

Concentration of Various Forms of Water in Silica Precipitated from a Hydrothermal Solution

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Abstract—The physicochemical properties of the surface of silica precipitated from a hydrothermal solution have been studied. The concentration of physically adsorbed water, and the net concentration of surface and bulk (internal) hydroxyl groups have been found by low-temperature adsorption of nitrogen and thermogravimetric data. The concentration of internal silicone (internal water) under different temperatures of the silica specimens under study has been estimated from the difference between the net concentration and the Zhuravlev physicochemical constants. The type of noncrystalline silica containing substantial amounts of internal water has been identified. The difference in mechanisms involved in internal and surface water extraction has been established.

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INTRODUCTION

To improve models of hydrothermal mineralization it is necessary to clarify the role of colloidal silica [3, 6]. Considerable amounts of material are known to be transported and precipitated in fractured porous rocks in colloidal form during a volcanogenic hydrothermal process [3, 6]. It is necessary to study the formation of colloidal silica particles in hydrothermal solutions, their precipitation, the sorption on the surface of colloidal particles and codeposition of compounds, as well as further transformation of the matter precipitated from a colloidal noncrystalline to crystalline forms. The physicochemical properties of hydrothermal minerals whose formation involves colloidal silica are related to the conditions for formation and precipitation of colloidal particles. Knowledge of colloidal silica is also in demand for developing the technology of extracting it from the hydrothermal heat carrier and for using the extracted material in industry [4, 5]. The purpose of this study was the determination of the concentration of physically adsorbed water and the surface and external silanol groups in a silica that has been precipitated from the hydrothermal solution of the Mutnovsky field.

Types of silanol groups on silica surface and the content of internal water. Multiple papers and monographs by various authors, including the review [8], demonstrate the high potential of noncrystalline, variously hydroxylated silica for use in science and technology. Silanol groups $\equiv\text{Si}-\text{OH}$ are generally formed on surfaces by two thermodynamically favorable processes [8]. Firstly, the groups form during synthesis, for

instance, as a result of condensation polymerization of $\text{Si}(\text{OH})_4$, when an oversaturated solution of monosilicic acid is transformed to polysilicic acids with further formation of SiO_2 sols and gels containing OH groups. After drying, the terminal product is xerogel, which preserves silanols partially or entirely on the surface as well. Secondly, silanols can form as a result of rehydroxylation when thermally dehydrated silica is treated with water or water solutions. A surface Si atom tends to preserve the final tetrahedral configuration. That is why the residual valency saturates with the OH group in water after disclosing the silicon bridge $\equiv\text{Si}-\text{O}-\text{Si}\equiv$.

Various groups on the surface and inside silica are illustrated in Fig. 1 [8]. They are (1) free single (isolated) surface silanols $\equiv\text{SiOH}$ (type Q^3), (2) free geminal (isolated) surface groups or silanediols $\equiv\text{Si}(\text{OH})_2$ (type Q^2), (3) vicinal bridge silanols which are single surface silanols, geminals and their combinations bonded with hydrogen (H-bond), (4) silicon bridges $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ having an O atom at the surface (type Q^4), (5) internal silanols located within the matrix and ultramicropores of SiO_2 . Consequently, noncrystalline silica, both untreated and hydrothermally treated within a wide range of temperature, has only two different types of OH groups at the surface, single and geminal ones, further subdivided into isolated and H-bonded vicinal silanols [8]. The taxonomy of surface groups frequently uses the Q^n -nomenclature suggested by D.V. Sindorf and G.E. Masiel on the basis of data derived by ^{29}Si nuclear magnetic resonance [8], where n is the number of bridges ($-\text{O}-\text{Si}$) joined to the central Si atom in an elementary $\text{SiO}_{4/2}$ tetrahedron.

[†] Deceased.

Adsorbing properties of noncrystalline dispersed silica are controlled, apart from their porous structure, mainly by chemical activity of the surface. This activity depends on the concentration of OH groups, i.e., the total quantity of silanols and their varieties, as well as on the temperature and energetic patterns of the silanol distribution and the occurrence of SiOSi silicon bridges.

Silanol groups $\equiv\text{Si}-\text{OH}$ could be located both on the surface (for surface silanols) and inside the particles of noncrystalline silica and/or in superfine pores less than 1 nm in diameter, which can accommodate only the smallest molecules, such as water molecules (for internal silanols). It was demonstrated in detail in [8] that OH groups at the surface of wide transport pores are easily involved in deuterium exchange (DE) reactions with heavy water D_2O in the form of steam or liquid introduced at room temperature. However, adhesive water inside the internal matrix of SiO_2 is almost not involved in the process, and the isotopic exchange with silanols in ultramicropores is very slow.

Internal silanols, i.e., OH groups that are bonded covalently with Si atoms, but are found inside the silica particles (see Fig. 1) and are not responsible for the surface processes, are a widely occurring form of noncrystalline silica. It should be stressed that the $\equiv\text{Si}-\text{OH}$ groups inside SiO_2 particles are to be excluded from consideration, when the goal is to calculate the surface concentration of OH groups (silanol number α_{OH} , OH/nm^2) and to study the surface silanols activity alone because of their controlling influence in various processes at the surface.

