Refractories and Industrial Ceramics *Vol. 48, No. 6, 2007*

SCIENTIFIC RESEARCH AND DEVELOPMENTS

NANODISPERSE SILICA AND SOME ASPECTS OF NANOTECHNOLOGIES IN THE FIELD OF SILICATE MATERIALS SCIENCE. PART 1

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Translated from *Novye Ogneupory*, No. 11, pp. 44 – 55, November, 2007.

Original article submitted August 14, 2007.

Some general concepts concerning nanosystems, characteristics of their dispersions, and the main ways for producing nanoparticles are considered. Main data on the silica-water system are presented. Recent information on the fabrication, properties, and use of various kinds of nanosilica, which is a leader in the world market of nanomaterials, is considered as applied to the processes of production of ceramic, refractory, and building materials. It is shown that the VKVS dispersion medium is a composite nanodisperse system.

Objects of nanosize scale (10^{-7} – 10^{-5} cm, 0.001 – 0.1 μm or 1 – 100 nm) have attracted much interest in the recent years. From the standpoint of the history of development of science we can see that the events that have occurred at the beginning of the 20th century repeat quite remarkably at the start of the 21st century. At that time, Wolfgang Ostwald (the eldest son of Wilhelm Ostwald, a physical chemist and a Nobel Prize winner) applied the term "a world of by-passed quantities" to the domain of material particles with sizes ranging between the sizes of individual atoms and molecules on one end and the sizes of macroscopic bodies on the other end [11]. The advances in colloid chemistry, which was a relatively young science at the beginning of the 20th century and is one of the ancestors of nanoscience, are connected with the names of such prominent scientists as P. Zsigmondy (Austria) and T. Svedberg [2, 3] (Sweden). Zsigmondy was the first to construct a slot light microscope (1903) and to use it for studying the Brownian motion of colloid particles. In 1911 he studied the structure of gels and put forward a theory of capillary condensation of steam in adsorbent pores and developed methods for obtaining a sol of gold and colored glass. In 1912 he created an immersion ultramicroscope and suggested a classification for colloid particles. In 1925 Zsigmondy was awarded the Nobel Prize in chemistry for determining the heterogeneous nature of colloidal solutions. In 1907 T. Svedberg confirmed the theory of Brownian motion experimentally and in 1919 created a method of ultracentrifuging for separating colloid particles. In 1923 Svedberg constructed ultracentrifuges for studying highly disperse sols. In 1926 he was awarded the Nobel Prize in chemistry for his work on dispersions.

However, the experimental methods of the time were not efficient enough and researchers had to limit themselves to studying relatively coarse (micron) particles. For this reason, despite the fact that nanosize objects have been known since the penultimate century, such notions as nanocluster, nanostructure, and the related phenomena were merged into a special field of physical chemistry only in the last decades of the 20th century. This qualitative jump can be associated with the progress in the research methods employing tunnel and scanning microscopy, x-ray and optical methods, use of synchrotron radiation, optical laser spectroscopy, etc. [4 – 6].

Unfortunately, the terms "nanotechnology" and "nanomaterials" have become so fancy and marketable that many traditional studies and developments are preceded by the prefix "nano." Yu. D. Tret'yakov mentions in [4] that present scientific society is experiencing a nanotechnological boom that resembles the twenty-years-earlier boom connected with the discovery of high-temperature superconductivity.

The following types of nanomaterials are distinguished in accordance with the recommendations of the 7th International Conference on Nanotechnologies (Wiesbaden, 2004): nanoporous structures, nanoparticles, nanotubes and nanofibers, nanodispersions (colloids), nanostructured surfaces and films, and nanocrystals and nanoclusters. The latter are

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particles with ordered structure that have a size ranging from 1 to 5 nm and contain up to 1000 atoms.

GENERAL CONCEPTS OF NANOSYSTEMS

Where the historical aspects related with the appearance and development of nanosystems and nanotechnologies are concerned the author sticks to the following concept. This sphere of science, which is described as a principally new one by many, has a more than century-long fundamental prehistory. R. Hoffman, a Nobel Prize winner, once wittily reacted to the question of what nanotechnology is by noting that he is glad that people have found a new term for chemistry. Now they have a stimulus to study what they have neglected at school. In fact, chemists have worked with nanotechnologies for more than two centuries and a half [4]. Modern nanotechnology requires a combination of the talents of a synthesizing chemist and a master engineer, and this very union has made it possible to create quite intricate nanostructures.

We can mention a lot of studies made in the last years and related to this or that degree with the now finally formed direction of “nanotechnologies.” Specifically, it is noted in [7] that the effects of the action of ultrafine particles, which are now called nanoparticles, have been implemented several decades prior to the recent “nanoboom.” In the first publication of the 1960s devoted to the technology of quartz ceramics, which appeared more than ten years prior to the birth of “nanosystems,” the high mechanical strength of castings (the binding properties of suspensions) was explained by “working” of the system during wet milling of silicic acid, i.e., by the presence of particles of colloid dispersion (the level of modern nanoparticles).

Colloid chemistry should be treated as a scientific base of the processes of fabrication of various silicate materials obtained with the use of nanoparticles l [8 – 11]. A very important problem is the determination of the variation of the properties of the system upon growth in the fineness of the disperse phase. Colloid chemistry considers systems with particle size ranging from coarse ones (1 – 100 μm) to ultrafine ones (up to 1 nm) in microheterogeneous systems (nanosystems). Judging by the data issued in the Russian journal of abstracts in chemistry (Khimiya) more than half of the recent publications on topics of colloid chemistry and dispersions are devoted to nanoscience and nanotechnologies.

