World Applied Sciences Journal 25 (1): 119-123, 2013
ISSN 1818-4952

DOI: 10.5829/idosi.wasj.2013.25.01.7032

Prospects of Application of Zero-Cement Binders of a Nonhydration Hardening Type

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Submitted: Aug 19, 2013; **Accepted:** Sep 20, 2013; **Published:** Sep 24, 2013

Abstract: The paper presents the evolution scheme of zero-cement binders of nonhydrational hardening type. That scheme allows determinining the prospects of using these systems. It also describes the process of obtaining binders, main characteristics of highly concentrated binding systems (HCBS) with different methods of modification and nanostructured binders (NB), their distinctive features. It was stated that NB in the production of materials for various purposes can be used as an additive to the modifier and the main binding component, which improves the main technical and operational characteristics of based on it composites. The positive effect of NB on the processes of structure formation was stated with a comparative analysis of the cellular microstructure of non-autoclaved cellular composites with application of NB and silica slurry.

Key words: Nanostructured binder · Cellular concrete · Autoclaved materials · Structure formation

INTRODUCTION

Nowadays cement is one of the mostly wide-spread binders that are used in manufacture of bilding materials. But in connection with negative influence of cement production on ecology, energy intensity of technological process, lack and high price of raw meterials in certain regions and countries thare is a necessity in development of new alternative binding systems. NB can be considered as one of them. Basic raw materials for manufacturing of nanostructured binder are siliceous and aluminosilicate natural and anthropogenic rocks.

Similar binders have been received before, but their application was mostly for production of materials for special purposes. Scientific researches of Y.E. Pivinsky were fundamental for development of HCBS and based on it materials (including unfired ceramics and refractory concretes). Limit possible areas of HCBS application for manufacture of building materials can be explained by specific rheological charcteristics of the system, notably by insufficient sedimentation stability which is unfavorable for process of formation based on it materials, high dilatancy, low mechanical strength after thermal treatment [1].

Analysis of theoretical data allowed designing an evolutional scheme of nonhudrational hardening binders, to reveal their basic advantages and disadvantages, areas of application (Table 1).

Researches of scientific school of BSTU named after. V.G. Shoukhov resulted in establishment of mechanisms of regulating the rheological properties and aggregative stability of HCBS of silicate and aluminosilicate compositions by directional spatial structure optimization [2, 3].

Main Part: Nanostructured binder is the inorganic polydispersed and polymineral system with high concentration of active solid phase and concentration of nanodispersed component in amount of 3–15 %.

Percentage rating of nanodispersed particles in the System directly depends on the type of used raw material.

Production of HB is based on HCBS's directional spatial structure optimization through the introduction of modifying additives. This process is based on the detected ability of traditionally considered as inert siliceous and aluminosilicate materials (quartzite, quartz sand and alumina-silicate rocks) to form a binding suspension as a result of mechano-chemical activation in industrial grinding units [4].

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Table 1: Evolution of non-hydration zero-cement binders

	Dry milling binder	Mechano-activation of wet milling binder	High concentrated binder sysmems (HCBS)	Complex HCBS	Plasticized HCBS	Modified HCBS	Nanostructured binder (BN)
Technology	Fine grinding of rocks	Silica-based cementation material obtained in alkaline medium at hydrostatic pressure	Single-stage wet milling at high temperature and critical concentration and additional stabilization when gravitation mixing	One-component system based on aluminosilicate raw with tailored properties	HCBS including clay as a plastifying agent (2-10% by weight)	HCBS + organomineral additive	Three-dimensional structural optimization of matrix phase of HCBS+ plastifying agent+ organomineral additive
Application	Fired materials exposed hydrothermal treatment, ceramic concrete	Refractory materials produced by compacting method	Infill ceramic concrete, silica-based ceramics items without preroast	Molded and unmolded refractory products	Molded and unmolded refractory products and binders for fired construction materials production	Binder for wide range of construction and specific-purpose materials	Binder for production materials with controlled properties and improved performances
Advantages	Non-hydration binder (10 MPa compressive strength)	Increased strength (54 MPa) and low porosity (16%) materials after hydrothermal treatment	High strength (50-90 MPa), low porosity (8,5 – 12%) due to silicic acid formed after milling which has cohesive properties. Fewer alkaline additives percentage	Increasing of the system operating time due to its chemical and mineral composition	Increased sedimentation stability of HCBS, possible change of the rheological system type. Volume constancy during drying process	High workability, expanding of application field	High sedimentation stability at smallest viscosity. Possibility to control binder structureinmicro-andnanoscale
Disadvantages	Reasonable strength the samples obtained by compactible method can be achieved only after hydrated lime adding. The synthesis mechanism upon this hypothesis not fully discovered	Synthesis conditions: hydrostatic preassure; temperature 2000 °C, low processability	Dilatation is a complicating factor for production process	Lack of sedimentation stability, high viscosity, chemical composition unavailability to refractory materials	Low water resistance of items and low workability of molding mixture	Low sedimentation stability	It is not studied now
Researchers	V. N.Young	G.V. Ferbern	Y.E. Pivinsky	Y.E. Pivinsky	Y.E. Pivinsky A.V. Cherevatova	A.V. Cherevatova N.A. Shapovalov	V.V. Strokova A.V. Cherevatova N.A. Shapovalov