We reiterate that the internal OH groups are subdivided into two basic types (a) those in the matrix of noncrystalline silica particles and (b) those inside superfine ultramicropores.

There are many means of silanol formation in the matrix and in the ultramicropores of silica, an incomplete list of these is as follows:

(1) Specific silanols could remain in the structure of an inorganic polymer of the silica recovered by condensation of low-molecular polysilicon acids, if no suitable reactants are available. As well, in the silica formed from sodium silicate, a certain number of OH groups could be captured inside as initial small particles are being aggregated, as well as later during the aging of the SiO_2 gel.

(2) Large spherical particles (globules) 10–20 nm in diameter of pyrogenic silica are formed by aggregation of elementary initial globules of diameter 1–2 nm that have been obtained by condensation from flame. Initial particles contain some surface silanols, and thus such OH groups could be captured inside a large globule of the terminal product.

(3) According to R. Iler's work [1], when colloid particles form by growing in alkaline solution ($\text{pH} \sim 9$), sodium ions can be adsorbed on the particles simulta-

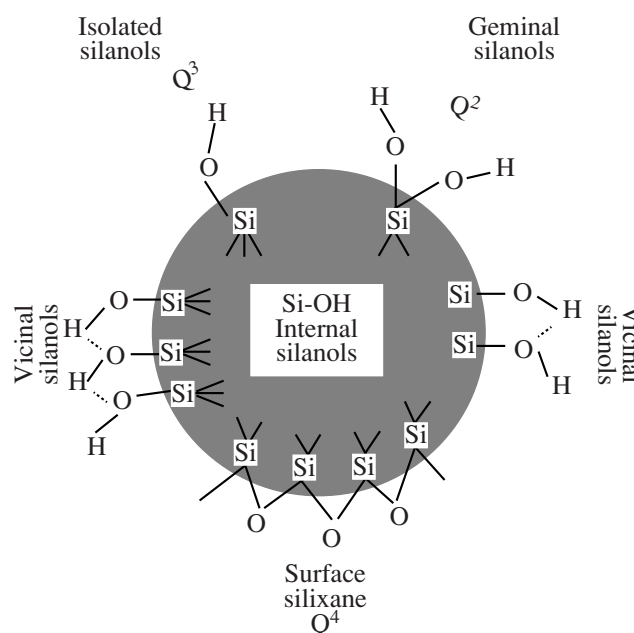


Fig. 1. Types of silanol groups on silica surface.

neously with the precipitation of SiO_2 , facilitating capture of silanol in the silica structure.

(4) The occurrence of internal silanols can also be explained by diffusion of H_2O molecules into the SiO_2 solid structure down to 15 nm depth at increased temperature [8].

(5) A popular method of silanol formation in the matrix and ultramicropores of SiO_2 is hydrothermal treatment (HTT). For noncrystalline silica under HTT, which means increased temperature and pressure, the complex processes of silica dissolution and redeposition, as well as water diffusion inside the solid phase occur. As a result, secondary, geometrically modified silica is produced having a different pore structure that can retain silanols or adhesive water both inside the particles and in ultramicropores.

(5a) Using HTT in the autoclave at the stage of SiO_2 hydrogels, a series of silica gels with mesoporous structures, dense particle packing, and lack of ultramicropores has been obtained. Such silica samples typically contain silanols both at the surface and inside the silica particles.

(5b) Using HTT at the stage of xerogels yielded silicagels of globular, transient and spongy porous structures [8]. These samples contain silanols at the surface, inside the particles, as well as in ultramicropores.

(5c) HTT applied to initial pyrogenic silica (aerosils) in the autoclave yielded a series of aerosilgels having various porous structures, with the samples containing silanols both at the surface and inside the silica particles [8].

(5d) Various treatment methods applied to initial porous glasses, including HTT (long-lasting boiling in

Table 1. Chemical composition of a silica sample (wt %) precipitated from hydrothermal solution

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅
AK1b	97.69	0.024	0.494	0.084	0.108	n/d	n/d	n/d	0.72	0.349	0.072

Note: n/d means not detected.

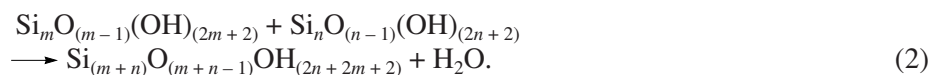
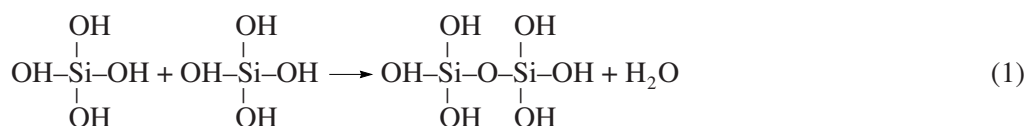
water) produced geometrically modified porous glasses having various porous structures. Apart from surface OH groups, these samples contain silanols inside the particles and in ultramicropores [8].

