SCIENTIFIC RESEARCH AND DEVELOPMENT

NANODISPERSED SILICA AND SOME ASPECTS OF NANOTECHNOLOGY IN THE FIELD OF SILICATE MATERIALS SCIENCE. PART 3[*1]

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On the example of highly concentrated binding suspensions (HCBS) of fuzed quartz the effect of their concentration with wet grinding is specified governing the content of nanoparticles in a system. On the basis of the limiting concentration of HCBS ($C_V = 0.82$) castings are prepared with a nanoporous structure. As applied to the technology of different silicate materials theoretical aspects are specified connected with preparation and control of colloid-chemistry and rheological properties of nano-containing dispersed systems for their preparation.

CONCENTRATION OF HCBS AS A FACTOR DETERMINING NANOPARTICLE CONTENT

In preparing and studying numerous types of HCBS it has been established that in the field of concentrations approaching critical there is a sharp change in properties both of suspensions and castings based on them. For example, with an increase in quartz glass suspension concentration by 5% in the range $C_V = 0.70 – 0.75$, Π_{cas} decreases by $25 – 30\%$ (rel.), but σ_{ben} increases by a factor of $1.5 – 2.0$. As C_V increases further the intensity of the change in properties increases. Analysis of this feature has shown that dependences of the change in HCBS properties on their concentration should be considered from the position of the volumetric solid to liquid ratio (SLR) that is the ratio in a system of volume fractions of solid C_V and liquid C_W phases, i.e. SLR $= C_V/C_W$.

As follows from Fig. 1, in the field of high values of C_V the SLR indices increase more markedly than in the field of low values. For example, with an increase in C_V from 0.7 to 0.8 (i.e. by 14%) the value of SLR increases by 71% (from 2.33 to 4.00).

In publication [41] in order to establish regularities in the change in properties of suspensions and castings based on them in relation to SLR index a study was made of fuzed quartz suspensions prepared both in an industrial mill ($C_V < 0.70$) and in a 50-liter laboratory vessel ($C_V < 0.77$). Here the grain size composition was about the same (< 5 μm $28 – 35\%$, > 50 μm $3 – 10\%$) and pH ($5.5 – 6.0$), but the temperature differed markedly (~90°C in the industrial mill and 65°C in the laboratory). Thus, in the range of change of C_V within the limits $0.68 – 0.77$ or SLR within the limits $2.12 – 3.34$ the dependence of fuzed quartz suspension phase composition (volume concentration of solid phase C_V, kinetically free C_{Wk} and bonded C_{Ws} of a dispersed medium), critical concentration C_{Wcr} and casting porosity Π_{cas} on SLR index were studied (Fig. 2). As SLR increases there is a reduction in the system of both kinetically free and bonded liquid. Here a rectilinear dependence of index C_{Wcr} and Π_{cas} on SLR is noted.
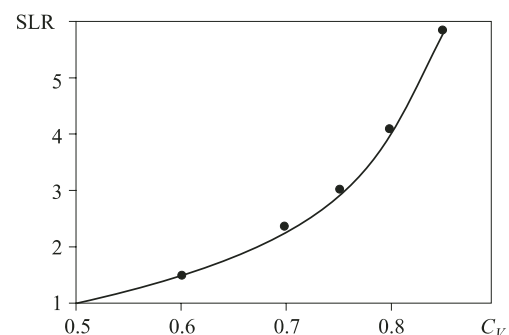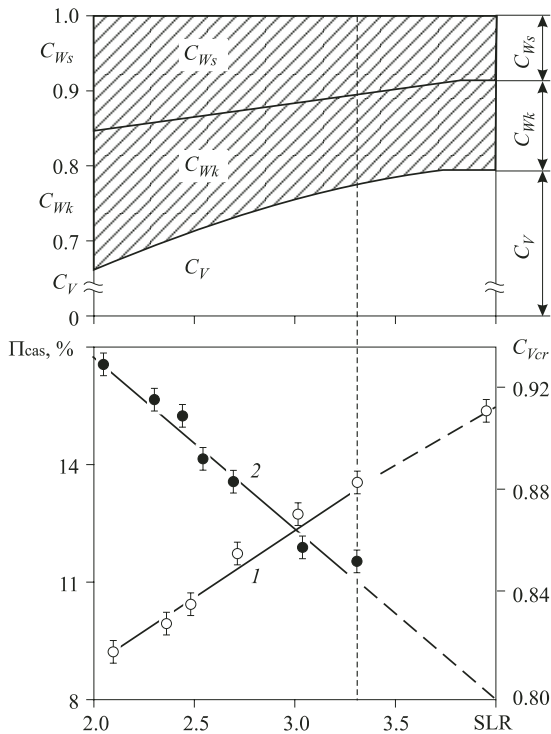

Fig. 1. Interconnection between indices of volume concentration C_V and SLR.
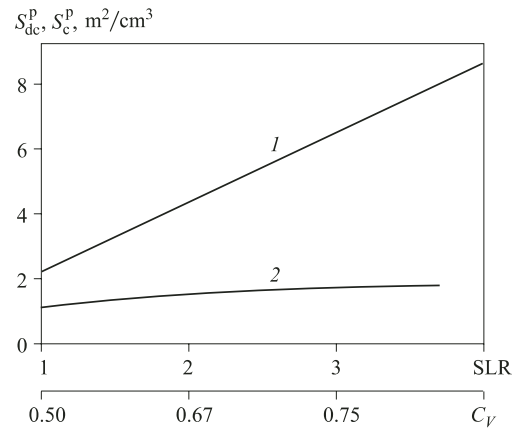
Fig. 2. Effct of SLR during wet grinding of HCBS based on fuzed quartz on their C_{Wcr} (*1*), Π_{cas} (*2*) and volumetric phase composition (C_V, C_{Wk}, C_{Ws}).

Fig. 3. Dependence of specific phase interface in a unit volume of dispersed medium S_{dc}^{p} (*1*) and HCBS S_{c}^{p} (*2*) on SLR and HCBS C_V respectively with a specific dispersed phase surface of 2.2 m²/cm³.

Taking account of analysis of both the data in question and similar data in many other forms of HCBS in publication [41] empirical rules were formulated for the first time describing the interconnection between suspension characteristics and concentration (SLR) during their preparation.