Production of binder is usually carried out by wet milling in a ball mill with stepwise loading grinding material. Selecting of the concentration on the first grinding step was carried out with view to the starting material packing factor and its other characteristics and overall dimensions of the mill. All amount of liquid that was calculated according to the final concentration of the suspension is usually administered at the first grinding step. The dispersion thus should provide the average particle size that at least 10-20 times less than the particle size of raw materials introduced at the next load of material. Optimum results can be obtained if after the first stage of grinding fineness, characterized by a considerable (20-40 %) content of solids fraction less than 5 microns is achieved. In this case the suspension is like a condensed that speeds up the subsequent grinding after the introduction of the next portion of the raw material. During the stepwise loading of material with increasing volume concentration the effective grinding body density decreases.

Gradual decrease of the volume content of the fluid and increase of the friction leads to the rise of temperature of the system, which largely determines its rheological properties in the grinding process, as well as the characteristics of the finished binder. As the temperature raises the overall viscosity of the system decreases, its fluidity increases, there is the effect of dilatancy, which allows carrying out the grinding process at elevated concentrations.

After the preparation of the binding system, its complex spatial modification is held in order to obtain NB. Modification consists in sequential introduction of the plasticizing additive-highly dispersed kaolin clay (Mark LT-1, the content of Al_2O_3 – 35-37%, SiO_2 – 48-

50%), with 33% humidity in an amount of 1.5-5% and complex deflocculation agent in an amount 0.02-0.1% by weight of binder based on the dry substance.

The principle of optimization of the matrix phase structure is based on a complex display of the three mechanisms of influence on the system: the structural-mechanical (the introduction of a clay component), electrostatic and adsorption-solvation (the introduction of a complex deflocculant). Prospects of application of complex deflocullants consisting of sodium tripolyphosphate and superplasticizer SB-for binding systems based on silicate materials were determined. High efficiency of complex additive ia s result of summation of different influence mechanisms of components on the dispersed phase binder. For mineral additives such as sodium silicate or sodium tripolyphosphate dilution is caused by the formation of the electric double layer (EDL), changes in pH of the dispersion medium of HCBS, increased value of zeta potential, but for the organic additives (such as SB-5) their adsorption on the surface of the particles and hydrophilization due to the presence of polar groups is typical.

Thus, the complex effects of deflocullants and plasticizing component (clay fraction), the presence of a rational ammount of nanoparticles has a positive influence on the processes of structure formation, rheological characteristics of the system and the technical and operational properties of the materials produced on its basis.

Demonstration of NB's binding properties is substantiated by the presence of inorganic acids, chlorides (or sols) as a dispersion medium, which is formed directly during the preparation of the slurry due to the interaction of phases. In this case, the system is usually modified by fluxing additives and dissolution catalysts. Depending on the acid-basic characteriatics of the NB solid phase the mechanism of demonstration of its binding properties can be different. So, the most common systems of silica and silica-alumina compositions hardens mainly by polycondensation effects. Particularly, binders on the basis of silicate raw materials during heat treatment is characterised by steady icrease of strength, that is explained by formation of polycondensation matching with transition of silanol bond into siloxan:

$$\equiv Si - OH + HO - Si \equiv \xrightarrow{t} \equiv Si - O - Si \equiv + H_2O$$

Analysis of the characteristics of binders, obtained from different types of raw quartz material, demonstrates the effectiveness of using these rocks as a raw component in the production of NB (Table 2).