In accordance with the classification accepted in colloid chemistry nanosystems (nanoparticles) belong to ultradisperse colloid systems with particles from 1 to 100 nm in size. It can be seen in Fig. 1 that the level of dispersion of domain II of nanosystems lies between those of molecular disperse systems (I) and microheterogeneous (III) systems. Thus, the range of particle sizes of nanosystems corresponds to the ultimate degree of fineness at which a colloid system still preserves heterogeneity.

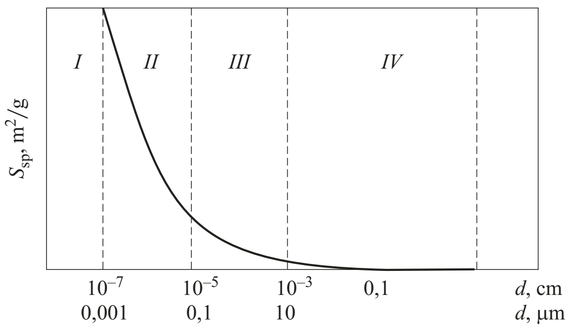


Fig. 1. Specific surface of particles S_{sp} as a function of their diameter d. The domains of the systems are as follows: *I*, molecular disperse one; *II*, colloid one (nanosystems); *III*, microheterogeneous one; *IV*, coarse disperse one.

It should be noted that the question of how we should call particles from 1 to 100 nm in size is more terminological than conceptual, because “nanosystems” appeared only after the introduction of SI units in 1981, i.e., much later than the long-used term “ultradispersion” or a similar concept of “colloid particles.” The works devoted to HCBS and ceramic concretes contain the term “colloidal component” for denoting nanoparticles until the late 1990s [7, 12 – 15].

Nanosystems are usually understood as a set of bodies surrounded by a gas or liquid medium and having a size not exceeding 1 – 100 nm. In some cases the maximum size of nanoparticles is assumed to be 1 μm (1000 nm). A special feature of nanobodies (nanoparticles) is the fact that their size is commensurable with the radius of the action of forces of atomic interaction. For this reason nanobodies interact and react with the ambient in a manner different from that of macroscopic bodies. It is assumed that the appearance of new properties within the nanoscale is not an obligatory consequence of the presence of such properties within the macroscale. The most important changes in the properties are not a consequence of the order of magnitude of the size but are a result of phenomena that occur within the nanoscale or become prevalent in this scale.

Practical interest in nanoparticles is explainable by the possibility of considerable modification and even of principal change of the properties of known materials upon their transformation to a nanocrystalline state and by the new possibilities opened by nanotechnologies for creating materials and articles from structural components with nanometer size.

The peculiar properties and the effect of nanoparticles are usually associated with the relatively higher fraction of surface atoms [5]. If the sizes of particles are decreased to 100 nm or a smaller value, they start to exhibit “quantum-size effects” that manifest themselves in changes in the atomic and crystal structure and in the physicochemical properties [4, 5]. These concepts are used in [10] for developing a classification of nanoparticles and showing the numerical relation between the size of a particle and the proportion of surface atoms in it. The authors consider a spherical nanoparticle with radius *r*, which is formed by atoms with diameter δ. The number of atoms n_V in such a particle is determined as follows:

$$n_V = \frac{\frac{4}{3}\pi r^3}{\frac{4}{3}\pi\left(\frac{\delta}{2}\right)^3} = 8\left(\frac{r}{\delta}\right)^3.$$

The number atoms n_S on the surface of such a particle will be

$$n_S = \frac{4\pi r^2}{\pi\left(\frac{\delta}{2}\right)^2} = 16\left(\frac{r}{\delta}\right)^2.$$

Then the proportion of surface atoms in the total number of atoms in the particle will be determined by a simple expression

$$\frac{n_S}{n_V} = \frac{16\left(\frac{r}{\delta}\right)^2}{8\left(\frac{r}{\delta}\right)^3} = 2\frac{\delta}{r}.$$

For macroscopic particles with $r \to \infty$ the proportion of surface atoms is negligibly small as compared to the total number of atoms in a particle ($n_S/n_V \to 0$). Particles with radius $r = \delta/2$ are single ones. Therefore, only objects with radius exceeding δ can be classified as nanoparticles. The quantities n_S, n_V, and n_S/n_V in particles of various sizes vary as follows:

r	n_V	n_S	n_S/n_V
δ	8	16	2
2δ	64	64	1
4δ	512	256	0.5
8δ	4096	1024	0.25
16δ	32768	4096	0.125
32δ	262144	16384	0.0625
64δ	2097152	65536	0.03125

Computations show that as the radius of a particle increases, the ratio n_S/n_V decreases markedly. The lower boundary of a nanoparticle corresponds to $r = 5$, whereas the upper boundary is indeterminate. Since the quantity δ is equal to 0.2 – 0.4 nm, the smallest size of a nanoparticle amounts to about 0.3 nm and it contains from 8 to 16 atoms. As applied to nanomineralogy [10] the upper boundary of nanoparticles is estimated at a level of 9 – 12 nm. As a rule, the same boundary is assumed to be 100 nm (0.1 μm). The size of particles of a silica sol ranges from 5 to 50 – 100 nm [9].