1. The product of indices of volumetric solid-liquid ratio and kinetically bonded liquid in HCBS or the porosity of castings based on them is a constant value, i.e. $\mathrm{SLR} \cdot C_{Ws} \approx$ $\approx$ const, $\mathrm{SLR} \cdot \Pi_{cas} \approx$ const.

2. Index C_{Ws} in stabilized HCBS or the porosity of castings based on them is inversely proportional to suspension SLR during wet grinding, i.e. $(\mathrm{SLR})_l \cdot (C_{Ws})_l \approx$ $\approx (\mathrm{SLR})_s \cdot (C_{Ws})_s$, $(\mathrm{SLR})_l \cdot (\Pi_{cas})_l \approx (\mathrm{SLR})_s (\Pi_{cas})_s$, where indices "l" and "s" signify indices SLR, C_{Ws} and Π_{cas} with large and small values of concentration respectively.

It is undoubted that these regularities, depending on SLR, are caused by several different factors, including the specific "packing" capacity of HCBS solid phase particles during structure formation, and also interphase reaction during HCBS preparation and stabilization. The latter determines the composition, dispersed medium properties and it depends markedly on concentration of the system. In order to evaluate this factor an understanding was proposed for the specific interface of phases in a unit volume of suspension, determined by the dispersion of solid phase particles S and concentration of the system $S_c^p = S C_V$. In order to analyze this regularity a similar index is proposed below for the

specific interface of phases in the calculation per unit volume of dispersed medium S_{dc}^p, i.e. $S_{dc}^p = S \cdot \mathrm{SLR}$.

It can be seen from Fig. 3 that S_{dc}^p depends rectilinearly on SLR. With an increase in SLR by a factor of two the S_{dc}^p also increases by a factor of two. As suspension concentration in the system increases there is a marked acceleration of the process changing properties of the dispersed medium and connected, for example, with solid phase solubility. Due to this in preparing HCBS in a system there is more rapid formation of the content of nanoparticles required for providing the optimum rheological and binding properties. According to preliminary experimental data, HCBS that have a high SLR under stable uniform conditions contain a considerable fraction of colloid component (nanoparticles). Substantiation of this feature is given below.

We shall proceed from the assumption that the solubility of quartz glass or another form of silica during wet grinding is determined by the volume fraction of solid phase in the suspension, i.e. the volume of solid substance in the system is a function of the solid–liquid phase interface. Here a condition for the concentration of dissolved SiO_2 in the dispersed medium of the suspension (in g/liter of dispersed medium) will be a function of index C_V or SLR, as follows from curve 1 in Fig. 4. By comparison with a suspension that has the minimum concentration of those shown in Fig. 4 ($C_V = 0.4$, SLR = 0.66), the content of dissolved SiO_2 in HCBS ($C_V > 0.72$) increases repeatedly. The real difference appears to be markedly greater in view of the fact that as suspension C_V increases there is an increase in the temperature of the wet grinding process. If the latter with $C_V = 0.40 -$ 0.50 does not exceed 30°C, then on reaching $C_V = 0.75 - 0.80$ under certain conditions the temperature increases to 90 – 95°C. Taking account of published data for the effect of temperature on the solubility of amorphous silica [19] and real values of temperature during wet grinding in relation to suspension concentration, an estimate of the relative solubility of SiO_2 for this case is shown in Fig. 4 (curve *2*). It fol-
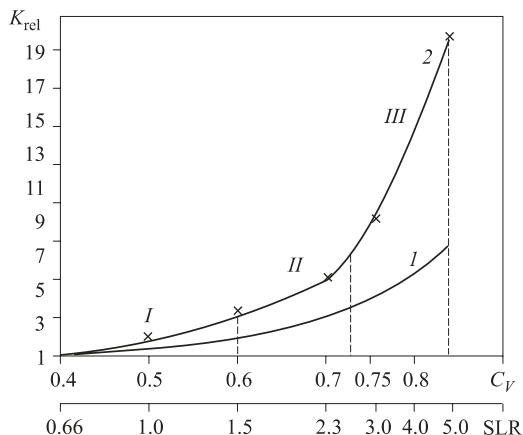
Fig. 4. Effect of C_V or SLR of a silica suspension on the relative concentration of dissolved silica K_{rel} on their dispersed medium: *1*) without considering the factor of suspension temperature during grinding; *2*) taking account of the latter; *I*) field of low concentration suspensions; *II*) field of medium concentration suspensions; *III*) HCBS.
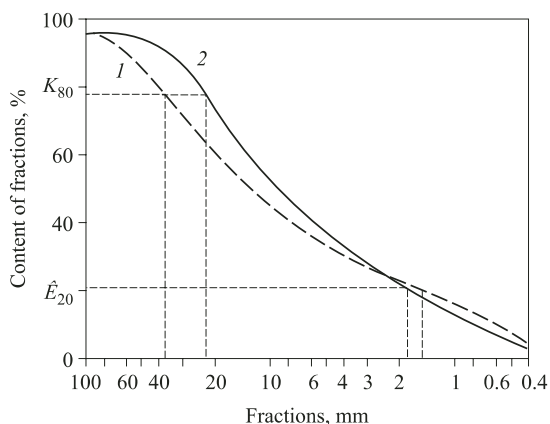
Fig. 5. Integral curves for grain size distribution of solid phase of a fuzed quartz suspension prepared by wt grinding with stagewise charging with a final value of C_V equal to 0.77 (*1*) and 0.675 (*2*).

lows from Fig. 4 that even with values of $C_V = 0.75 - 0.77$ ($\rho_d = 1.90 - 1.92$ g/ñm³) normal for quartz glass HCBS the K_{rel} with respect to a low-concentration suspension increases by a factor of $9 - 12$.

The following example points to the existence of an effect of HCBS C_V during grinding on concentration of the colloid component $C_{c.c}$ formed. Stabilized suspensions of quartz glass of comparable dispersion (Fig. 5), but differing in the value of C_V are characterized by the values of $C_{c.c}$ of 17.3 and 49.5 g/liter of dispersion medium respectively. The ultimate strength in bending of castings based on the suspensions being compared was 1.8 and 5.0 MPa respectively [41]. These data confirm experimentally the competence of the results of calculations shown in Fig. 4.

