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SILICA SOLS PRODUCTION BY MEMBRANE CONCENTRATION OF HYDROTHERMAL SOLUTIONS

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Key words: hydrothermal solution, orthosilicic acid, colloidal silica, silica sols, membrane filters, ultrafiltration, silica powder.

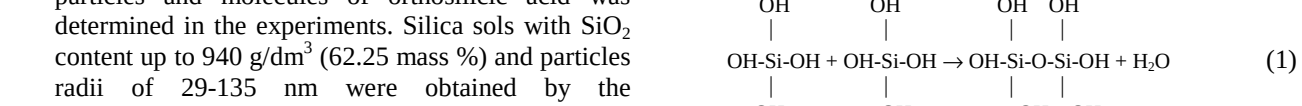
ABSTRACT

The experiments on concentration of hydrothermal solutions by membrane filters for silica sols production were carried out. Three types of membrane processes were tested: microfiltration, ultrafiltration, reverse osmosis. Temperature of solution varied from 20 to 90 ^{0}C. Selectivity of membrane layers with respect to colloidal silica particles and molecules of orthosilicic acid was determined in the experiments. Silica sols with SiO_2 content up to 940 g/dm^3 (62.25 mass %) and particles radii of 29-135 nm were obtained by the ultrafiltration. Silica powders with the specific surface of 110-400 m^2/g, mean pores diameter of 3-10 nm, pores volume of 0.2-0.3 sm^3/g were obtained by cryochemical vacuum-sublimation drying of sols with liquid nitrogen use. Particles sizes of the powders are within the range of 10 - 100 nm. The characteristic of powders extracted from silica sols such as particles sizes, diameters, surface areas, pores volumes were studied. The methods of scanning electron microscopy, X-ray phase analysis, thermogravimetry, low temperature nitrogen adsorption were used. In accordance with measurement results the influence of process conditions on powders characteristics was determined

INTRODUCTION

Colloidal silica particles appear in a natural hydrothermal solution due to polycondensation of orthosilicic acid molecules (OSA) coming under the dissolution of silica-alumina minerals containing in the rocks under the increased pressure and temperature in deposits interior. When the solution raises to the surface the temperature and pressure reduce, the solution becomes supersaturated and nucleation and polycondensation of OSA molecules take place in it and they cause to the forming of colloidal silica particles of spherical form with the radii of 5-100 nm. Other components are also in the initial solution in addition to silica; their concentration is shown in table 1.

Nucleation and polycondensation of silicic acid molecules take place due to condensation of silanol groups, siloxane bonds formation and partial dehydration on the following reactions:



(1)

$$Si_mO_{m-1}(OH)_{2m+2}+Si_nO_{n-1}(OH)_{2n+2}\rightarrow Si_{m+n}O_{m+n-1}OH_{2n+2m+2}+H_2O. \quad (2)$$

Finite sizes of silica particles first depend on the temperature and pH under which nucleation and polycondensation of OSA take place. Temperature increase of polycondensation results in increase of particles finite sizes. pH reduction results in increase of particles finite sizes too. During polycondensation the temperature was varied within the range from 20 up to 72 ^{0}C, pH – from 9.2 up to 4.0. At the same time finite mean radii of silica particles were within the range from 5 up to 100 nm subject to the temperature and pH.

Table 1. The concentration of the main components of the initial hydrothermal solution

Component	Na^+	K^+	Li^+	Ca^{2+}	Mg^{2+}	$Fe^{2+,3+}$	Al^{3+}
Concentration, mg/l	282	48.1	1.5	2.8	4.7	<0.1	<0.1
Component	Cl^-	SO_4^{2-}	HCO_3^-	CO_3^{2-}	H_3BO_3	SiO_2	Cl^-
Concentration, mg/l	251.8	220.9	45.2	61.8	91.8	780	251.8

To develop of the technology of membrane silica concentration the main stages must be worked out:

nucleation and polycondensation of orthosilicic acid (OSA), sol filtering in membrane facilities and sol cleaning from electrolytes, sol stabilization (addition of stabilizing additives).