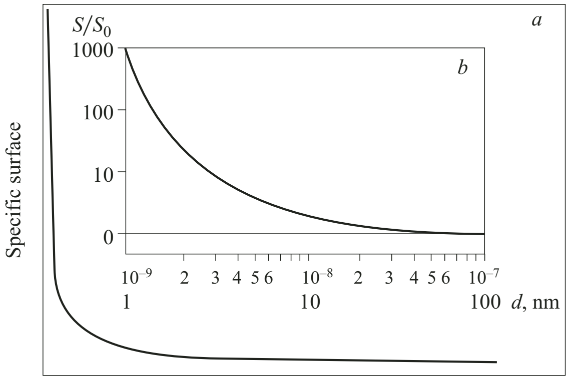


Fig. 2. General behavior of the relations between the specific surface of crystals and their sizes (*a*) and relative solubility of small quartz grains with respect to the solubility of the total mass of quartz S/S_0 (*b*).

The difference in the properties of nanosize individuals and microscopic bodies is connected with the relation between the specific surfaces of the particles and their size (Fig. 2). When the diameter of a quartz particle decreases from 100 to 1 nm, the solubility of the particle increases by a factor of 1000.

The size effects and, in the first turn, the functional dependence of the properties of a material on the size of particles in three dimensions form the physical basis of nanoscience just like the Schrödinger equation forms the basis of quantum mechanics. Virtually any property (magnetic, electric, catalytic, or mechanical) obeys this dependence [4 – 6, 10 – 11].

When developing and converting a technology connected with nanoparticles we should take into account its high-end and expensive nature. The probability of solution of problems by the quite popular trial-and-error method should be reduced markedly in the field of nanotechnologies. The path from laboratory development to commercial process in this field is much more complicated than in conventional technologies [4].

Even in the initial stages of implementation of a nanotechnology it is expedient to analyze and predict the risks for human health and environment. We imply primarily respiratory and pulmonary diseases including pulmonary cancer. A discussion on this topic was conducted at the end of 2006 at the Shubnikov Institute for Crystallography of the Russian Academy of Sciences within the framework of the National Conference on Crystal Growth [16]. It was noted that particles with a size below 10 μm (to say nothing of nanoparticles!) are the main sources of toxicological influence on human beings. More and more people suffer from air contamination (due to fuel combustion products, industrial effluents, etc.).

The positive effect of nanomaterials on our life can be accompanied by an extremely negative effect in the case of uncontrolled use. The transition from the microlevel to the nanolevel of a substance is accompanied by qualitative changes in the negative influence of matter on living organisms and environment. Today we lack data on this influence due to the absence of control, and the consequences can be unpredictable. In the absence of an international legislative base concerning the development and spread of nanotechnologies (like the International Non-proliferation Treaty) the use of nanotechnologies for war purposes can be more catastrophic than a nuclear blast [16]. In this respect the advantage of "*wet technological synthesis*" of nanoparticles becomes more and more obvious; as applied to the production of many silicate materials this concerns the process of fabrication of highly concentrated suspensions obtained by wet disintegration [7, 12 – 15, 17].

Two principally different methods are commonly distinguished in the field of synthesis of nanoparticles, i.e., dispersion and condensation. The method of dispersion is based on grinding solid bodies primarily in an inert medium; this raises markedly the degree of dispersion and yields a system possessing a considerable boundary surface [9, 11]. The condensation method includes three directions, i.e., liquid-phase condensation (the basis of the sol-gel process), condensation from a gas phase, and high-temperature (baking) processes. A common condition for all these methods of synthesis of nanoparticles is supersaturation of the system with the phase-forming substance [9]. Nanoparticles of the same composition (for example, SiO_2) can be obtained by virtually any of the methods mentioned. For example, the microsilica (MS) widely used in the production of unshaped refractories [15] and structural concretes [18] is a waste in the production of silicon or ferrosilicon. In the high-temperature (> 2000°C) processes gaseous SiO_2 is reduced by carbon and then oxidized by air oxygen in the cooling process and condensed in the form of amorphous spheres up to 0.25 μm in diameter [15, 18], i.e., the process is in fact condensation from the gas phase.

Another known and widely used method is pyrogenic synthesis of nanosilica (Aerosil) by firing silicon chloride in an oxygen atmosphere (deposition from the vapor phase) according to the following reaction: $SiCl_4 + O_2 \rightarrow SiO_2 + 2Cl_2$. A classical and widely used example of liquid-phase condensation is fabrication of silica hydrosols [9, 19].

A distinctive feature of synthesis of nanoparticles in the processes of fabrication, stabilization, and utilization of siliceous and silicate highly concentrated ceramic binding suspensions (HCBS) consists in the following. In the process of wet milling under conditions of ultimate concentration and elevated temperature that promotes dissolution of silica or silicates a certain amount of silicic acid (or aluminosilicic acid) is formed in the system on the one hand, and very fine "silicosol" particles produced by dispersion are formed on the other hand [7, 12 – 15]. A detailed analysis of the effect of nanoparticles contained in HCBS on the processes of production and properties of materials based on them is made in [12 – 15]. The task of the present work consisted in continuing these studies and making a wider generalization of the problem of dispersed silica used as a basis for developing nanotechnologies of various silicate materials.