Proceeding from this it is also evident that similarly there will be a dependence of nanoparticle content in a system

produced as a result of mechanical dispersion. An important conclusion follows from this that dispersion of a HCBS medium is a concentrated polydispersed silica gel governing the unique technological properties of a suspension.

Apart from the effect of the factors considered, an important role of the SLR index (increased concentration of HCBS with wet grinding) consists probably of the fact that as concentration ("constraint") of the system increases the effect of factors responsible for achieving its increase in "packing capacity" both in the state of a suspension and also in material with structure formation. On one hand with an increase in SLR (C_V) there is an increase in polydispersion promoting achievement of improved packing. On the other hand there is an increase in "matching" and "rubbing" of particles with respect to size and surface relief in order to provide more dense packing of the solid phase in the system and thereby reduce to a minimum the energy for changing the system under "constraint" conditions. These processes, promoting an increase in density, are not geomechanical; they are connected with the action of surface forces and with structure formation typical for colloidal systems. It is entirely probable that movement of anisometric (less rounded or "rubbed") particles, characterizing a lower degree of packing regularity, in suspensions with equal C_V cause a more clearly defined dilation than their movement in a more polydispersed system. In view of the fact that dilation is connected with an increase in shear stresses, governing the wear mechanism, in fact it favors an increase in packing capacity for the system. These features appear most clearly in comparing HCBS with low C_V (dilation is insignificant) and with high C_V (dilation is strongly expressed).

The effect of the concentration factor with wet grinding on the polydispersion index follows from data shown in Fig. 5. suspensions of different concentration ($C_V = 0.77$ and $C_V = 0.675$) were prepared by wet grinding in a 50-liter mill for crushed fuzed quartz powder with an original particle size of $0.1 - 1.0$ mm. Here a stagewise charging method was used with a grinding duration of 23 and 42 h for a suspension with C_V equal to 0.675 and 0.77 respectively. The suspensions have about equal content of fine ($3 - 4$ μm) fractions. However their polydispersion, evaluated by the polydispersion coefficient K_p, differs markedly. The value of K_p is 24.0 and 13.5 for curves 1 and 2 respectively in Fig. 5. with stable uniform conditions the degree of polydispersion markedly governs the rheotechnological properties of a suspension, and also the density of materials prepared based on them.

PREPARATION OF LIMITING CONCENTRATION FUZED QUARTZ HCBS

As shown in Fig. 5a suspension with a high concentration is characterized both by higher polydispersion and also a higher nanoparticle content. In this connection the problem was posed of preparing under industrial conditions the
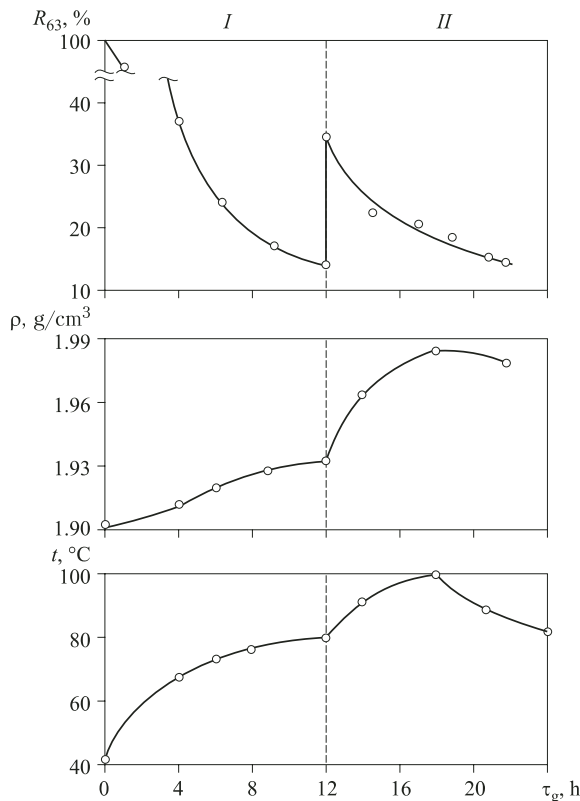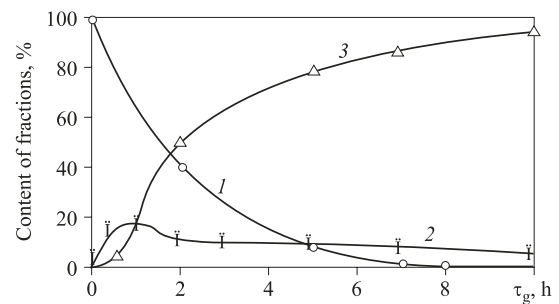
Fig. 6. Effect of wet grinding duration τ_g for fuzed quartz in a ball mill ($V = 3.5$ m^3) on content in HCBS of fraction > 63 μm R_{63}, HCBS density ρ and temperature t of the process after the first (I) and second (II) charging of material.

Fig. 7. Effect of τ_g for fuzed quartz in a ball mill ($V = 3.5$ m^3) after the first charging material on content in the suspension of fractions > 1 mm (1), $0.3 - 1.0$ (2) and < 0.315 μm (3).

Fig. 8. Integral curves for grain size composition of fuzed quartz HCBS with a density of 1.93 g/cm^3 (1) after grinding for 12 h (end of stage I) and with a density of 1.98 g/cm^3 (2) for 22 h (after the end of stage II).
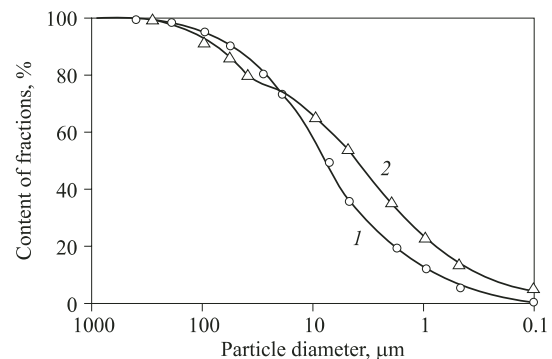
limiting concentration fuzed quartz HCBS. It was assumed that the latter, by analogy with data of Fig. 5, will exhibit a higher concentration of nanoparticles with a significant content of coarse fractions, i.e. HCBS will be characterized by markedly higher polydispersion.