EXPERIMENTS ON MEMBRANE CONCENTRATION

After the completion of OSA polycondensation of hydrothermal solutions and formation of silica colloidal particles of given sizes the water removal was made to obtain nanodispersed powders. Water was removed in accordance with a two-stage scheme (Potapov V.V. et al., 2008; Generalov M.B., 2006; Brazhnikov S.M., Generalov M.B., Trutnev N.S., 2004; Generalov M.B., Trutnev N.S., 2006; Onopko K.D., Platov I.V., Trutnev N.S., 2008): the 1st stage is filtering through the membrane filters; the 2nd stage is cryochemical vacuum-sublimation drying with liquid nitrogen use.

During the first stage hydrothermal mediums were filtered through the ultrafiltration membrane units. Under ultrafiltration silica colloidal particles were stopped by the membrane layer and water molecules and ions of dissolved salts passed through this layer. Thus, the electrolytes content reduces as silica was concentrated, it provided sols stability. Colloidal particles were concentrated in aqueous medium, at the same time SiO_2 content increased up to 10-62.2 mass %, and water content reduced up to 90-37.5 mass %. Concentrated water sols with a high content of SiO_2 were subjected to cryochemical drying under vacuum then.

The possibility of use of the main membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis for concentration of hydrothermal solutions were studied. The experiments with membranes showed the ultrafiltration advantage for the obtaining of stable concentrated silica sols. When nanofiltration and reverse osmosis were used both silica concentration and mean ions content increased, and the obtained sols were unstable. Microfiltrational membranes have a low selectivity on silica colloidal particles and they can't be effective during the initial concentration stages under a low SiO_2 content. So ultrafiltration or ultrafiltration with microfiltration were used to store a considerable sols volume. Ultrafiltration was used first, then during the later stages microfiltration was used. The ultrafiltration membranes of capillary type were used, the material of membrane layer was made of polyethersulfone and polyacrylonitrile. The diameters of the membrane layer pores were within the range of 2-100 nm. Ceramic microfiltration membranes were of tube type, mean pores size was 70 nm (0,07 micron). The concentration was made in three stages: SiO_2 content from 3 up to 10 g/dm^3 was obtained during the first stage, during the second stage it was 10-30 g/dm^3, during the third stage - 100-940 g/dm^3 (10.0-62.25 mass %). During the first stage the filters of a large standard size were used, during the second stage – the filters of a mean standard size, during the third stage – the filters of a small standard size. The sols density was in the range of 999-1510 g/dm^3, the dynamic viscosity was1-150 mPa·s, the radii of silica particles were 5-135 nm, the particles zeta-potential was from -32,4 up to - 42,5 mV.

The concentrated water sols of silica were used to obtain low-aggregated nanodispersed powders. Cryochemical technology includes the following order of the main technological stages of the production:

- Preparing of the concentrated water sol of silica;
- Sol dispersing and cryocrystallizing of the dispersion medium drops under the temperature of 77 K;
- Sublimation removal of water solution from the cryogranulated material obtained during the previous stage;
- Water solution (desublimation) utilization.

Solutions dispersion for separate drops is used to make developed interphases surfaces providing a high intensity of heat and mass exchanged processes that accompany the technological phases of cryocrystallization and sublimation.