NANODISPERSE SILICA. SiO_2–H_2O SYSTEM

Silicon is the second element after oxygen in the lithosphere of the Earth. Due to the high strength of the Si–O bond (445 kJ/mole) the Earth crust is represented by over 50% silica, silicates, and aluminosilicates, which explains the wide range of application of these materials. On the other hand, in contrast to the traditional uses of SiO_2 the production and use of various colloidal (nanodisperse) and microheterogeneous forms of silica and sols, gels, and powders with developed surface has grown intensely in the last decade. Recent data on nanosilica are generalized in [9, 20]. Today nanodisperse SiO_2 is a leader in the world market of nanomaterials (28.5% in 2000; 43.9% in 2005). Quite frequently the term "nanodisperse silica" is used for the entire variety of its forms (sols, gels, suspensions, pastes) encountered under natural conditions (quartz, opal, chalcedony) or created by man (Aerosil, hydrosols, silica gels, carbon white) [9, 19, 20]. Nanodisperse silica is a very important natural object and the main component of oxide materials obtained by the sol-gel method. Sols (ultramicroheterogeneous dispersions with liquid or solid dispersion medium and solid disperse phase), the particles of which participate in Brownian motion, are the most interesting and important representatives of nanodisperse silica. The term "colloidal silica" is frequently used to denote stable dispersions or sols consisting of discrete amorphous particles [19, 20]. Silica hydrosols are representatives of nanodisperse oxide systems used very widely due to the polymer nature of the particles and the presence of well-developed surface and functional (silanol) groups, which ensures a high reactivity and a possibility of adsorption modification of the surface of particles. Judging by the degree of significance and the level of practical implementation the process of fabrication of silica sols or hydrosols seems to be a quite demonstrative example of the use of nanotechnology in the field of inorganic materials science [9, 20].

The chronology of studies in the field of the chemistry of disperse silica is analyzed in [21] on the basis of works published from the second half of the 18th century to the beginning of the 20th century. It follows from this book that topics of the chemistry of silica have interested primarily prominent scientists who were leaders of the chemical science of the time. Specifically, the classical work of P. Zsigmondy (see [21], p. 135] in 1911 should be mentioned from the standpoint of the beginning of nanoscience. Prior to this publication the pore diameter in a clear dry gel of silicic acid was assumed to be 1.0 – 1.5 μm. Using the theory of capillary phenomena and the formula of Laplace and Thomson Zsigmondy showed that the pore diameter is hundreds of times smaller and amounts to about 5 nm (in the now-used dimensionality). It seems that Zsigmondy was the first to identify nanopore structures. The objectiveness and accuracy of the almost hundred-year-old result is confirmed by the fact that modern estimates of the size of pores [22] are virtually the same.

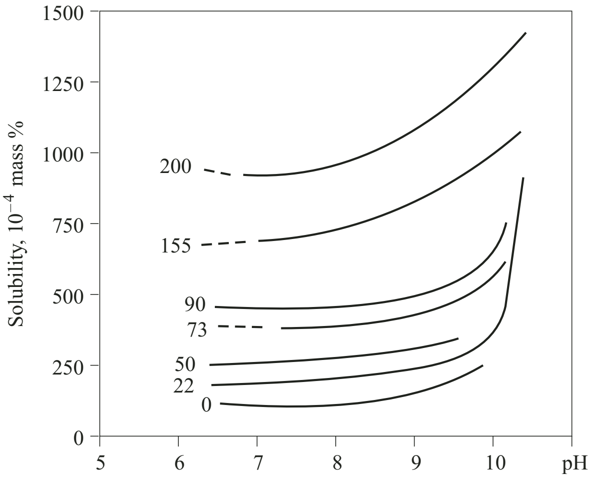


Fig. 3. Solubility of silica as a function of pH at various temperatures (given at the curves, °C).

Silicon in a highly disperse state can have the form of a solid or of a liquid. In the latter case we distinguish soluble and colloidal silica. All nanodisperse forms of SiO_2 are obtained using aqueous systems in the production process, which makes it necessary to consider the SiO_2–H_2O system.

In the fundamental monograph [19] R. Iler comments on the works of many of his predecessors in the study of the SiO_2–H_2O system and notes that the uniqueness of amorphous silica as a solid substance is similar to its uniqueness as a liquid. Specifically, it says that some properties of water and silica are so close that there is a gradual changeover between hydrated silicic acids and the water matrix. Both water and amorphous silica possess a temperature at which the volume of the substance is minimal. It is also reported that there exists a relation between the water density and the solubility of different forms of silica, because both properties are determined by the packing of oxygen atoms. Oxygen atoms are the primary occupants of volume in the structure of silica and water. These atoms are packed with a characteristic density. Small atoms of hydrogen and silicon fill the voids between oxygen atoms and make a considerable contribution to the volume.

Polymerization of silicic acid, which is accompanied by the formation solid silica and water, causes separation into two phases, i.e., silica, where the silicon atoms are surrounded by oxygen atoms at denser packing, and water, where the atoms of hydrogen are surrounded by oxygen atoms at looser packing. In amorphous silica one cubic centimeter contains 1.17 g oxygen, whereas in water, which has a density of 1.0 g/cm^3, one cubic centimeter contains 0.89 g oxygen. Dissolution and precipitation of silica in water includes the reactions of hydration and dehydration catalyzed by OH^- ions, i.e.,

$$(SiO_2)_x + 2H_2O \underset{\xleftarrow[\text{Dehydration}]{}}{\xrightarrow{\text{Hydration}}} (SiO_2)_{x-1} + Si(OH)_4 .$$

For massive amorphous silica the equilibrium concentration of $Si(OH)_4$ at 25°C corresponds to 70 weight parts SiO_2 per million parts water or 0.007 mass %. This is just the "solubility" of anhydrous nonporous amorphous SiO_2. On the other hand, crystalline silica (quartz, for example), which is encountered virtually anywhere in the form of sand, has a much lower solubility (on the order of 0.0006% SiO_2). At the same time, it is known that the solubility of various kinds of silica is substantially affected by the temperature, the pH of the medium, and the fineness of the particles. In particular, Fig. 3 presents the effect of the value of pH and of the temperature on the solubility of amorphous silica in accordance with the data of [19]. Growth in the temperature from 22 to 90°C more then doubles the solubility. Below we present data on the solubility of amorphous silica in water at various values of pH, i.e.