(5e) It should be expected that internal silanols must be found in samples of various noncrystalline silica forming as solid deposits on the walls of wells, pipelines and thermal equipment of heat and electric power plants operating with natural high temperature hydrothermal heat carriers in the fields of Russia, New Zealand, Japan, the United States, Philippines, Mexico, Iceland, Italy and others [4, 5].

The mechanism involved in the production of colloidal silica in hydrothermal solutions. Colloidal silica forms in hydrothermal solutions as a result of successive physicochemical processes. The initial concentration of silica is controlled by the temperature of

chemical equilibrium between water and aluminosilicate minerals of the host rocks of geothermal fields [5]. In an equilibrium environment, the net concentration C_t of silicon dioxide SiO₂ in solution is in close agreement with the solubility of alpha-quartz in pure water [5]. The silica in the solution is mostly found in the monomer form as molecules of orthosilicic acid H₄SiO₄.

During ascending filtration in rocks or when rising to the surface in producing wells of geothermal power plants (GPP), because of decreasing pressure and temperature, as well as partial transition of the solution to the steam phase, silica becomes oversaturated with respect to the solvability C_e of noncrystalline silica [5]. The oversaturation is the driving force of nucleation and polycondensation of orthosilicic acid molecules, producing silicon bonds and partial dehydration [1, 5, 7], as follows:



As a result of polycondensation, the colloid particles of hydrated silica are formed in the solution. Dissociation of surface silanol groups SiOH and separation of proton H⁺ result in negatively charged particle surface. Electrostatic repulsive forces prevent the coagulation of particles and are responsible for the stability of colloidal silica in hydrothermal solutions.

Physicochemical properties of silica precipitated from hydrothermal solutions. Silica was precipitated by freezing from a dispersoid solution of the Mutnovsky field wells [4]. Drops of the solution were frozen on the snow, colloidal silica particles concentrated in spaces between ice crystals, drawing the particles together and accelerating the coagulation. As a result, a gelatinous mass of precipitated silica and snow mixed together formed on the surface, which became a fine powder after drying at 105°C.

The silica precipitated was removed from the plot and dried. The density of the gelatinous silica sampled from the snow surface was 2.0 g/cm³. After a drying treatment lasting 12–16 h at 110°C the material became a fine powder of density 0.22–0.24 g/cm³. The chemical composition of silica is shown in Table 1. The weight percentage of silicon dioxide in the samples after sub-

traction of the losses due to drying at 110°C and ignition at 1000°C was 95.0–97.69 to 99.02%, while the combined weight percentage of calcium, aluminum and iron did not exceed 0.6%.

The silica samples precipitated by freezing were amorphous to X-rays, as illustrated by Fig. 2a. X-ray diagrams support this by the occurrence of a halo-amorphous phase having the maximum at 0.387–0.40 nm. After ignition at 1000°C the silica was transformed to cristobalite (see Fig. 2b).

Infrared (IR) spectra of the silica samples have been acquired with a Fourier IR spectrometer Vector 22/N (Bruker) in the wave number range 250 to 4250 cm⁻¹. There are three maxima in the range 250–1200 cm⁻¹ associated with oscillations of Si–O–Si bonds in the SiO₄ tetrahedron: two low maxima between 500 and 750–850 cm⁻¹, and a third higher one in the interval 1096–1104 cm⁻¹ (Fig. 3). The range 1200–4000 cm⁻¹ always contains two low peaks around 1600–1640 cm⁻¹ and 2344–2368 cm⁻¹, as well as a higher one in the interval 3440–3480 cm⁻¹, which represent the oscillations of hydroxyl groups OH.

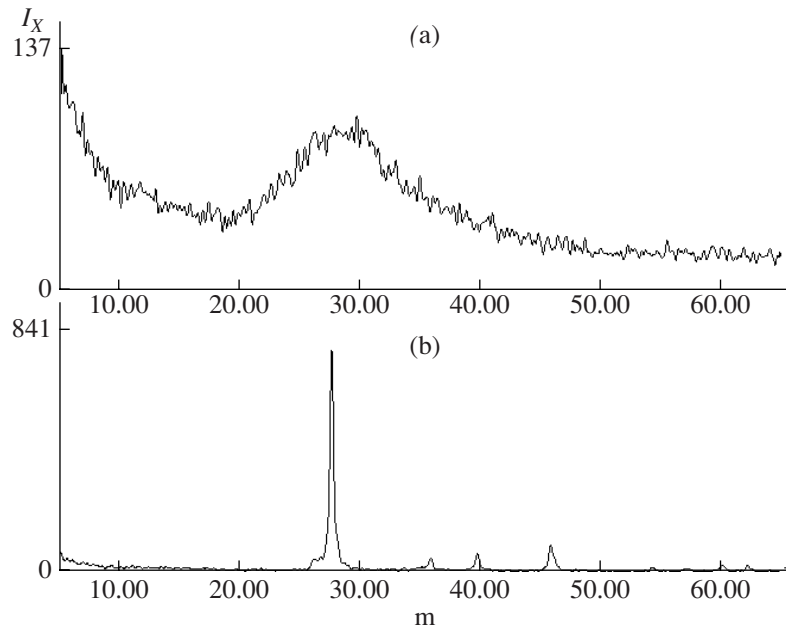


Fig. 2. X-ray diagrams of a silica sample before (a) and after (b) ignition.