In the middle of the 1990s in the Pervoural Dinas Plant on an industrial scale single stage wet grinding of fuzed quartz HCBS with a density of $1.90 - 1.93$ g/cm^3 ($C_V = 0.75 - 0,775$) was assimilated. In order to accelerate grinding in the initial stages about 10 wt.% of solid phase from drainage, i.e. production waste during centrifugal formation of articles [13, 27], was added to the mill charge. The essence of the process making it possible to increase significantly density or concentration C_V of a suspension (up to a density of $1.98 - 2.0$ g/cm^3 and a corresponding $C_V = 0.82 - 0.83$) includes the following.

In contrast to the normal method providing single-stage charging of material, the new process, as follows from Fig. 6, is accomplished with two charges: the main (stage I) providing introduction of wet grinding with a suspension density of $1.91 - 1.93$ g/cm^3 and an additional (stage II) making it possible to increase HCBS density to $1.98 - 2.0$ g/cm^3. The second charging (replenishment) of fuzed quartz is accomplished in this grinding stage when the grain size composition

of the HCBS solid phase of grinding stage I is already quite finely dispersed (the content of particles with a size of < 5 μm is not less than 25%, and > 63 μm is not more than 15%). Grinding kinetics for the material in stage I are shown in Fig. 7, and the overall nature of the process is shown in Fig. 6. The original fuzed quartz containing 99.3% SiO$_2$ with a particle size of $1 - 5$ mm is loaded without drainage material in an amount of 1000 kg and ground with a moisture content of $11.5 - 12.0$% to a density of $1.90 - 1.93$ g/cm^3 (see Fig. 6, stage I). It is apparent that after 6 h of wet grinding the content of fractions coarser than 63 μm is reduced to 24%, and after 12 h it is reduced to 12%. The integral curve for grain size distribution of the suspension after 12 h of grinding is shown in Fig. 8 (curve 2). Here the temperature of the process increases from 40 to 80°C. In stage I of the process, corresponding to $\tau_g = 12$ h, replenishment of the material is carried out in an amount of 200 kg, and the grinding process lasts 10 h (see Fig. 6, stage II). It follows from Fig. 6 that the grinding intensity, characterized by the content of coarse fractions (63 μm) in this stage, is comparable with the initial stage I. In stage II of the process there is a sharp increase in suspension temperature up to 100°C which leads to the requirement for reducing it as a result of introduction of 10 liters of water (reduction in

suspension density from 1.99 to 1.98 g/cm³). The grain size composition of the suspension in the concluding grinding stage II ($\tau_g = 22$ h) is specified by curve 2 in Fig. 8.

From comparison of the corresponding integral curves of Fig. 8 it follows that HCBS after the final grinding stage II, in spite of the comparable value of the content of coarse fractions (> 63 μm) is characterized by a high degree of dispersion. The content of particles with a size of less than 1 μm for curves 1 and 2 in Fig. 8 is 12 and 23%, and for particles with a size of 5 μm it is 36 and 55% respectively. A significant difference (almost by a factor of three) is noted with respect to the content of nanoparticles (< 0.1 μm).

The suspensions compared are also have a different degree of polydispersion. Whereas index K_p for a suspension corresponding to stage I of wet grinding (curve 1 in Fig. 8) is about 17 ($\approx 30/1.8$), then for stage II K_p increases to 50 ($\approx 40/0.8$). It is possible to suggest that fuzed quartz ($1 - 5$ mm) of the secondary charge (20 wt.%) as a result of 10 h of grinding is predominantly ground to a particle size of $40 - 400$ μm. This is indicated by the marked deflection of curve 2 with a particle diameter of about 40 μm. Particles similar with respect to size ($40 - 200$ μm), present in a suspension after grinding stage I, are ground in stage II to significantly smaller sizes. In spite of the existence of high viscosity in a suspension in grinding stage II the rate of the grinding process according to the index for the content of fine fractions appears to be comparable, but may also be greater than in stage I. A possible reason for this effect and the grinding mechanism in Stage II consists of the following.

Introduction into stage II of fuzed quartz grains with an average particle diameter $d_m \approx 2$ mm with respect to particles of solid phase in the suspension, prepared in stage I ($d_m \approx 7$ μm) may be considered as self-formed "microspheres". The latter, combined with ground suspension, are arranged within the gaps between the grinding objects ($d = 30 - 40$ mm) and promote an additional grinding effect. Here the maximum grinding rate for coarse fractions (microspheres) is noted in the initial (up to $2 - 3$ h) part of the grinding period. Taking account of the fact that in the suspension particles with a size up to 10 μm predominate, the efficiency and function of microspheres is retained with a reduction in coarse grain size to $0.1 - 0.2$ mm.

Thus, the markedly greater degree of HCBS polydispersion, obtained by the method in question, is determined by a marked increase in their content of highly dispersed particles (< 1 μm). With use in grinding stage II of additions of highly dispersed quartz glass in the form of drainage material fuzed quartz HCBS is prepared with a density of $1.99 - 2.00$ g/cm³ (value of C_V increased to 0.83).

Rheological curves for fuzed quartz HCBS with a density of 1.98 g/cm³ are presented in Fig. 9. In spite of the very high volume concentration of the suspension there is considerable dilation, i.e. with a tenfold increase in shear stress, viscosity increases only by a factor of two. The mini-
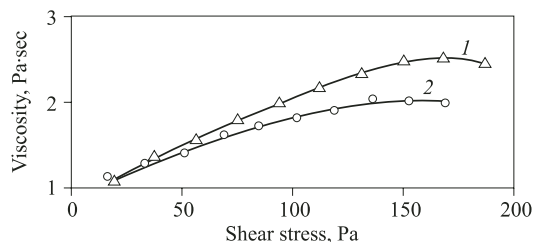

Fig. 9. Dependence of viscosity on shear stress for fuzed quartz HCBS with a density of 1.98 g/cm³ after stabilization lasting 4 (1) and 24 h (2).
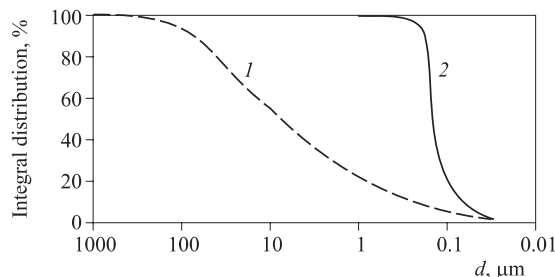

Fig. 10. Integral curves fort he distribution of solid phase particles of limiting concentration fuzed quartz HCBS (1) and pores in a casting based on it (2).

mum viscosity (1 Pa·sec) with $C_V = 0.82$ corresponds to viscosity calculated by the Pivinskii equation [36].