pH	6 – 8	9	9.5	10	10.6
Solubility of amorphous silica at 25°C, mass %	0.0120	0.0138	0.0180	0.0310	0.0876

The total content of "soluble" silica can grow due to the attainment of the following equilibrium:

$$Si(OH)_4 + OH^- = H_3SiO_4 + H_2O,$$

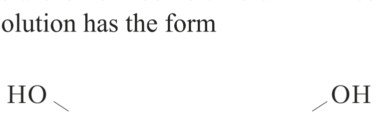
$$[H_3SiO_4] = 1{,}85 \cdot 10^4 [Si(OH)_4][OH^-],$$

where 1.85×10^4 is the chemical equilibrium constant computed using the considered data on the solubility.

Thus, the solubility of silica increases at high values of pH due to the formation of silicate ions in addition to the $Si(OH)_4$ monomer present in the solution. The solubility of SiO_2 is also influenced considerably by the size of the particles. For example, the solubility of finely milled quartz sand is 20 times higher than its solubility in unmilled condition.

The soluble phase of silica is its monomer that contains only one silicon atom and is commonly described as $Si(OH)_4$. It is frequently called monosilicic or orthosilicic acid. It is assumed that the structure of monosilicic acid includes a silicon atom that coordinates four oxygen atoms both in amorphous quartz glass and in crystalline quartz.

The structure of orthosilicic acid in a freshly prepared hydrolyzed solution has the form



Gradual removal of water transforms the solution into a gel. After drying and baking a gel of silicic acid can contain a crystalline structure, i.e.,

$$H_4SiO_4 \xrightarrow{\text{Drying}} SiO_2 \cdot 2H_2O \xrightarrow{\text{Heating}} SiO_2 + 2H_2O.$$

The rate of dissolution of silica is proportional to the silica surface, and the rate of the inverse process (polymerization of orthosilicic acid H_4SiO_4 in the form of which silica is present in solutions) is proportional to the concentration of SiO_2 in the solution.

The dissolution of SiO_2 is especially affected by the value of the pH of the medium (the presence of alkali). This effect is used as a basis for the production of various alkaline silicate binders or water-soluble silicates. The latter are usually understood as concentrated solutions of silica in alkalis (liquid glasses) and microheterogeneous (nanodisperse) systems containing silica polymerized to different degrees at $pH > 7$ and capable of adhesive hardening upon drying. Binders of this type are classified in accordance with the following features [23 – 25]:

The degree of polymerization of silica. In the process of polymerization of SiO_2 its molecular mass increases and the particles grow in size. Colloidal silica in the form of a sol or of hydrated SiO_2 forms under specific conditions;

The chemical composition. The alkalinity of water-soluble silicates is characterized by the SiO_2/R_2O molar ratio ($n = SiO_2/R_2O$). In accordance with this parameter silicate binders can be arranged in the following succession: highly alkaline systems ($n < 2$) → liquid glasses ($n = 2 – 4$) → polysilicates ($n = 4 – 25$) → silica gels ($n > 25$);

The kind of cation. In accordance with this parameter the systems in question are classified into potassium, sodium, and lithium silicates and organic-base silicates;

The water content. The classification includes high-water systems (low-viscosity liquids), low-water systems (pastes), and powders.

Commercial liquid glasses are represented by a comparatively narrow range of compositions and are a particular case of alkaline silicate binders. Liquid glasses are understood as potassium-sodium silicate solutions with silicate modulus $n < 4$. Alkaline silicate binders are characterized by a considerably wider range of compositions and properties. Their specific feature is the fact of progressive variation of the chemical composition upon decrease in the alkalinity and the respective changes in the properties of the binders. This is explained by a sweeping change in the physicochemical nature of the solutions including the formation of high-polymer SiO_2 in colloidal condition. The process of polymerization of SiO_2 consists of mutual condensation of the Si–OH silanol groups. This gives rise to molecule-bonded formations of SiO_2 with increasing sizes. Sodium and potassium liquid glasses are products of dissolution of vitreous soluble sodium and potassium silicates also known as “impure disilicates.” Vitreous soluble sodium and potassium silicates are produced at glass plants by melting in tank furnaces. Production of liquid glass (dissolution of impure disilicate) is organized at many enterprises that consume this material. Impure sodium disilicate is dissolved in rotary or stationary autoclaves at a pressure of 0.3 – 0.7 MPa and a temperature of 120 – 150°C. Liquid glass is used for three purposes. The first application is connected with the binding properties of the material. Liquid glass has high adhesive properties with respect to substrates (surfaces) of different chemical nature. This makes it a good gluing agent for various materials, a material for depositing coatings, and a binder for fabricating various inorganic materials [23 – 26]. The second application is the use of liquid glass as an initial raw component for synthesizing silica-bearing substances, i.e., silica gels, carbon white (Aerosil), and catalysts. The third application is the use of liquid glass as a chemical reagent and an additive in the composition of various substances.