Currently, a number of materials with NB were developed. In particular, compositions of autoclaved silicate material pressed with application of NB as a modifier were [5, 6]. The use of nanostructured modifier (NM) increases the compressive strength of the composite by 1.5 times, that allow producing effective high-porous products with enhanced durability, as well as compositions of colored silicate materials with improved color stability during prolonged inpact of external natural and anthropogenic environmental factors.

Composite binders with application of NB were developed. The use of HB promotes binding activity to 35%, while saving clinker component up to 50%. Increase the strength after the introduction is explained by the formation of a denser, defect-free cement stone structure [7, 8].

The specificity of nanostructured binders makes it possible to recommend them for the production of heat-insulating and structural heat insulating cellular concretes of different hardening type [9]. The use of HB in the production of cellular nonautolaved materials helps to simplify, reduce the cost and increase the efficiency of the technological process of their manufacturing due to significantly reduced period of hardening of cellular concrete products with improved thermal characteristics [10, 11]. Due to the fact that cellular concrete has recently been widely used in the construction in Russia and abroad [12-14], we are going to pay more attention to that material.

Table 2: Characteristics of binders

	Characteristics of binders			
Type of binder	Density, kg/m^3	Total specific surface,[1] m^2/g	Volume concentration of the solid phase	Flow type[2]
Nanostructured binder	2120	6,1	0,76	T–N
Highly conentrated binding systems	2102	5,1	0,68	D

[1] Results were obtained on instrument SoftSorbi-II ver.1.0 in BSTU named after V.G. Shoukhov.

[2] T – thixotropic; N – newtonian; D – dilatant.