One aspect of the efficiency of materials prepared using limiting concentration HCBS, illustrated by the example provided below (Fig. 10), that has the pore structure of a casting based on it. Integral curves for the distribution of solid phase particles of limiting concentration fuzed quartz HCBS and pores in a casting with a porosity of 10.5% prepared based on it are compared in Fig. 10. The original suspension has a high degree of polydispersion ($k_p = 50$). The value of d_m for particles is 8 mm with a nanoparticle content (< 0.1 μm) of 6%.

However, in spite of the content in the original suspension of a significant volume of coarsely dispersed particles ($d_{max} = 0,4$ mm) the pore structure of a casting, prepared by slip casting, has a very fine capillary structure (see Fig. 10, curve 2). The latter is characterized by 95% content of pores with a diameter of less than 0.2 μm with $d_m = 0.12$ μm, i.e. the median pore diameter is almost 70% less than for solid phase particles of the original suspension. Thus, in spite of the fact that in the original HCBS the median diameter of particles is about 8 μm, the pore structure that forms in a casting is governed by a significant fraction of very finely dispersed particles ($0.2 - 0.3$ μm). During partial dehydration in a polydispersed highly concentrated and limiting deflocculated system (Fig. 11a) the optimum particle distribution is provided consisting of the fact that in spaces between relatively coarsely dispersed particles ($20 - 400$ μm) particles of average size ($5 - 20$ μm) are laid down. Within
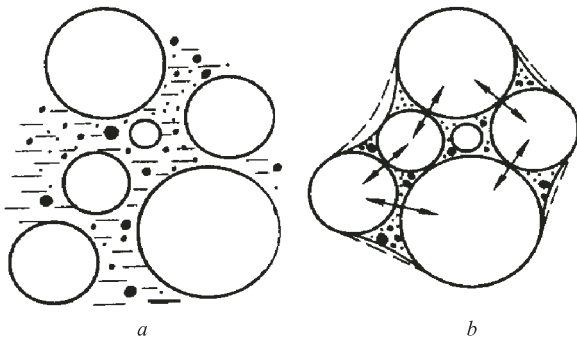
Fig. 11. Fundamental layout of casting structure formation during assembly of a mass: *a*) state of particle in an original suspension; *b*) state of particles in the stage of casting formation.

the skeleton of coarse and medium particles, occupying about 50% of the volume, there is packing of finely dispersed $(1 - 5 \ \mu m)$ particles, and between them there are nanoparticles (Fig. 11*b*). Formation of a fine capillary structure of a casting during mass assembly is the main "brake" for acceleration of the process. In addition, this structure of quartz ceramic or refractory is connected with its high metal and slag resistance. Pores at this level, even taking account of their specific coarsening during firing or service, appear to be impenetrable for corrosive melts.

COLLOID-CHEMICAL
AND RHEOLOGICAL ASPECTS
OF NANO-CONTAINING DISPERSED SYSTEMS

Independent of the technology for preparation and the composition of nano-sized particles they are primarily characterized by a strongly developed specific surface, and as a consequence a high value of uncompensated surface energy that governs their marked affinity for each other. This leads to aggregation of nanoparticles if their concentration in the system exceeds a threshold value.

In this connection in technologies based on preparation and application of fluid (cast) dispersed systems containing nanoparticles [7 – 9, 13, 18, 27, 36, 42 – 46] particular attention is devoted to the development and application of additions providing both dilution and stabilization of them (stability with respect to time). Introduction of these diluting, plastifying or surface active additions should normally be accompanied by intense mixing. The mechanism of the effect of diluting additions and subsequent suspension deformation according to [43] is shown in Fig. 12.

Structural changes in suspensions are illustrated in Fig. 12 that are achieved both as a result of introduction of defloculents and also shear deformation. An original suspension without addition of diluent is characterized by agglomeration (adhesion) of solid phase particles and as a result of which high viscosity and clearly expressed thixotropy (see Fig. 12, curve *1*). Deformation of a suspension without a deflocculant (curve *1*) leads to partial dispersion of
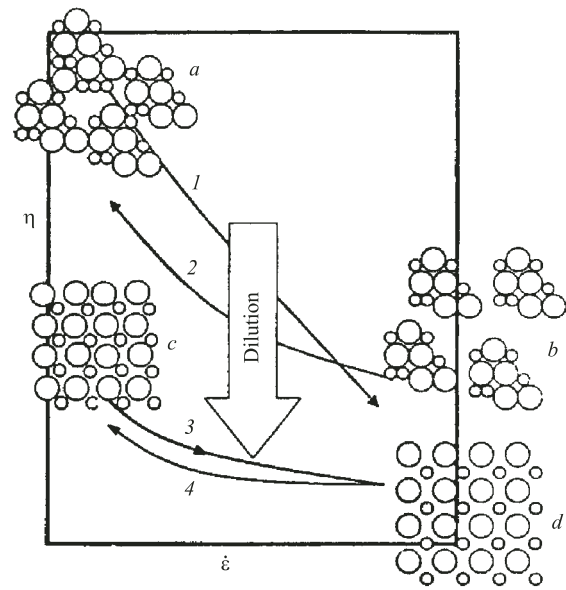
Fig. 12. General nature of the dependence of viscosity η (1 – 4) and structural state of solid phase particles in the system ($a - d$) on shear rate $\dot{\varepsilon}$: *1, 2*) flocculated suspension (arrows indicate the direction of shear application); *3, 4*) deflocculated system; *a*) flocculated original structure; *b*) same after deformation; *c*) deflocculated original structure; *d*) same after deformation.

agglomerates (condition *b* in Fig. 12). However, even for a disturbed thixotropic structure suspension viscosity is quite high; hysteresis of viscosity is significant (curve *2*). Introduction of deflocculant leads to a marked change in the structure of a suspension of both an original (*c*) and also after shear deformation (*d*). There is an equivalent change in suspension viscosity (curves *3, 4*). Deflocculation leads to colloid disintegration (dispersion) of solid phase particles in a suspension, to a sharp reduction in thixotropy (curve *3*) and viscosity hysteresis (curve *4*). Proceeding from general assumptions of colloid chemistry and rheology, features of the change shown in Fig. 12 for structure and rheological properties characterize an example of a combination of colloid-chemical and rheological (mechanical) principles of stabilization and dilution of dispersed systems [13, 36].