Solutions of liquid glass are often used as water-reducing admixtures in the production of ceramic suspensions that are characterized by optimum values of pH in the alkaline range. Specifically, a liquid glass admixture is used in wet milling of HCBS of quartz glass, bauxite, and other aluminosilicate suspensions [12 – 15, 27]. However, in this case its function is not only to liquefy the suspension. It is known [19, p.165] that liquid glass contains undissolved silica in the form of nanoparticles 1 – 2 nm in diameter in addition to sodium and silicic acid ions. The nanoparticles and the silicic acid that polymerizes in drying are sources of effective nanosilica. By analogy with nanoparticles generated due to milling of HCBS the latter exerts a noticeable hardening action on the properties of castings or binders from the corresponding HCBS. In addition, liquid glass is the most effective reagent for the process of fabrication of unfired materials hardened by chemical activation of contact bonds (UKhAKS ceramics) [13, 27].

The very wide range of application of liquid glass in various branches of economy is explainable by the high level of binding properties, the low cost and availability of the raw material, nontoxic nature, inflammability, and absence of emission of gaseous substances. High-modulus aqueous silicate systems comprise alkaline silicate binders that cannot be obtained by dissolution of silicate glass in water or alkalis. Two groups of such binders are produced, i.e., polysilicates having a silica modulus $n = 4 – 25$ and silica sols with $n > 25$. The content of colloidal silica in polysilicate solutions is 50 – 92%. These are obtained by introducing liquid glass into a concentrated silica sol when adding the alkali to the sol. In this case the colloidal SiO_2 is represented by high-polymer highly hydrated SiO_2 with particle size of 1 – 7 nm at a size of the initial sol particles equal to 10 – 20 nm.

Dry alkaline silicate binders (powders) have found considerable application in recent years. Fabrication and use of powder binders instead of aqueous solutions has a number of advantages. Such binders are produced in two forms, i.e., in high-alkali and low-alkali variants. The powders are obtained by dry milling of impure sodium disilicate in a ball mill. This type of binder is used in the production of refractory concretes [26]. The particles dissolve in the composition of moistened mixtures and, during drying under temperature-and-moisture conditions, pass to a liquid phase and thus form a liquid-glass binder that makes a monolith with concrete particles. This principle is used in some processes of production of unfired refractory concretes and building materials based on HCBS [27, 28].

Silica sols are dispersions of nanosize particles of SiO_2 in water [9, 19, 20]. They are produced by polymerization of monomer silica, which yields siloxane bonds according to the following scheme:

$$\equiv SiOH + {-}OSi\equiv \rightarrow OH^- + \equiv Si{-}O{-}Si\equiv,$$

$$\equiv SiOH + OH^- \rightarrow H_2O + \equiv SiO^-.$$

The sol particles are charged negatively due to adsorption of hydroxide ions on their surface, which makes the system stable. The most important characteristics of the sols are the content of SiO_2 in them and the particle size. Commercially produced sols have particles from 5 – 7 to 30 – 50 nm in size. The content of the stabilizer (the Na_2O alkali) fluctuates within 0.1 – 1.0 mass %; that of SiO_2 fluctuates within 20 – 30 mass %. The principle of fabrication of a silica sol consists in passing a diluted (< 4%) solution of liquid glass through a layer of H+ cation and adding the required amount of alkali at the outlet for stabilization. When the solution reacts with the surface of the cation exchanger, the cation of the alkali metal (Na^+) is exchanged for protons. Then the solution is concentrated by evaporation and progressive addition of the solution arriving from the ion exchanger (sol feeder). Silica sols are widely used as binders for refractory materials and coatings due to that fact that they contain virtually pure silica with an insignificant amount of alkali (in contrast to liquid glass). In recent years foreign producers and consumers have turned to cement-free refractory concretes on colloidal silica-sol binders [29]. In the casting production silica sols are used in the form of coatings for precision casting molds. Sols are widely used for fabricating silica gels, adsorbents, and catalysts.

Until recently all the binders mentioned have been characterized as aqueous systems. At the same time, we know of analogous (with respect to the inorganic component) systems obtained with the use of organic liquids. Examples of the latter are ethyl silicates. This is a commercial term for oligomer esters of orthosilicic acid. Ethyl silicates are obtained from silicon tetrachloride and ethyl alcohol by the reaction

$$SiCl_4 + 4C_2H_5OH \rightleftarrows Si(OC_2H_5)_4 + 4HCl.$$

Ethyl silicates contain up to 30 – 40% SiO_2 and are used primarily as binders for fabricating molds for casting metals. As for the ceramic technology, a considerable volume of studies devoted to the sol-gel process with the use of ethyl silicate binders is described by the author in [30].

It should be noted that solutions or powders of liquid glass as well as silica sols and ethyl silicates have been used in the technology of quartz ceramics and refractories in various stages and for various purposes.

Polycondensation is the main chemical process in all stages of the sol-gel process used for fabricating oxide materials including those based on silica. A nucleating sol is formed as a result of polycondensation of silicic acids in an aqueous medium, and its particles grow [9, 19]. A monomer silicic acid can be obtained by hydrolysis not only from silicates of alkali metals (liquid glasses) but also from halides, esters, and silicon alkoxides. The reaction of hydrolysis of sodium silicate (liquid glass) in an aqueous solution occurs by the following scheme:

$$Na_2SiO_3 + 3H_2O \rightarrow Si(OH)_4 + 2NaOH.$$

The silicic acid produced in the reaction of hydrolysis contains silanol groups (≡Si–OH) capable of polycondensation reaction that yields siloxane bonds (≡Si–O–Si≡). The polycondensation process yields hyperpolymerized silicic acids, i.e.,

$$(OH)_3 \equiv Si{-}OH + HO{-}Si \equiv (OH)_3 \rightarrow$$
$$\rightarrow (OH)_3 \equiv Si{-}O{-}Si \equiv (OH)_3 + H_2O.$$

It is assumed that polycondensation of silicic acid in the process of stabilization and subsequent use of HCBS with siliceous composition is conducted according to this scheme [12, 13, 27].