The structure of the IR spectral curves, together with two major peaks at $1096\text{--}1104\text{ cm}^{-1}$ and $3440\text{--}3480\text{ cm}^{-1}$, are characteristic for various forms of noncrystalline silicon dioxide.

A thermal analysis of silica sample AK1b was carried out with a Pyris Diamond TG/DTA instrument manufactured by Perkin Elmer. The data is presented in Fig. 4, while values of the thermogravimetric (TG) curve are listed in Table 2. The measurements were made in open air at a heating rate of $20^\circ\text{C}/\text{min}$. The differential TG curve has an extremum at 68°C , which lies in the range of typical values for noncrystalline silica [8].

Measurements of the reflection index for light at the surface of dispersed silica in the range of $400.0\text{--}760.0\text{ nm}$ were made with a MSFU-K spectrophotometric microscope. The reflection index (whiteness) of geothermal silica samples reached 91–95 to 94–98%, increasing with increasing wavelength as follows: 0.9402 at 480 nm, 0.9531 at 500.0 nm, 0.95029 at 520.0 nm, 0.95394 at 540.0 nm, 0.96534 at 560.0 nm, 0.96592 at 580.0 nm, 0.97425 at 600.0 nm, 0.97911 at 620.0 nm, 0.97679 at 640.0 nm, 0.97182 at 660.0 nm, 0.97274 at 680.0 nm, and 0.98265 at 700.0 nm. These values of the reflection index demonstrate the potential of silica for use in various industries, including paper production.

Measurements of specific surface area and pore volume in a silica sample by low temperature adsorption of nitrogen. The area and pore volume in silica samples were measured by means of low temperature adsorption of nitrogen using an ASAP-2010N porometer (Micrometrics, United States). The tech-

nique is based on measurements of adsorption/desorption isotherms for nitrogen at the temperature of liquid nitrogen [2]. The experiment was done in order to measure changes in the mass of the dispersed sample to find the amount of adsorbed nitrogen at a fixed relative pressure of nitrogen P/P_0 (P is the nitrogen pressure in the system and P_0 the pressure of saturated nitrogen vapor at the experiment temperature) in a vial containing the sample. The volume of adsorbed nitrogen V was first determined for successively increasing values of the relative pressure P/P_0 from 0.01 to 1.0 (the adsorption curve), and then for the pressure P/P_0 decreasing from 1.0 to 0.04 (the desorption curve). The $V(P/P_0)$ relation is presented in Fig. 5.

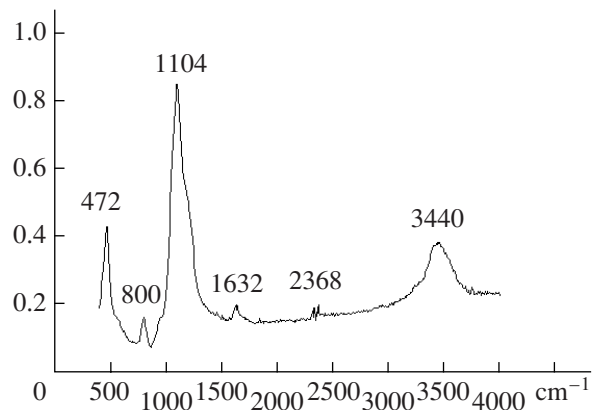


Fig. 3. IR spectrum of a silica sample.

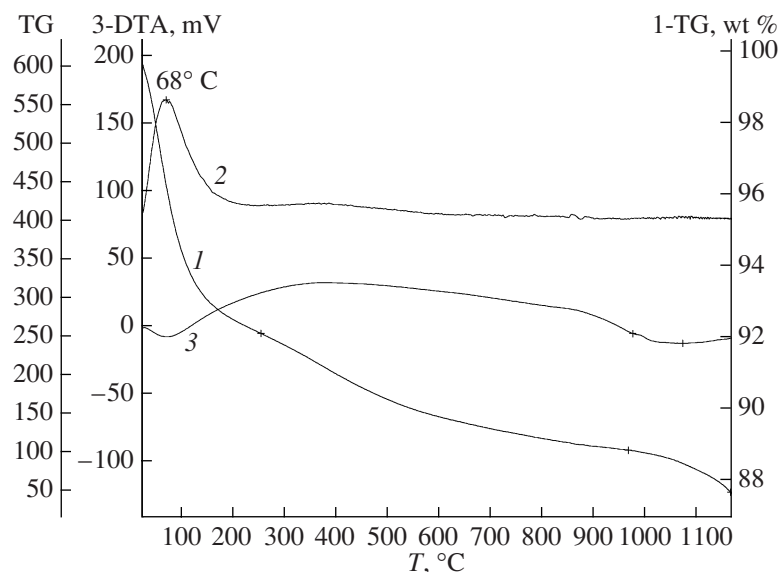


Fig. 4. Curves from thermal analyses of a silica sample: (1) thermogravimetric analysis; (2) differential thermogravimetric analysis; (3) differential thermochemical analysis.