As applied to use of microsilica according to data in [46] an example is considered of effective realization of the principle of dilution and stabilization of dispersed systems. It is well known that microsilica (MS) is used extensively in industry is supplied in a bulk or previously compacted state. According to data of the Norwegian firm Elkem AS, supplied microsilica has a bulk density of $200 - 400 \ kg/m^3$ in a normal condition and $500 - 600 \ kg/m^3$ in a compacted condition. This corresponds to a packing coefficient value overall of $9 - 18$ and $22 - 27$ respectively. On the basis of studies at NIIZhB [46] in the Chelyabinsk Electrometallurgical Combine industrial production has been accomplished of fluid concentrated suspensions (pastes) and MS.

The method has been realized as a result of preventing gel formation of a suspension and increasing its fluidity as a result of introducing stabilizer FOK-2. An important component of it is a complex-forming agent, i.e. nitryltrimethylenephosphonic acid and water-soluble polymer (superplastifier S-3). For aqueous MS suspensions an important role is played by the reaction of polycondensation that is accompanied by formation of silaxane bonds, growth of colloid particles and gel formation, i.e. a reduction in aggregate stability. Since MS contains, apart from microsilica, significant impurities of iron, calcium, magnesium and aluminum oxides, then during hydration there is formation of polymer chains of the type –Si–O–M–O–Si–. These chains are an additional factor leading to particle aggregation and gel formation, i.e. to suspension thickening. Therefore in order to stabilize the latter it is necessary to avoid this factor, i.e. to block metal cations. In order to stabilize MS suspensions it is necessary to prevent or slow down formation of siloxane bonds and polymer chains. This may achieved as a result of ion charges that provide retention of particles separately due to repulsion forces and as a result forming an absorbed film of inert substance. According to [44] the first case is electrostatic stabilization and the second is steric.

Introduction of the optimum complex addition FOK-2 (0.25%) made it possible to prepare fluid suspensions with a weight concentration up to 60 – 70% that corresponds to a volume concentration of 40 – 50%, or a solid content of 900 – 1100 kg/m^3. In addition, an advantage of using similar systems consists not only in a reduction in transport losses or in an ecological respect (replacement of a "dry" process by a "wet" process). As shown in the publication [46] the main features of concrete mixes and structural concretes with additional of MS paste based on FOK-2 is an increase in concrete mix mobility and a lower loss in mobility during storage for 2 h, and also a slowdown in concrete hardening kinetics that subsequently intensifies compensating the comparatively low strength in earlier times.

An important colloidal-chemistry and production characteristic of multiphase dispersed systems of casting consistency is their sedimentation resistance. As shown in studies summarized in publications [13, 36], a significant increase or achievement of total resistance to layering is possible in the case of an increase in suspension concentration and a high degree of polydispersion of their solid phase particles. Also important is presence of nanoparticles in the latter. In addition, it has been established experimentally for a long time that sedimentation resistance of quartz glass suspensions increases markedly after dilution and stabilization. In studying quartz glass suspensions [35] it has been established that stabilization by mechanical mixing increases sedimentation resistance. Considering that viscosity of a stabilized suspension is markedly lower than for the original, a question arises about the mechanism of this effect: why a reduction in viscosity should lead to an increase in deposition rate.

Apparently this effect is caused by the fact that during stabilization there is a marked increase in aggregation resistance of a suspension characterized by the value of the electrokinetic ξ-potential of particles of their solid phase [36]. It is well known that this is one of the most important parameters of a double electric layer (DEL) determining the effect of particle repulsion. To all appearances this effect prevails in the sedimentation behavior of concentrated suspensions. As applied to a quartz glass suspension the value of the ξ-potential is markedly governed by the purity of the original material, preparation conditions, the degree of stabilization, and pH, etc. In this connection a study was made of the sedimentation resistance of quartz glass suspensions characterized by the maximum value of ξ-potential, i.e. 98 mV. The latter was prepared by technology adopted in the production of high purity quartz ceramics [35], and it was characterized by a density of 1.875 g/cm^3, pH = 4.9, viscosity 8 °E, content of fractions finer than 5 mm 28.5%, coarser than 63 mm 5.3%. As shown in part 1 of the present article, quartz glass suspensions also contain nanoparticles.

Studies consisted of the following*[3]. An original suspension in a volume of 1.5 liters was subjected to 50-day settling in a polythene cylinder 30 cm tall, i.e. 1 cm of column has a volume of 50 ml. during settling kinetics were determined for deposit accumulation in the lower part of the vessel. It was established that accumulation of deposit to maximum height of 28 – 30 mm was only noted over the first 10 – 12 days of settling, i.e. the maximum height of deposit achieved was only 10% of the total volume of the original suspension. After 50 days of settling suspension density and viscosity were measured over the height of the column followed by analysis in samples of the content of "screened" fractions, whose size did not exceed 40 μm. The upper level was taken as the zero point. The two upper samples were taken as a volume of 50 ml and the rest as a volume of 100 ml.

Experimental data for the distribution of density and viscosity indices for a suspension over a the height of a column after settling are shown in Fig. 13, and the content of different groups of fractions are shown in Fig. 14. It follows from Fig. 14 that only in the very upper part of the settled column of the suspension is its density below 1.24 g/cm^3. At the level of 2 cm it increases to the value of 1.75 g/cm^3, and with $h = 8 – 10$ cm it becomes comparable with the original. A marked increase in density compared with the base commences after the level $h = 20$ cm. The maximum density (at the boundary with the deposit) reaches 1.96 g/cm^3 ($C_V = 0.80$). It is entirely natural that the indices of nominal viscosity correlate with those for suspension density. It is notable that up to a value of $h = 10$ cm for settled suspension its viscosity is entirely comparable with the original (8 – 12 °E). This points to insufficient thickening during holding (storage). A sharp increase in viscosity corresponds to the interval of marked suspension concentration ($h = 20 – 26$ mm).

