# PRINCIPLES OF CREATING NANOSTRUCTURED BINDERS BASED ON HCBS

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The combined interaction of factors is presented determining the principles of creating nanostructured binders based on highly concentrated ceramic binder systems (HCBS). Presence in HCBS of particles at a nano-level, and also intentional optimization of the spatial structure of this system has a comprehensive favorable effect on structure, rheotechnological properties of HCBS, and the technical and operating properties of materials prepared based upon them.

**Keywords:** HCBS, nanostructured binder, nanoparticles, matrix phase, synergism effect, complex deflocculants.

Creation of a new generation of high quality materials is impossible without controlling the process of structure formation at the micro- and nanolevel. Practical interest in nanosystems in the area of material science of ceramics and refractories is due to the possibility of creating rational composite structures as a result of their significant modification with a change-over to the nanolevel accompanied both by a fundamental change in the properties of traditional materials and the creation of neocomposites.

However, use of nano-objects in existing technology is connected with certain difficulties, including the following. As particle sizes are achieved close to the nanolevel, there is a considerable reduction in their packing density, and preparation of dense materials is accompanied by considerable shrinkage. A more promising version from a technical point of view may be consideration of the presence in a composite of a small content of nano-dispersed particles, an example of which is a highly concentrated ceramic binder systems (HCBS). In addition, currently in view of the increasing requirement for effective binder substances, including binders of the unhydrated hardening type and materials based on them, exhibiting high operating properties, it is important to develop a new class of nanostructured binders with a capacity to partly or completely replace cement in molding systems over the maximum broad range of material classes.

HCBS technology is one of the newest areas in contemporary material science, whose theoretical basis was developed by Yu. E. Pivinskii. HCBS are mineral aqueous suspensions, obtained primarily by wet grinding of natural or technogenic silica, aluminosilicate or other materials under conditions of a high solid phase concentration, increased temperature and limited dilution. These conditions on one hand promote “production” in a system of a specific amount of nanoparticles (gel, obtained by dispersion), and on the other hand provide mechanical activation of particles of the main solid phase. Solidification of these systems and their strength are based predominantly on a contact-polycondensation method. In view of this in creating HCBS the task was resolved of realizing under industrial conditions a capacity for the original raw materials for spontaneous polymerization structure formation [1, 2].

The limited application of these systems is due to the dilation properties inherent for them, that considerably reduce the possibility of choosing a compaction method for a molding mix based on HCBS, and complicate the production technology for objects. The problem may be resolved by obtaining new theoretical and experimental data about the mechanisms of mechanochemical activation and the role of deflocculants in stabilizing the nanosystems developed, establishing features for regulating the rheotechnological properties of HCBS for their intentional complex modification, and also revelation of features of structure formation kinetics and optimization of nanosystems taking account of the method for object manufacture.

Recently the fundamental possibility has been demonstrated of obtaining refractory binders of a mixed type based on highly concentrated silica binder suspensions of quartz sand with addition of refractory clay [3]. On the basis of morphostructural features of the formation of nanosize

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HCBS particles and clay mineral particles, and also inorganic and organic modifiers, creation has been proposed for an aggregative-stable medium by direct optimization of HCBS composition.

It is well known that clay of an incomplete stage of mineral formation with a high content of x-ray-amorphous substance in nature is a natural nanosystem. The content in clay of particles with a size of less 5 mm reaches 60%. Features have been established for regulating rheological properties and the aggregative-stability of HCBS of silicate and aluminosilicate compositions. A principle has been proposed for plastifying HCBS as matrix systems, making possible to change their rheological properties from dilation to thixotropic as a result of introducing a very fine clay component.

The principle is based on additional introduction into HCBS of a clay component in an amount of 2 – 10%. Here there is change in rheological type of system from dilation to dilation-thixotropic and then to thixotropic. An increase in sedimentation stability of HCBS, provides high volume constancy both in the drying stage and during heat treatment. Presence of an optimum amount of nanoparticles makes it possible to improve the rheotechnological properties of molding systems, and leads to an increase in mechanical strength in the stages of structure formation and drying. In addition, the optimum nanoparticle content predetermines a marked increase in strength at 300 – 400°C below the sintering temperature of the original materials, makes it possible to form fine porosity, and as a rule an impermeable microstructure.

The possibility has been established of regulating the rheological properties and aggregative-stability of highly concentrated mineral suspensions by means of deflocculants. An effective complex organomineral additions has been developed, consisting of sodium tripolyphosphate and a superpastifier SB-5 [4, 5]. Use of complex organomineral additions makes it possible in fact to reduce by a factor of two the moisture content of molding systems based on HCBS and increase their rheotechnological quality indices. Due to this there is a reduction in porosity of the finished objects, and an increase in their physicomechanical properties.