The experimental data were processed to construct plots of nitrogen volume $V(P/P_0)$ versus relative pressure, also referred to as adsorption and desorption curves. In these plots the curves exhibit characteristic hysteresis loops. The resulting experimental curves are of the fourth type of adsorption isotherms according to [2]. The curves are convex from zero to the point $P/P_0 = 0.3$, a flexion point around $P/P_0 = 0.3$ – 0.5 , after which the curves are concave. Near the point $P/P_0 = 1.0$ the curves become convex again (Fig. 5).

The specific surface area was found by the Brunauer–Emmet–Teller (BET) and Brunauer–Deming–Helthy (BDH) techniques. The calculations of the specific surface area according to the BET were based on measurements in the range of relative pressure $P/P_0 = 0.0$ – 2.0 , and the BET equation for multimolecular adsorption of vapor was used [2].

We used the $V(P/P_0)$ relation in the classical adsorption/desorption theory [2] to calculate differential distributions of the volume V_p and the area S_p of the pores with diameters d_p in a specified range, as well as integral values of the pore volume and area with diameters between 1.7 nm and a specified value d_p . Differential characteristics of pore volume $dV_p/d\log(d_p)$ and pore area $dS_p/d\log(d_p)$ have been calculated.

The $dV_p/d\log(d_p)$ curves have maxima around $d_p = 18.0$ nm, and the $dS_p/d\log(d_p)$ curves have maxima at $d_p = 11.7$ nm.

Properties of the pores of the geothermal silica samples found by the adsorption technique are demonstrated in Table 3. This data shows that the specific surface area of a silica sample acquired from the solution of Mutnovsky field wells reaches $300 \text{ m}^2/\text{g}$, the porosity is $1.1 \text{ cm}^3/\text{g}$, and the mean pore diameter is 12.7 – 16.6 nm.

The micropore volume and area in samples of hydrothermal silica are relatively small. The ratio of micropore area to total pore area was 0.09 – 0.107 , the respective volumetric ratio is even smaller, 0.005 – 0.0085 (Table 3).

The area and volume of the pores in relation to the pore diameter are presented in Table 4. It is seen that the pore size of the AK1b silica sample clusters in a narrow range of diameter. The differential distribution of pore volume over pore diameters has a maximum around $d_p = 33$ nm, while the area distribution over the diameter is characterized by two close and roughly equal maxima at 13 and 9 nm (see Table 4).

The pores of 5.18 to 20.61 nm diameter occupy 71.1% of the total volume, the respective percentage figures being 79.8% for $d_p = 5.18$ – 26.47 nm and 88.3% for $d_p = 5.18$ – 40.00 nm. We note that 60.9% of the total

Table 2. Temperature dependence of the AK1b sample mass during thermogravimetric analysis, wt %

Temperature	22.6	100	200	300	400	500	600	700	800	900	1000	1100
Mass, %	100	94.65	92.81	92.10	91.30	90.58	90.09	89.76	89.49	89.27	89.09	88.61

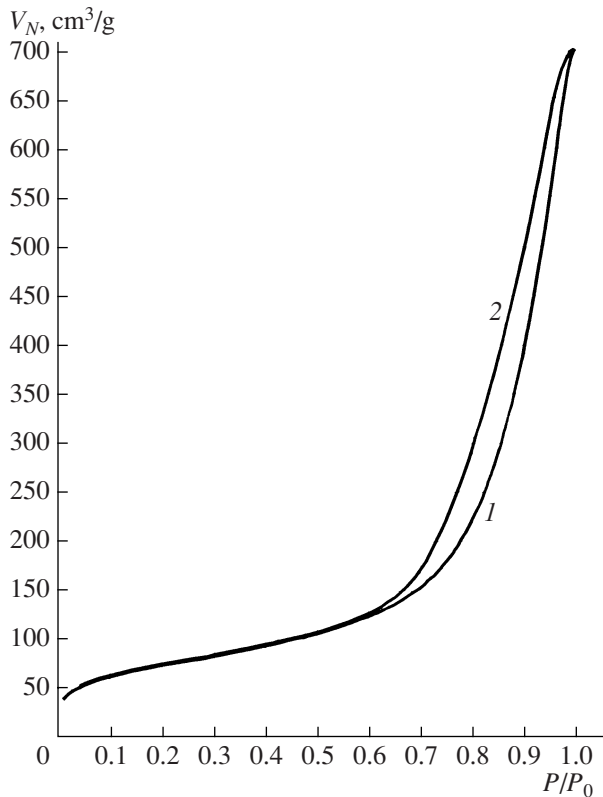


Fig. 5. Nitrogen adsorption/desorption curves for a silica sample: (1) adsorption curve; (2) desorption curve.

surface area is for the pores in the range of diameters $d_p = 5.18\text{--}26.47\text{ nm}$, while the pores with diameters of $d_p = 5.18\text{--}40.00\text{ nm}$ make 76.4% of the total area.