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*[3] A. D. Buravov and P. V. Dyakin took part in these studies.
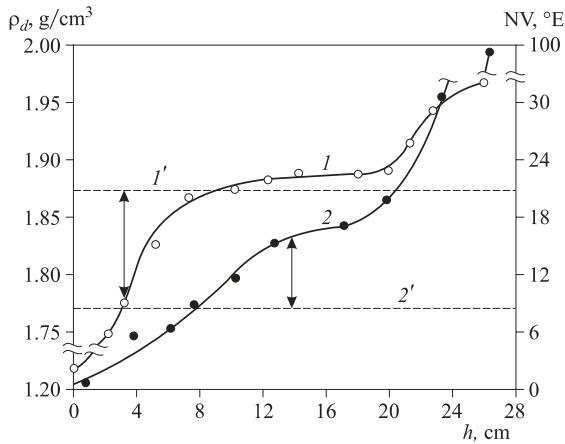
Fig. 13. Distribution of density ρ_d (*1*) and nominal viscosity NV (*2*) over the height *h* of a column settled for 50 days of quartz glass suspension with $\rho_d = 1.875$ g/cm³; *1′* and *2′* are original values of ρ_d and NV respectively.
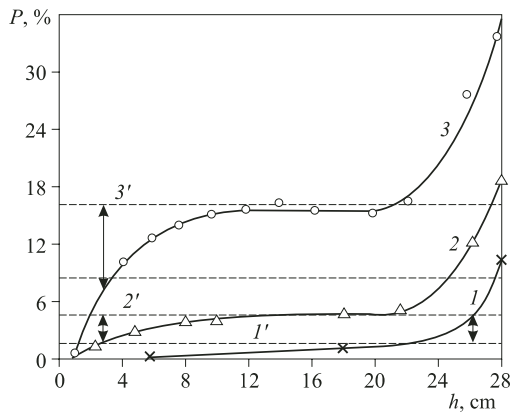
Fig. 14. Distribution P of the content of coarse fractions 100 (*1*), 63 (*2*) and 40 μm (*3*) over the height *h* of a settling column during 50 days of a suspension of quartz glass with $\rho_d = 1.875$ g/cm³; *1′–3′*) content of fractions in the original suspension.

It follows from Fig. 14 that marked impoverishment of the suspension with respect to the content of a group of fractions coarser than 40 and 63 mm is only noted at the level up to $10 - 12$ cm. As far as a coarse fraction is concerned (> 100 μm), then up to the level $h = 8$ cm it is entirely absent. The fraction > 63 μm is absent at the level of $2 - 3$ cm. Proceeding from these data for deposition rate of narrow groups of fractions ($63 - 100$, $100 - 160$, $160 - 200$ μm) it has been established by calculation that the actual deposition rate even for very coarse fractions ($0.5 - 1.0$ mm/day) compared with the rate calculated by the classical Stokes equation, is less in the test suspension by about a factor of one million (six orders of magnitude).

The content of different "screened" fractions in the original suspension and the deposit are compared in Table 1. The latter was characterized by a density in the dried state of 1.88 g/cm³ (porosity 14%). Taking account of the fact that

TABLE 1. Content and Ratio of Grain Size Fractions in a Suspension (R_1) and in a Deposit (R_2)

Fraction	Content, %, fraction, μm				
	$40 - 63$	$63 - 100$	$100 - 200$	> 40	> 63
R_1	11.80	3.75	1.55	17.1	5.3
R_2	17.05	7.4	10.4	34.85	17.8
$K = R_2/R_1$	1.44	1.97	6.7	2.04	3.35

the value of the specific concentration of the original suspension Q_V is 1.60 g/cm³, the value of additional concentration $\Delta Q = 1.88 - 1.60 = 0.28$ g/cm³. Whence it follows that the deposit formation factor $K_{de} = (0.28/1.60) \cdot 100\% = 17.5\%$.

It follows from Table 1 that the difference in content of fractions increases with coarsening of them. The maximum difference is typical for the fraction $40 - 63$ μm, and the maximum (difference a factor of 6.7) is for fraction $100 - 200$ μm. It is evident from the data provided that deposition of suspensions is determined primarily by the coarsest particles (> 100 μm) contained within them. Particles with a diameter of less than 40 μm in suspensions hardly precipitate. As applied to casting, a test quartz glass suspension may be considered entirely stable in a sedimentation respect for a duration up to several hours.

WATER AS AN ACTIVE COMPONENT OF NANO-DISPERSED SYSTEMS

As a result of the exceptional reaction capacity of nanoparticles in general and nano-dispersed silica in particular it is useful to consider separately the role of water in dispersed systems containing it. Water as a component of a dispersed system may only be considered neutral in the initial instant. Subsequently within it, as a liquid medium, there is dissolution, dissociation, flocculation or deflocculation, peptization, typical for the stages of dispersion and condensation of dispersed systems [36, 48]. Water is subject to electrolytic dissociation in accordance with the equation $2H_2O = OH_3^+ + OH^-$. As a result of these phenomena there is a continuous change in dispersion medium activity with respect to the dispersed phase of the system. Water becomes a solution of electrolytes and therefore its properties change in proportion to the concentration of dissolved substance [15, 36, 48].

Exceptionally important is the effect of water in processes of structure formation not only of hydrated binders, but also ceramic (HCBS) or desiccation binders (clays). Formation of surface films and layers of water at the surface of particles, determining the effect of binding properties, is caused by three physicochemical processes: adsorption, surface osmosis and capillary absorption. The activity of water, according to various data, in view of various factors (defects and pores of the boundary surface, temperature, pressure, presence of electrolytes, impurities, etc.) changes

in the range from 10 to 1600 kJ/mole. Thus, bond energy in water molecules embraces all the possible range from van der Waals to chemical interaction that develop during structure formation of mineral binders. Water may be considered as a matrix base during solidification of oxide and aluminosilicate materials. For some systems the proportion of water in the energy of formation of a material is 50 – 80% [27, p.345]. on the other hand, as applied to dehydrated material based on HCBS presence in the latter of water also has a marked effect on their strength. For silica ceramic concretes [49] the ultimate strength in compression σ_{co} in the absolutely dry state (immediately after drying) is 20 – 30% higher than for specimens in the air-dried state. Strength of the same specimens in a water-saturated state is 40 – 790% of the strength of air-dried material.