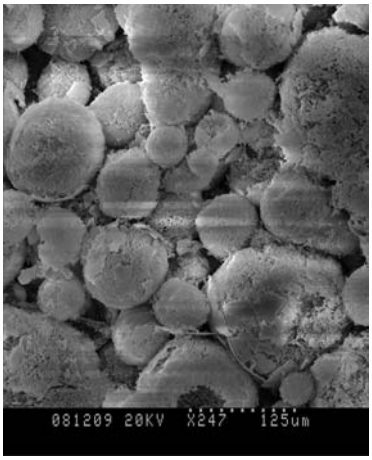
The principal aim of cryocrystallization is to keep a high chemical and granulometric uniformity which is inherent to the soluble sol. Cryogranulation feature is the following: the process of water sol crystallization is made under the temperatures that are considerably lower than the ice point is. Such temperature decreasing is necessary to increase the freezing rate; it gives the possibility to eliminate the aggregation and fix a uniform diffusion of the silica particles presenting in a solid state in the sol. Later on during the sublimation water extraction the low-aggregated silica powder with the dispersity corresponding to silica dispersity in water sol takes place.

The stage of ice sublimation was made under the pressure which is lower than the pressure corresponding to a triple point of water. For this point the parameters are the following: the pressure is (p = 610 Па) and the temperature is (T = 0,0076 ^{0}C). It gave the possibility to minimize the agglomeration of silica particles formed during the freezable stage due to eliminate the formation of the condensed moisture.

During the sublimation stage the heat using for ice evaporation was supplied to the material using conductive heat transfer (heat conductivity).

In accordance with electron microscopy under the increasing in 250-7000 times the sizes of structures obtained by the vacuum-sublimation drying of sols cryogranules were within 20,0-100,0 micron. Fig. 1 a-d shows the image of powder structures after water solution sublimation under the increasing in 247, 500, 800 and 1000 times in sequence: after water solution removal porous-net structure of powder particles remains; this structure has features of a spherical form and sizes of solid cryogranules. Inside of residual structures, in their center part, the cavities were formed after the water solution removal. It shows the mechanism of water removal from the solid cryogranules (fig. 1 d). If the influence was light the residual structures were destroyed forming the flakes of 0,1-0,2 micron thick.

a)



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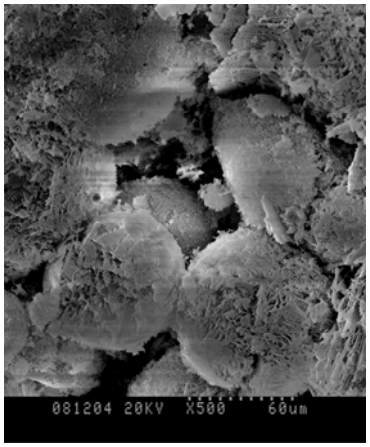
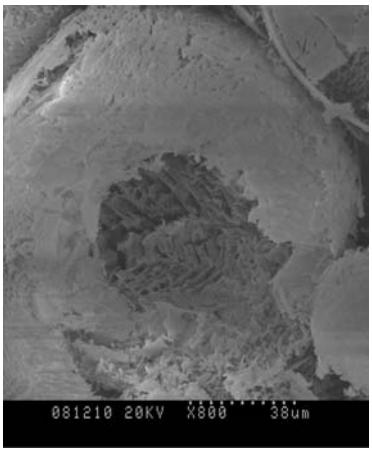


Fig. 1.a,b Structures images from the particles of silica powder formed from cryogranules after water solution sublimation. Magnification factors on the scanning electron microscope: a)-247; b) 500;

c)



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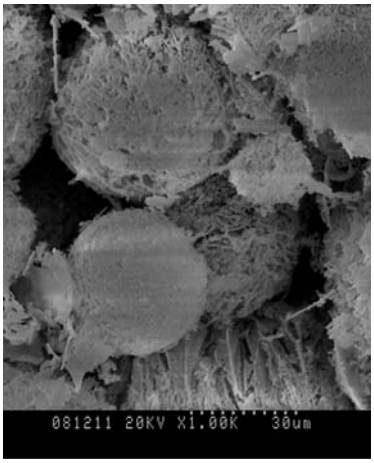


Fig. 1.c,d Structures images from the particles of silica powder formed from cryogranules after water solution sublimation. Magnification factors on the scanning electron microscope: c) 600; d) 1000;