Concentration of internal silanol groups. Knowing the specific surface area of silica S_{BET} (m^2/g) and the weight percentage $\Delta m_{\text{H}_2\text{O}}$ (wt %) of the mass losses incurred by the thermogravimetric analysis, one can find the concentration of silanol groups in a silica sample δ_{OH} (nm^{-2}):

$$\delta_{\text{OH}} = (\Delta m_{\text{H}_2\text{O}} \times 2 \times 6.02 \times 10^3) / (18 S_{\text{BET}}). \quad (3)$$

The value of $\Delta m_{\text{H}_2\text{O}}$ in (3) equals the mass loss due to heating at temperatures higher than the boundary temperature T_{BR} . Below this temperature, the mass losses due to heating results from removal of physically adsorbed water from the silica surface, while above T_{BR} , the sample loses its mass owing to condensation of silanol groups accompanied by siloxane bond formation.

Taking $S_{\text{BET}} = 300\text{ m}^2/\text{g}$ for the AK1b sample, assuming 1000°C as the terminal temperature of complete removal of silanol groups, and substituting the data of Table 2 into (3), we found the following theoretical values of δ_{OH} for a variety of temperatures T_{BR} , arranged in pairs as follows: $T_{\text{BR}} = 200^\circ\text{C}$, $\delta_{\text{OH}} =$

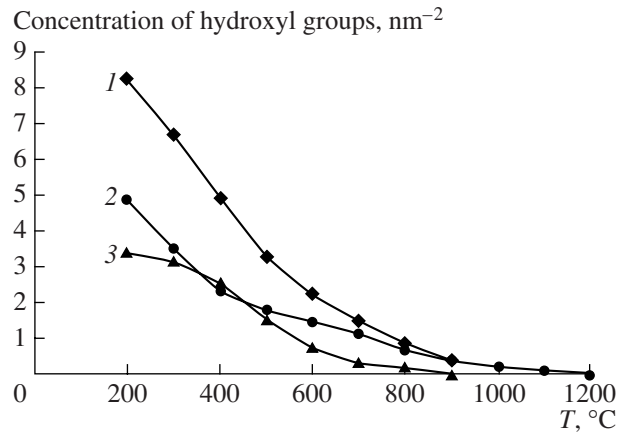


Fig. 6. Temperature relationships for δ_{OH} , α_{OH} , γ_{OH} : (1) δ_{OH} ; (2) α_{OH} ; (3) γ_{OH} .

8.29 nm^{-2} ; 300°C , 6.71 nm^{-2} ; 400°C , 4.92 nm^{-2} ; 500°C , 3.33 nm^{-2} ; 600°C , 2.23 nm^{-2} ; 700°C , 1.49 nm^{-2} ; 800°C , 0.89 nm^{-2} ; 900°C , 0.40 nm^{-2} . According to Kiselev–Zhuravlev model [8], the limiting value of α_{OH} for a surface saturated with silanol groups at 200°C equals $4.6\text{--}4.9\text{ nm}^{-2}$.

Assuming the removal of physically adsorbed water from the AK1b silica surface to occur below 200°C , the concentration of adsorbed H_2O molecules would make 5.96 nm^{-2} according to the thermogravimetric data in Table 2 and relation (3).

Comparison of the Zhuravlev constants with the theoretical results shows that the silica precipitated from a hydrothermal solution is likely to have the limiting concentration of silanol groups α_{OH} , which is equal to the maximum value $4.6\text{--}4.9\text{ nm}^{-2}$ (the Kiselev–Zhuravlev constant) at 200°C [8].

According to the earlier results of Zhuravlyov [8], the limiting concentration of OH groups at the surface of various types of silica reaches 4.9 nm^{-2} at 200°C , afterwards decreasing with increasing temperature to generate a set of Zhuravlev's physicochemical constants α_{OH} . If we assume all this, the concentration of internal silanol groups (internal water) γ_{OH} per unit surface area of the AK1b sample could be found as the difference:

$$\gamma_{\text{OH}} = \delta_{\text{OH}} - \alpha_{\text{OH}}. \quad (4)$$

The results of calculations based on (4) are summarized in Table 5. They reflect the temperature control on the spatial patterns of OH groups on the surface and in the body of the AK1b sample. The curves of δ_{OH} , α_{OH} , $\gamma_{\text{OH}}(T)$ are shown in Fig. 6.

