer level and so adjusting its rheological properties. Maintaining a high concentration of solid phase, results in formation of nanostructured binder (NB), which is highly fluid, stable system. 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 [1, 9-11].

In NB, the nano-, micro and macro–sized particles are located in the vacancies between the relatively large structure-forming particles of the matrix. 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 and resulting in a matrix with larger capillary pores. Therefore, the use of nanoparticles helps reducing the viscosity of the NB mixture at certain water-solid ratio, or reduces the latter, while maintaining the same viscosity.

At present, the effect of a nanoscale mineral modifiers such as layered alumosilicate minerals of kaolinite $Al_2Si_2O_5(OH)_4$, montmorillonite $(Na, Ca)\cdot 0,3(Al, Mg)_2Si4O_{10}(OH)\cdot nH_2O$, talc $Mg_3Si_4O_{10}(OH)_2$, pyrophyllite $Al_2Si_4O_{10}(OH)_2$, antigorite $(Mg, Fe^{2+})\cdot 3Si_2O_5(OH)_4$, 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 was investigated [10].

2. NANO-DIMENSIONAL COMPONENTS IN NANOSTRUCTURED BINDER

Investigation of nano-structure of the NB centrifugate demonstrated the presence of nano-sized silica components (Fig. 2). It was observed that the main distribution peak of NB corresponds to the particle size of ~30 nm. The nano-scale structure of NB was confirmed using Transmission Electron Microscope, Fig.2, left. 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.2, right).

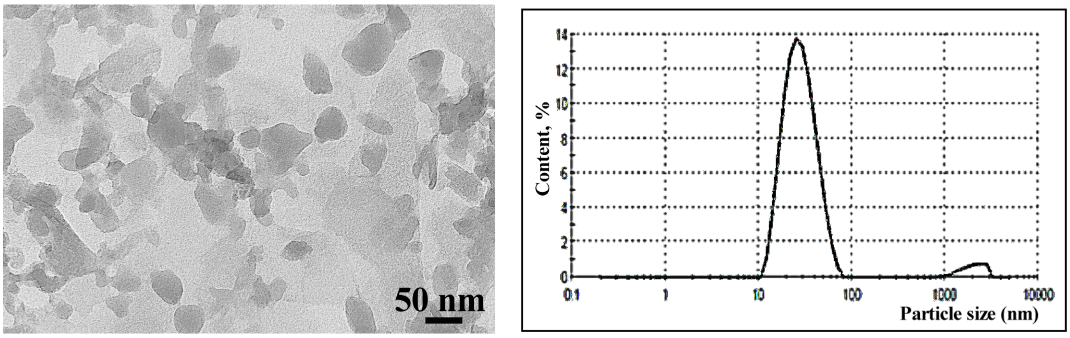

Fig. 2 Morphology of nano-dispersed fraction of NB based on silica sand under TEM (left) and particle size distribution of NB centrifugate (right)

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 have low costs due to the availability and wide distribution of raw materials and, consequently, minimal transportation costs energy saving due to elimination of high temperature processing and due to virtually unlimited shelf life. High flexibility of proposed technology is associated with the unique performance characteristics at low water demand and a wide temperature range for application or service.

Green eco-friendly NB may replace the portland cement in number of applications. Currently, NB can be used as an active component in the refractory materials (which required high-temperature firing), but also in construction materials cured in natural conditions or by autoclaving. The use of NB technology for the production of refractory materials can reduce the average density by 45 % and the thermal conductivity by 30 %. For the systems cured at natural conditions the increase in the strength by up to 20–40 % was achieved.

The developed NB concrete has an ultimate fire-resistance and even improves its strength at elevated temperatures. At elevated temperatures, reference materials based on cement and autoclave silicate materials are destroyed, however 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 buildings. Thus, despite of many advantages of silica-lime bricks, the problem of obtaining a durable wall material based on autoclaved lime-silica mixtures remains relevant. One solution to improve durability is the addition of nanoparticles obtained with NB technology to silica-lime compositions.

The addition of NB into the portland cement system increases the strength up to 35 %, while saving the cement component by 50 %. The increase in strength is due to the formation of a denser structure of cement paste [8-10]. 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 portland cement is a subject for further research.

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 development 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 (foamed concrete) based on NB. 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]. Cellular concrete based on NB can be used as conventional insulating foam, and foamed concretes for special purpose such as insulating foam concrete.

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 materials such as cellular concrete it is possible to significantly reduce the energy consumption required for the production. New green zero-cement composites with significantly reduced energy consumption create the sound conditions for the incorporation of nanomaterials in industrial and civil construction.

ACKNOWLEDGEMENTS

Authors acknowledge the support of RAS Institute of Crystallography, Moscow with the SAXS studies and the Department of Materials Science, Lomonosov Moscow State University for investigation using high-resolution SEM.KS gratefully acknowledges the financial support from Ministry of Education and Science of the Russian Federation, Grant 14.132.21.1702, Strategic Development program of Belgorod State Technological University named after V.G. Shoukhov; Russian Foundation for Basic Research, Agreement 12-08-97603, and Grants 16.740.11.0770, 14.B37.21.0930, Government Contract 3.4601.2011.

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