Electric power consumption E_m to obtain mass unit of silica powder consists of power consumption for pumps drive of membrane unit for sol concentration and power consumption for vacuum pumps drive and refrigerating machine for the desublimator unit of sol cryochemical drying. Power consumption for sol membrane concentration depends on selectivity of ultrafiltration membranes and process temperature. When pores membranes size was 50 kiloDalton and the temperature was 20 ^{0}C power consumption for membrane concentration was 0.32 – 0.18 kW·h/kg, when pores size was 10 kiloDalton specific consumption reduced considerably: up to 0.3 - 0.025 kW·h/kg. During cryochemical drying power consumption reduces if SiO_2 content in the sol increases: if SiO_2 content is 25 mass % (300 g/dm^3) power consumption is 14.0 kW·h/kg, when SiO_2 content is 45 mass % (600 g/dm^3) power consumption is 7.0 kW·h/kg. Thus, total power consumption for obtaining of silica powder is E_m = 14.32 – 7.18 kW·h/kg.

There are different methods to obtain nanopowders (dispersion in solid and liquid states, electrolytic deposition, chemical methods, evaporation and recondensation) with different chemical composition: Mg, Al, B, Si, Ti, Zr, borides, carbides, nitrides, metal oxides (Storozhenko P.A., Guseinov Sh.L., Malashin S.I., 2009; Kotov Yu.A., 2009). In accordance with (Storozhenko P.A. et al. 2009) specific power consumption for production of powders SiO_2 and ZrO_2 by plasma method by recondensation of large-dispersed powders with the help of high-frequency reactors with low plasma velocities are 600-1000 kW·h/kg. The production of metal nanopowders can be made by levitating crucibleless. This method is based on evaporation of drop material which is kept in a gas volume by the electromagnetic field, it is characterized by power consumption of 150-200 kW·h/kg (Storozhenko P.A. et al. 2009). The obtaining of nanopowders of silica and silicon carbide in accordance with the process flowsheet including plasma reactor with an extended zone of vortex plasma stabilization, collection apparatuses (cyclones, filters) and capsulating unit needed power consumption of 100-125 kW·h/kg. Power consumption was 50-25 kW·h/kg to obtain nanopowders of different metals by the method of wire electric blast with a mean size of particles d_{BET} = 50-100 nm in accordance with (Kotov Yu.A., 2009).

When SiO_2 content increases the specific cryogenic liquid – nitrogen consumption in the sol reduces. 100 kg of liquid nitrogen is necessary for the work of the unit of cryochemical drying of the sol of 20 l/day productivity(output) during one cycle of 20-24 hours. If SiO_2 content is 25 mass % (300 g/dm^3) in a sol the specific nitrogen onsumption is 16.66 kg/kg, when SiO_2 content is 62.25 mass % (600 g/dm^3) nitrogen rate is 8.33 kg/kg.

3. THE MEASURING OF COLLOIDAL SILICA PARTICLES SIZES

Silica colloidal particles size in the initial hydrothermal solutions and concentrated water sols was determined by the method of photon correlation spectroscopy (PCS) or dynamic light scattering. This method is based on the measurement of the diffusion coefficient of colloidal particles on basis of an analysis of dynamic fluctuations of scattered light intensity; these floctuations appear due to chaotic heat motion of the particles. Information about the diffusion coefficient of the particles is contained in the time-dependent correlation function of intensity fluctuation:

$$G(\tau)=\left\langle I_{FC}(\tau)\cdot I_{FC}(T_p-\tau)\right\rangle=\lim_{t_m\to\infty}\frac{1}{t_m}\int_0^{t_m} I_{FC}(T_p)\cdot I_{FC}(T_p-\tau)dT_p, \quad (3)$$