As applied to structural concrete technology in [50] the problem has been formulated of nano-modification as a principle for controlling formation of a material structure from the nano-level to the macrostructure, and to a concrete mix. The concept has been introduced of nano-structuring of mixing water using nano-dispersed modifiers (plastifiers S-3 and F_k-03) in molar fractions close to 10^{-7}. This makes it possible to control the kinetic process, and to increase strength, water- and frost-resistance.

As applied to the technology of refractory materials prepared using colloidal SiO_2 (silica gel) solutions, the authors in [51] with the aim of increasing material strength studies introduction into the composition of the latter of organically based ammonia that promotes a reduction in the silicate modulus, an increase in solution alkalinity with an increase of its pH to 12 – 12.3. As a result of this part of the silica gel is converted into a highly active soluble form from the point of view of binding properties. This provides hardening of the binder according a "liquid-glass" mechanism with formation of a stronger skeleton compared with the skeleton based on normal silica gel. During heat treatment there is decomposition and burning-off of the organic part of the binder, and the strength of the material as a result of the increase in concentration of the dissolved form of SiO_2 increases markedly.

NANOSILICA QUARTZ GLASS AND CERAMIC TECHNOLOGY

In view of the expansion of the production of semiconductor silicon in recent years there has been a marked increase in interest in preparing quartz ceramics of high purity applied to crucible preparation. They are prepared primarily by casting into porous dies from casting suspensions prepared on the basis of high purity quartz glass or synthetic SiO_2 [52 – 54].

In view of this methods are being developed fro preparing high purity quartz glass, including synthetic material. From data provided in [55] it follows that recently in order to synthesize monolithic quartz glass dispersions and powders

of nanosize silica are used that are prepared by hydrolysis in a flame and plasma-chemical synthesis. The most widespread used are aerosils in the form of binder and original materials for preparing quartz glass. In this article works are cited devoted to studying processes that occur during sol-gel synthesis of monolithic quartz glass using aerosil OKh50. Preparation of xerogels, an intermediate synthesis product, has been accomplished on the basis of both a dry powder and aqueous suspensions of aerosil. In the first case isostatic compaction is used and the aerosil is used in the form of both basic material and a binder for more coarsely dispersed silica powders. Aerosil powder OKh50 has also been used as a filler added either to tetraethoxysilane before the start of hydrolysis, or to commercial SiO_2 sols. Here fine particles of SiO_2 serve as a binder for the relatively coarsely dispersed particles of aerosil OKh50. In the second case aerosil OKh50 has been used in order to prepare highly concentrated dispersions in aqueous and nonaqueous media. As noted in [55], sols and suspensions of aerosils due to the high degree of chemical purity, narrow particle size distribution, their spherical nature may serve as model systems in particular for studying the electrosurface properties of particles, the aggregate stability of sols and interconnection of these properties with physicochemical and mechanical properties of dispersions prepared based on them.

For a long time (1960 – 1980s) in GosNIIKS studies have been carried out and specific objects have been prepared from quartz ceramic (kersil) prepared on the basis of synthetic silicon dioxide (SSD). Then tetraethoxysilane was synthesized by hydrolysis with an aqueous solution of ammonia followed by heat treatment of the hydrolysate at 750°C [56]. The production complexity of preparing quartz ceramic based on SSD consisted of a requirement of prior dehydration (calcining) of the original material. It has been established [56] that the optimum calcining temperature is in the range 1100 – 1150°C. If it is exceeded the danger develops of forming cristobalite. Subsequently SSD were subjected to grinding and suspension. The density of suspensions for slip casting was 1.8 – 1.88 g/cm³, and material porosity after firing at 1200°C was 13 – 16%. An increase in firing temperature to 1230°C and above had an undesirable effect of cristobalite formation, and therefore the level of material sintering achieved was characterized by porosity of 11.8% with a content of 5% cristobalite.

In order to prepare synthetic silica the authors in [54] used a sol-gel method. Sols of SiO_2 were prepared by hydrolysis of silicon tetrachloride $SiCl_4$. Silicon tetrachloride exhibits an advantage compared with other forms of raw material due to the fact that the contemporary semiconductor industry has moved to use of trichlorosilane. In view of this silicon trichloride, formed during hydrogen reduction of trichlorosilane and exhibiting semiconductor purity, needs utilization or conversion into trichlorosilane. Here silicic acid sol was prepared during titration of $SiCl_4$ into water with continuous mixing of the solution. The hydrolysis reaction that occurred may be presented in the following

form: $SiCl_4 + 4H_2O \rightleftarrows Si(OH)_4 + 4HCl$. With the passage of time (2 – 3 h) there was sol polymerization with transfer of the system into a gel-like state. The sol-gel transition process was accelerated by means of mixing. After titration freshly deposited gel was filtered and washed with deionized water and then the gel was dried at 100 – 140°C. In the concluding stage the xerogel obtained was subjected to firing with the aim of removing residual moisture at a temperature not below 800°C, that was accompanied by considerable aggregation of the sol particles. Here the size of the agglomerates formed was 300 μm. Mechanical grinding of agglomerates to a median particle size (10 mm) was performed in a planetary mill. The suspension method was used to prepare suspensions with a maximum possible concentration that to a considerable degree was determined by the temperature of prior material calcination. With an increase of it from 800 to 1150°C the value of C_V increased from 36 to 65%. On the basis a limiting concentrated suspension ($C_V = 0.65$) the slip casting method was used to prepare castings with a porosity of 15% that with a firing temperature of 1200°C sintered with shrinkage of 4 – 5% [54]. From the two examples provided [54, 56] it is evident that there are production difficulties in preparing ceramics connected with the problem of prior dehydration of the original synthesized materials.

Thus, the concentration of suspensions with which wet grinding is an important factor governing the content of nanoparticles within their dispersed medium. Under industrial conditions limiting concentration fuzed quartz HCBS have been prepared ($C_V = 0.82 – 0.83$) that have high polydispersion and containing nanoparticles. Castings based on them have a nanoporous structure. In the technology of materials using nano-dispersed particles an important role is played by control of their rheological and colloid-chemical properties. Stabilized HCBS have high sedimentation stability.

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