The values of α_{OH} rapidly decrease in the temperature range $190\text{--}400^\circ\text{C}$, while at higher temperatures, in the range 400 to $\sim 780^\circ\text{C}$, the rate of decrease slows down and the curve becomes less steep. In the $190\text{--}400^\circ\text{C}$ interval, α_{OH} can be fitted by the linear equation

$$\alpha_{\text{OH}}(\text{OH}/\text{nm}^2) = -0.0122T(^{\circ}\text{C}) + 7.218. \quad (5)$$

Table 3. Dimensions, area and volume of pores in AK1b silica samples

Sample mass, g	0.13
Volume 1, cm ³	17.45
Volume 2, cm ³	54.32
S_S , m ² /g	263.53
S_{BET} , m ² /g	274.64
S_{MP} , m ² /g	26.33
S_{AC} , m ² /g	260.25
S_{DC} , m ² /g	333.52
V_S , cm ³ /g	0.871
V_{MP} , cm ³ /g	0.00827
V_{AC} , cm ³ /g	1.078
V_{DC} , cm ³ /g	1.088
d_{BET} , nm	12.692
d_A , nm	16.575
d_D , nm	13.058

Note: Volume 1 and Volume 2 are the volumes of the vial automatically measured by the instrument at indoor temperature and after immersing the liquid nitrogen in a Dewar flask, respectively. They are further involved in the mathematics to define constants in the calculation; S_S is the area as determined at a fixed pressure $P/P_0 = 0.200$; S_{BET} is the total area of pores calculated by the BET technique; S_{MP} is the total area of micropores of roughly 1.7 nm diameter; S_{AC} is the total area calculated by the BDH technique from the adsorption curve for pores of 1.7–300.0 nm diameter (BDH-area); S_{DC} is the area calculated by the BDH technique from the desorption curve for pores of 1.7–300.0 nm diameter; V_S is the total volume of pores less than 40.0 nm in diameter measured at a fixed nitrogen pressure $P/P_0 = 0.950$; V_{MP} is the volume of micropores of roughly 1.7 nm; V_{AC} is the total volume calculated by BDH technique with the adsorption curve for the pores of 1.7–300.0 nm diameter (BDH-volume); V_{DC} is the total volume calculated by the BDH technique with the desorption curve for pores of 1.7–300.0 nm diameter; d_{BET} is the mean pore diameter equal to $4V_S/S_{BET}$; d_A is the mean pore diameter calculated from the pore volume and area found by the BDH technique on the adsorption curve, equal to $4V_{AC}/S_{AC}$; d_D is the mean pore diameter calculated from the pore volume and area found by the BDH technique on the desorption curve, equal to $4V_{DC}/S_{DC}$.

In the 400–780°C interval, $\alpha_{OH, T}$ can be fitted by the power-law equation

$$\alpha_{OH}(\text{OH}/\text{nm}^2) = 1155.6T(^{\circ}\text{C})^{-1.0367}. \quad (6)$$

At temperatures of 190–400°C the thermal desorption energy E_D is nearly independent of silanol concentration, being largely controlled by the set of perturbations available on the surface of H-bonded OH groups, and these perturbations disappear once the type of vicinal silanols in hand is gone at ~400°C. Consequently, H-bonds (lateral coupling) between neighboring vicinal OH-groups in conditions of high occupancy typically exist in this temperature region. At 400–780°C, the main agents include free single and free geminal OH groups, as well as SiOSi bridges. In the range 400–

1200°C, the energy E_D dramatically increases from 25 to 50 kcal/mol and even higher, accompanied by a decrease in α_{OH} . Under these conditions, the basic mechanism involved in the transfer of OH-groups to perform the condensation reaction could be an unordered migration of protons along the surface (the activated surface diffusion of OH groups). At the terminal stage a water molecule is precipitated owing to interaction between two OH groups that accidentally approach each other within a ~0.3 nm distance (a typical length of the H-bond). If the concentration of OH groups is low, the proton diffusion along the SiO₂ surface limits the condensation process itself. At 800–1200°C geminals are lacking, and the condensation reaction is limited by interactions of distant free single OH groups only. Accordingly, it is hard to approximate the range reliably.

At a temperature of 200°C the concentrations of internal and surface OH groups in the silica precipitated from hydrothermal solutions are comparable. In the range 200–400°C the internal water is removed slowly, and the values of γ_{OH} decrease slowly with increasing temperature. In the range 375–425°C, owing to a slow removal of internal water, the concentration of internal OH groups becomes equal to the concentration of the surface groups, and slightly exceeds it around 400°C, which is illustrated by the $\gamma(T)$ and $\alpha_{OH}(T)$ curves intersecting in Fig. 6.