where the intensity of scattered light I_{FC} has different values during T_p and $(T_p-\tau)$; t_m is the time of correlation function accumulation. Correlation function of intensity is connected with correlation time t_c:

$$g(\tau) = 9a\cdot exp(-2\tau/t_c) + b, \quad (4)$$

where a and b are the experimental constants. Reverse correlation time $1/t_c$ is connected with the coefficient of particles diffusion D_b, light wave length and scattering angle of light. Correlation time t_c is measured by a digital correlator, the diffusion coefficient is measured on its basis. The particles radius is calculated by Stokes-Einstein formula:

$$D_b = k_B\cdot T/(6\cdot\pi\cdot\mu\cdot R), \quad (5)$$

where k_B is the Boltzmann's constant; T is an absolute temperature; μ is the dynamic medium viscosity where the particles of radius R are suspended.

The results of measurement of the sizes and zeta-potential of silica colloidal particles surface in four different sols samples were obtained. Sizes measurement was made by PCS method, zeta-potential was measured by electrophoretic technology. Silica sols were obtained under different temperatures (72-30 ^{0}C) and pH (9,2-4,5). The sol corresponding to UF17 sample was obtained by the separate concentration after the ageing under the temperature of 72 ^{0}C. The separate for UF18 and UF19 sols aged in two-phase ageing: first it was made under 72-70 ^{0}C, then the cooling up to 50 and 30 ^{0}C was made. Separate cooling influenced on particles sizes little because the particles mainly formed under a high temperature 72-70 ^{0}C. However as a result the particles of UF19 sol are larger than in UF17 and UF18 sols. It is explained in the following way: UF19 sol was obtained in accordance with the deadlock scheme of the filtration when the outlet for the concentrate was closed, and the concentrated medium was recirculated through the element filter; it caused the aggregation of silica particles. Particles sizes in UF20 sol are larger than in other sols; it is explained by lower pH value during the stage of separate ageing.

The results are represented as dependence of amplitude of monochromatic laser light scattering with wave length of 633 nm on the logarithm of particles diameter. Data of measurement of zeta-potential of silica particles surface in these sols samples are shown opposite the graph of intensity dependence on logarithm of particles diameters. Measurement of sizes and zeta-potentials are made

on Zeta-Sizer unit, Malvern. Table 2 presents data of mean radii, zeta-potential and silica particles obtaining.

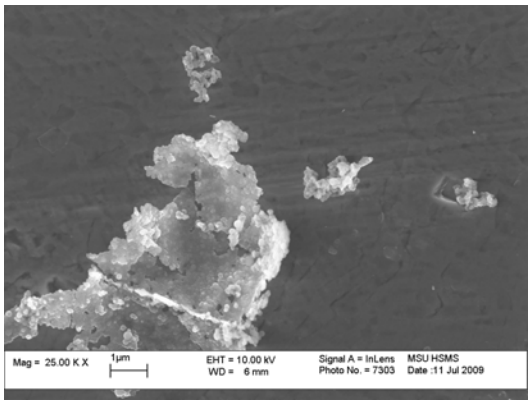
Table 2. The results of measurement of sizes and zeta-potential of silica colloidal particles surface in water sols.

Sample	The conditions of separate ageing before the membrane consentration		Mean radius of the particles in silica sol before the cryochemical drying, nm	Zeta potential of the particles surface, mV
	Temperature, ^{0}C	pH		
UF17	72	9.2	29.5	-39.5
UF18	70-50	9.2	29.55	-43.8
UF19	70-30	9.2	55.5	-56.0
UF20	30	4.5-5.0	135.0	-45.2

The method of scanning electron microscopy was also used to measure the size, form, structure of particles in the sols and powders of silica. Sols samples were prepared for electron microscopy by cryochemical vacuum-sublimation drying. The method of electron microscopy is based on the results analysis of scattering by the surface of solid sample of electrons beam. A high microscope resolution is possible due to a small length of electrons wave in comparison with the waves lengths of other light forms. Accelerating voltage was 7 kV, magnification factors were from 10^4 up to 10^5, low-energy (<<100 eV, ~ 20-50 eV) and secondary electrons appearing as a result of interaction of scanning beam with solid body surface were detected.