DISPERSION MEDIUM OF HCBS AS A COMPOSITE NANODISPERSE SYSTEM

It is known that the principle of optimum degree of dispersion and optimum grain distribution is very important for the technology of HCBS and materials based on them. Until the middle 1980s analysis of grain composition was performed at a kind of "macrolevel" by sedimentation and screen fractionation. At the same time it became more and more obvious that the content of microparticles undetectable in HCBS by conventional methods (particles of the "microlevel") was very important.

In order to obtain additional and important data on the characteristics of the dispersion composition of HCBS it was suggested in [31] to single out two conventional levels (ranges) of dispersity, i.e., (I) that of particles of solid phase with a size ranging from 0.2 – 0.5 μm to a maximum value of 30 – 100 μm and (II) particles with a size below 0.2 μm. The latter range can be conventionally treated as that of nanoparticles. From the standpoint of colloid chemistry and technology the principal difference in the suggested levels consists in the fact that the particles of the main level (I) represent the "true" disperse phase of HCBS, which is characterized by sedimentation of particles, and the particles of level II obey the laws of Brownian motion. Even after long-term settling (1 – 3 years) such particles do not precipitate in diluted HCBS. This has made it possible to assume that particles of level II are a part of a dispersion medium.

The content of particles with dispersity of level II in HCBS is determined primarily by the parameters of the process of preparation of the HCBS (concentration, total degree of dispersion of the solid phase, temperature and duration of wet milling, pH of the medium). The maximum size of particles in a dispersion medium is chiefly determined by the density of the solid phase ρ_s. To give an example of a sol of HCBS we present an electron micrograph of a silica sol separated from a dispersion medium of quartz glass HCBS after settling for two years (Fig. 4) [7]. Similarly to the polydisperse grain distribution of particles of the disperse phase of HCBS, the solid phase of the dispersion medium is also characterized by polyfractional composition. This is an important characteristic of the dispersion medium from the standpoint of the density and strength of the material obtained from HCBS. The content of the solid colloidal component in the dispersion medium (g/l) or its relative content reduced to the solid phase $C_{\text{c.c}}^{\text{red}}$ (%) can depend substantially on the experimental conditions of its separation.

In accordance with [19, p. 475] the particles of colloidal silica with a size below 30 nm can be separated from the rest of the solid phase of a suspension by ultracentrifuging with rotor speed of at least 10,000 rpm. In [31] we used an ultracentrifuge with rotor speed of 18,000 rpm rotated for 15 min for separating the colloidal component. We studied samples of a dispersion medium obtained by long-term settling of repeatedly diluted suspensions. Due to the use of the ultracentrifuge the "disperse phase" of the dispersion medium was in its turn conventionally divided into two levels of dispersity. The particles deposited due to centrifuging had a size ranging within 0.03 – 0.3 μm and the finer particles separated by drying of the centrifugate were less than 0.03 μmm in size. In accordance with [12], the value of S_{sp} for nanoparticles of the latter level separated from quartz sand HCBS amounts to 260 m^2/g, which corresponds to a mean surface diameter of the particles equal to 9.5 nm. It is expedient to express the concentration of the colloidal component $C_{\text{c.c}}$ in terms of the absolute value for the dispersion medium [1] or in terms of the reduced concentration $C_{\text{c.c}}^{\text{red}}$ determined as

$$C_{\text{c.c}}^{\text{red}} = \frac{C_{\text{c.c}} C_w}{C_V \rho_s} \times 100\,\%,$$

where C_w and C_V are the volume fractions of the liquid and solid phases.

Depending on the task the concentration of the colloidal component is determined as a total value or with respect to the two levels of fineness. In the former case a pipette method is used, which will be described in Part 2 of the present paper.

System studies of the content and characteristics of nanoparticles in fused quartz and quarts sand HCBS are presented in [12, 31, 32]. As an example, we characterize the fineness and the grain distribution of fused quartz suspension with different contents of nanoparticles in Fig. 5 using the data of [32]. The content of the particles was controlled by enriching or depleting the initial suspension with respect to $C_{\text{c.c}}^{\text{red}}$ and using the known method of [12]. It follows from Fig. 5*a* (for a grain size range from 1 to 100 μm) that the content of particles with a size below 1 μm for the analyzed suspensions ranges from 24% (curve *2*) to 7.5% (curve *3*). The concentration of the colloidal component varies accordingly. For example, the content of particles with a size below 0.3 μm is 11 – 4% and that of particles less than 0.1 μm in size (up to 100 nm) is 1.5 – 5%. For the initial suspension (curve *1*) the mass fraction of particles less than 0.3 μm in size is 6.2%; that of particles less than 0.03 μm in size (30 nm) is only 0.65%.

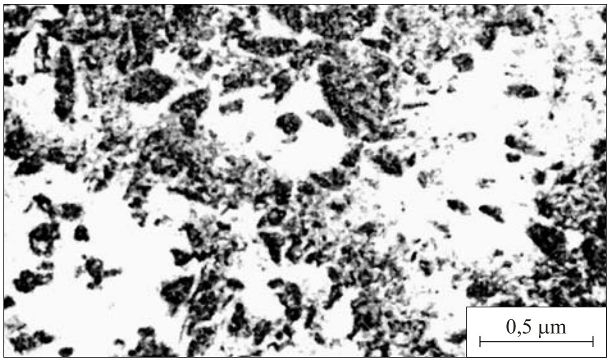


Fig. 4. Electron micrograph of a silica gel separated from a quartz glass suspension after two years of settling.