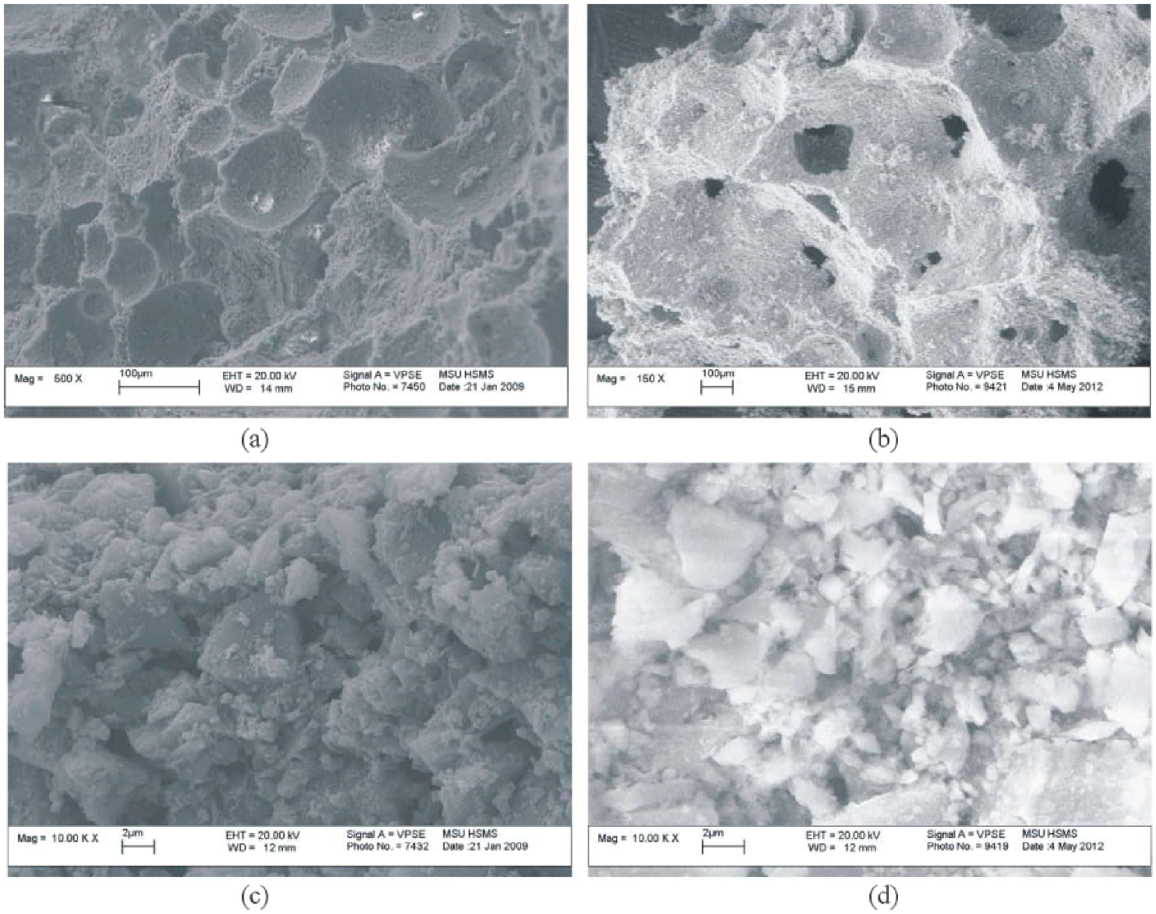

Fig. 1: Cell concrete on the basis of: a, c – nanostructured binder; b, d – quartz slurry

Management of processes of structure formation is a fundamental factor in the production of heat-insulating cellular materials. The application of NB helps to obtain composites with optimal cellular structure, which is characterized by uniformly distributed, closed, polydisperse pores with a glossy surface of pore-surrounding layer and separated by a thin, dense, identical in profile interporous partitions. Reducing porosity of interporous partitions is justified by polydispersity of a binding system, the presence of a rational quantity of nanosized particles in NB and in forming systems based on it (Fig. 1a, c).

In order to study the effectiveness of NB as a binder for cell concrete and positive influence of nanosized components on system structure formation processes, a comparative analysis of the microstructure of non-autoclaved foamconcretes based on NB and silica slurry obtained by the appropriate concentration of raw materials, but without the observance of technological and time parameters.

Foam concrete on the basis of NB differs by fierce cellular structure with sharp edges between the individual pores. Materials obtained by foaming the suspension of silica porosity have weakly traced porosity and significant defects of the structure. This is explained by a low polydispersity, the lack of nanoscale particles. In connection with the failure to comply with technology of NB production, lack of stepwise loading during mechanical activation of quartz suspension, binding properties are slightly manifested in the system. Quartz particles in the slurry are characterized by a size of 300 nm. Low concentrations of colloidal component lead to the increased hardening time, low binding activity and low aggregate stability of binding system (Fig. 1 b, d).

During production of cellular composites using NB particles with the lowest size are arranged in the gaps between the relatively large particles of the matrix systemthat promotes creating a thin film of mineralizer on the surface air bubble. This allows obtaining a material with a low bulk density and high strength characteristics.

Summary: The main advantages of NB are its low cost and high manufacturability. The low cost is explained by the availability of mineral raw materials for its production and, as a consequence, minimal transport costs, lack of energy in the high-temperature processing of raw materials in the production of binder and its unlimited shelf life.

Development and application of a new type of zero-cement binder and its use in the manufacture of building materials for various functionalities will significantly reduce the energy intensity of production of artificial composites and that will result in obtainment of raw mixes with a qualitatively new energy state, which would create the objective conditions for the introduction of nanomaterials in civil and industrial construction.

CONCLUSION

The mechanisms of regulation of the rheological properties and aggregate stability of HCBS of silicate and aluminosilicate compositions were stated. This research proposed principles of optimization of the structure of the matrix phase on the basis of a comprehensive display of three mechanisms of influence on the system: structural and mechanical, electrostatic, adsorption-solvation. All of that make it possible to extend the use of HCBS, to develop and identify promising applications NB as active siliceous modifying additive-nanostructured modifier (NM) and the main binder component-nanostructured binder (NB) in the production of materials for various applications.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Education and Science of the Russian Federation, the strategic development program of BSTU named after V.G. Shoukhov, state task 3.4601.2011, in the framework of the Grant of President of Russian Federation for support of young scientists MC 6170.2013.8.

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