Starting from 400°C, the removal of internal water is accelerated. At 600°C the internal OH groups are half as common as the surface ones. The curves of $\delta_{OH}(T)$ and $\alpha_{OH}(T)$ (Fig. 6) intersect at about 900°C, which indicates the existence of internal OH groups in AK1b silica at high temperatures. A complete elimination of internal OH groups occurs at 900–1000°C, when the concentration of surface OH groups becomes significantly lower than the initial 4.6–4.9 nm⁻². At 400–800°C the experimental values of γ_{OH} (nm⁻²) that correspond to the concentration of internal water in a sample of silica precipitated from a hydrothermal solution can be fitted by

$$\ln \gamma_{OH}(T) = 0.943 - 0.0065(T^2 - 673^2), T(\text{K}). \quad (7)$$

The data acquired highlight an essential difference between the removal of surface and internal water. In the range 200–400°C, $\alpha_{OH}(T)$ decreases at a high rate, while above 400°C the decrease slows down owing to dissipation of vicinal silanols on the surface. By contrast, $\gamma_{OH}(T)$ decreases slowly in the range 200–400°C, but at 400–600°C the rate of decrease of internal OH groups increases. We believe that the difference could be associated, firstly, with the fact that the reaction of silanol groups in the case of internal water occurs in the bulk sample rather than on its surface. Secondly, in order to remove the internal water the transport of water molecules from inside to the surface of the particles is needed. The transport of H₂O can occur by diffusion through the particles or through ultramicropores. The diffusion rate grows with the increase in temperature,

Table 4. Dependence of pore area and pore volume on pore diameter for an AK1b silica sample by low-temperature adsorption of nitrogen

Pore diameter d_p , nm	Mean diameter, nm	Pore volume, g/cm^3	Net pore volume, cm^3/g	Pore area, m^2/g	Net pore area, m^2/g
333.0–125.1	150.03	0.0238	0.0238	0.635	0.635
125.1–88.9	100.89	0.0333	0.0571	1.321	1.956
88.9–72.7	79.1	0.0284	0.0856	1.438	3.394
72.7–40.0	47.2	0.1539	0.2395	13.03	16.42
40.0–26.5	30.4	0.1669	0.4065	21.94	38.37
26.5–20.6	22.7	0.1303	0.5368	22.90	61.27
20.6–16.7	18.2	0.1182	0.6550	25.93	87.20
16.7–14.0	15.1	0.0960	0.7510	25.35	112.55
14.0–11.6	12.6	0.1005	0.8516	31.89	144.45
11.6–10.3	10.89	0.0550	0.9066	20.23	164.68
10.3–8.36	9.11	0.0764	0.9831	33.57	198.25
8.36–7.00	7.55	0.0425	1.0257	22.55	220.80
7.00–5.97	6.40	0.0243	1.0501	15.25	236.06
5.97–5.18	5.52	0.0141	1.0642	10.24	246.310
5.18–4.54	4.81	0.0079	1.0722	6.624	252.93
4.54–4.02	4.24	0.0039	1.0761	3.760	256.69
4.02–3.58	3.77	0.0011	1.0773	1.226	257.92
3.58–3.20	3.36	0.000061	1.0774	0.072	257.99
3.20–1.96	2.01	0.000059	1.0774	0.118	258.11
1.96–1.86	1.91	0.00046	1.0779	0.963	259.07
1.86–1.76	1.81	0.00053	1.0784	1.178	260.25

Table 5. The distribution of OH groups at the surface and in the volume of an AK1b silica sample precipitated from hydrothermal solution

T, °C	200	300	400	500	600	700	800	900	1000	1100	1200
δ_{OH}	8.29	6.71	4.92	3.33	2.23	1.49	0.89	0.40	n/m	n/m	n/m
α_{OH}	4.90	3.55	2.35	1.80	1.50	1.15	0.70	0.40	0.25	0.15	0.0
γ_{OH}	3.39	3.16	2.57	1.53	0.73	0.34	0.19	0.0	n/m	n/m	n/m

Note: n/m means “not measured”.

which leads to a steeper slope of the $\gamma_{\text{OH}}(T)$ curve in the range 400–600°C.

CONCLUSIONS

(1) Comparison of thermogravimetry analysis of silica precipitated from a hydrothermal solution in terms of the temperature relation $\delta_{\text{OH}}(T)$ with the set of Zhuravlev's physicochemical constants has revealed considerable amounts of internal OH groups, comparable with the amount of surface OH groups at 200°C. Hence we have established a new type of noncrystalline silica containing significant amounts of internal silanols. They are silica samples produced by coagulation

and precipitation of colloid silica particles from a hydrothermal solution or by adhesion of colloid particles at the walls of a transport channel as the hydrothermal solution was flowing in it.

(2) We believe that the high concentration of internal water in silica precipitated from hydrothermal solution can be attributed to: (i) the mechanism involved in the formation of colloid particles by polycondensation of orthosilicic acid molecules and by the presence of noncompensated areas in the structure of inorganic polymer; (ii) the action of the water solution at increased temperature and pressure that is equivalent to hydrothermal treatment leading to dissolution and redeposition of silica, and diffusion of water.

(3) Comparison of $\alpha_{\text{OH}}(T)$ and $\gamma_{\text{OH}}(T)$ relationships for silica precipitated from a hydrothermal solution points to an essential difference between the mechanisms involved in the removal of internal and surface water. In the range 200–400°C the rate of removal of internal water is low, but increases at 400–600°C. This difference could be associated with the fact that in the case of removal of internal water, the condensation of silanol groups occurs inside the particles or in ultramicropores, while the transport of condensation products to the surface of the particles occurs by molecular diffusion, the rate of which grows with temperature.

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