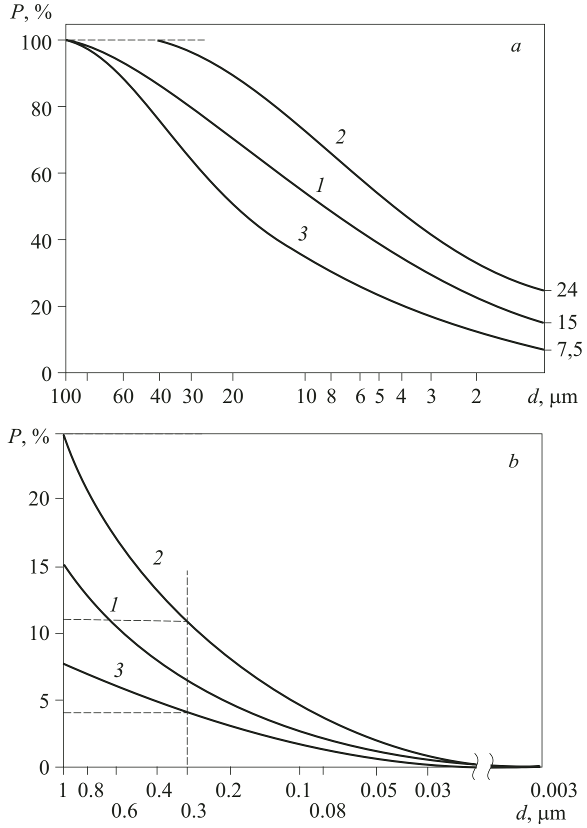


Fig. 5. Integral curves of grain distribution *P* for suspensions of fused quartz: *1*, initial; *2*, enriched; *3*, depleted of fine fractions.

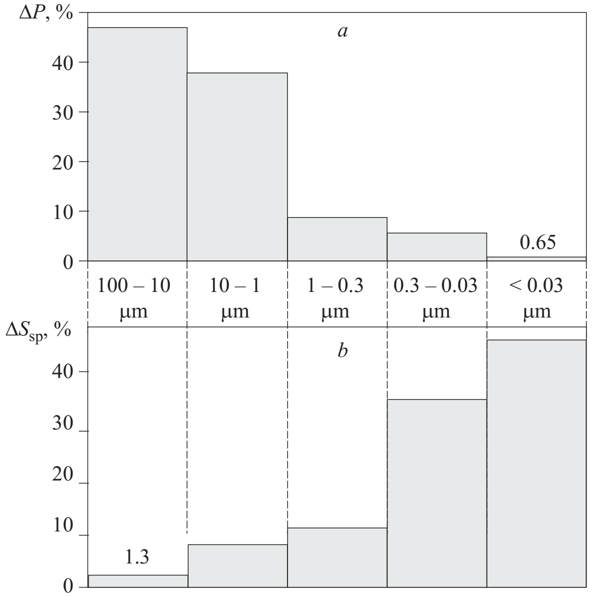


Fig. 6. Specific contributions (ΔP and ΔS_{sp}) of different fractions to the composition P (*a*) and to the specific surface of the solid phase S_{sp} (*b*) of quartz sand HCBS corresponding to curve *1* in Fig. 5 ($S_{sp} = 3.4$ m^2/g).

The exceptional effect of nanoparticles in the technology of HCBS and ceramic concretes is explainable by their enhanced reactivity. Despite the relatively low mass fraction of nanoparticles their contribution to the total specific surface S_{sp} of the solid phase of HCBS is enormous. It follows from Fig. 6 that the total specific contribution of particles less than 0.3 μm in size to the total specific surface is about 80%; the fraction of particles less than 30 nm in size (0.65%) takes about half of the entire surface.

Based on the presented and analyzed data it would be natural and logical to assume that the dispersion medium of HCBS of acid composition (quartz glass, fused quartz, quartz sand) is a relatively concentrated silica sol. The difference of the latter from conventional silica sols obtained by liquid-phase condensation [9, 19] is that they consist of particles formed both due to mechanical dispersion (30 – 300 nm) and due to condensation of soluble forms of silica (< 30 nm). In order to estimate computationally the concentration of a silica sol in a dispersion medium of quartz sand HCBS we will consider a suspension with grain composition corresponding to that presented in Fig. 6. This HCBS is characterized by $C_V = 0.75$. One liter of this HCBS contains 1650 g SiO_2 and 250 g water. A certain portion of particles of the solid phase in nanodisperse condition (see Fig. 6) enters the composition of the dispersion medium. Using the total content of the colloidal component with $d_{max} = 0.3$ μm in this suspension we find that its mass fraction in the dispersion medium is about 30%; at $d_{max} = 0.1$ μm (the upper boundary for nanoparticles) the value is 16%. The concentration of conventional commercial silica sols suits the same range [19].

Thus, it follows from the data presented that silica in a nanodisperse condition is characterized by exceptionally wide possibilities of both production and application. V. I. Vernadskii wrote at the beginning of the last century that such materials as silica and aluminosilicates “should attract much more attention in engineering than it does now, because they represent widely encountered bodies that surround us everywhere and are in fact quite available in any amounts. The wide occurrence of aluminum and silicon and of their compounds will make them a base for a technology of the future” [33]. Recent developments in the technology of quartz ceramics and refractories, HCBS, and ceramic concretes and the leadership of nanosilica in the world production of nanomaterials confirm the objectiveness of this prediction.

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