The mechanism of the plastifying action of complex additions, within whose composition there is SB-5, includes the following: molecules of the addition are adsorbed at the surface of particles, forming a monomolecular layer; adsorption of SB-5 at the surface of particles provides interaction forces between systems of aromatic rings of the additive and the surface of particles. Since the addition is an anion-active substances, the charge of the particle surface becomes more negative. It should be noted that the $\eta$-potential of complex additions increases significantly more than for individual components. This leads to an increase in the force of repulsion. This promotes formation of hydrate layers around particles as a result of the presence of hydrophyillic groups within the additive molecules.

These reasons give rise to the effect of synergism, i.e. reinforcement of the effect of components with their combined introduction. As a result of this forces of repulsion start to be exhibited over molecular forces of attraction, which gives rise to a combined effect of adsorption-solvation and electrostatic factors of aggregative-stability. A reduction in coagulation contact energy to values comparable with energies for thermal movement, leads to a total aggregative-stability for this system, peptization of aggregates to primary particles, and a change the rheological nature of the flow of suspensions with Newtonian structuring.

A principle is proposed for optimizing the structure of the matrix system (on the example of HCBS) based on combined development of three mechanisms of action for the system: structural-mechanical, electrostatic, and adsorption-solvate. An example of structural-mechanical action is a system in this case has been realized with additional introduction of a clay component into the HCBS.

The specific structure of clay particles promotes creation of a structure-mechanical barrier, that makes it possible to provide high stability of interlayers of a dispersed medium between particles of dispersed phase. The principle of optimizing the HCBS structure as a result of realizing two reaction mechanisms in a system (electrostatic and adsorption-solvate) has been proven, as already indicated above, in the development of complex deflocculants consisting of sodium tripolyphosphate and superplastifier SB-5. With complex modification of clay and an organomineral addition particles of clay minerals are concentrated only in the contact zone, and the optimum amount of clay component is established within the limits of 2 – 5%. In fact, on introducing deflocculants there is peptization of the surface of both the clay component and of the suspension particles. This makes it possible to "close" the surface of the solid phase of the system with the least amount of clay particles. A proposed scheme has obtained practical confirmation in analyzing the microstructure of suspensions.

Realization of the theoretical principles was carried out in model experiments. It has been established that this mechanism of spatial modification makes it possible to increase the rheotechnological quality of HCBS and in fact to reduce by a factor two the moisture content of molding systems based on HCBS, i.e. from 7.6 to 4.0 – 3.8%. As a result of this there is a marked increase in the mobility of raw material mixture, a reduction in the porosity of finished objects, an increase in their physicomechanical and operating characteristics, that has been demonstrated with use of this mechanism in technology for producing heat-resistant foam concretes, ceramic concretes and fine ceramic systems.

Ceramic concrete mixes of silica and aluminosilacte compositions, having within their composition a complex organomineral addition, have high operating properties. The porosity is reduced by 30%, and the ultimate strength in compression is increased by 50 – 60% compared with these indices for industrial analogs. Due to this effect ceramic concrete mixes with a complex addition exhibit higher thermomechanical properties, the temperature for the start of their deformation under load is higher by 40 – 60°C, than for factory analogs. This material is more resistant to corrosive action of media under service conditions.

The features established of regulation of the aggregative-stability of the HCBS system makes it possible first to increase their sedimentation stability, increase the volume concentration of solid phase (this is common for all of the test systems studied), and also to regulate the rheological properties.

Presence in HCBS of nanoparticles, optimization of the spatial structure of these systems based on the example of HCBS due to additional introduction of nanoparticles of a certain size and shape (clay component), and combined action of deflocculants, has a comprehensive favorable effect. The latter concerns both the microstructure and production aspects of HCBS manufacture and also the technical and operating properties of the materials prepared on a basis of them.

Practical expansion of the field of use of HCBS, based on intentional modification of the surface of a dispersed phase with the aim of increasing the aggregative-stability, opens up broad potential for developing and realizing energy saving technology, that is an undoubted priority in the current period of development of industry within Russia. Results of these studies extend to many forms of materials and objects.

Thus, as a result of the development and use of a new type of nanostructured binder the possibility arises of a marked reduction in energy content of producing artificial composites, i.e. to prepare raw material mixes with a qualitatively new energy state, that creates subjective conditions for introducing nanotechnology into the production of ceramics and refractories.

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