Silica colloidal particles images in the sols and powders were obtained on a scanning electon microscope JEM-100CX (JEOL, Japan) under the magnification factors from 10000 up to 500000. Before the images obtaining the sol sample was put on a copper plate and water solution was sublimated. The powders were preliminary dispersed in an absolute ethanol, the concentrated medium was put on a copper plate, the dispersion medium was sublimated. Particles images of silica powder obtained on a scanning electon microscope under an magnification factor in sequence in 25000, 50000, 100000 and 250000 times are presented on fig. 2.

a)



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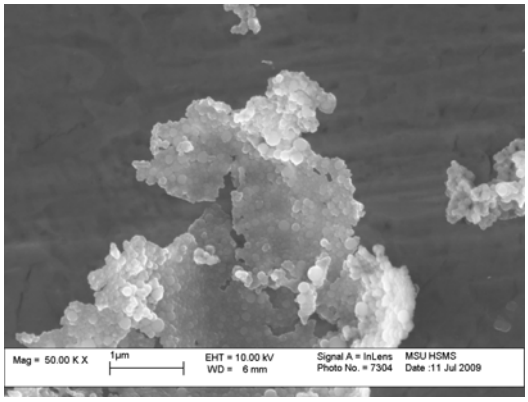

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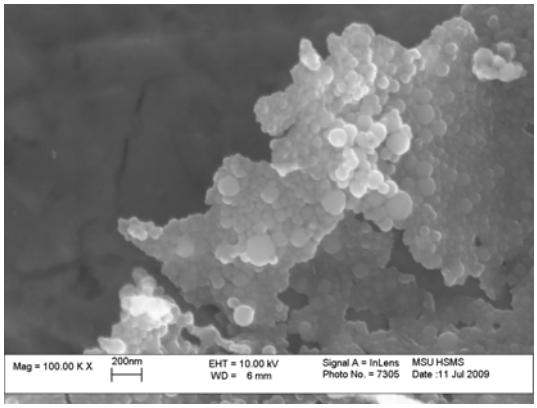

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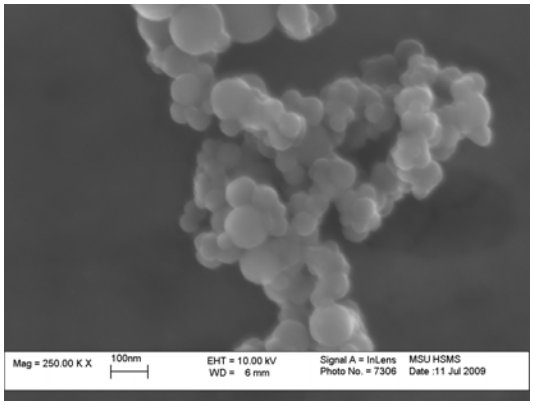

Fig. 2.a,b Silica powder pictures obtained on the scanning electron microscope.

Cryochemical sols drying in liquid nitrogen under 77 K with further ice sublimation under vacuum gave the possibility to reduce particles aggregation when silica was extracted from liquid phase. Particles size didn't enlarge; the sizes of particles of a sol differed from the sizes of powders particles little. Silica particles images of sols and powders obtained by cryochemical vacuum-sublimation drying of the sols under the magnification factors in 100000 and 250000 times were compared. In accordance with these images it was determined that the sizes of the main particles part of sols and powders are within the range of 10-100 nm.

THE CHARACTERISTIC OF SILICA POWDERS OBTAINED BY CRYOCHEMICAL DRYING

Data of thermogravimetric analysis of UF-20 powder were compared with thermogravimetry data for amorphous silica powder precipitated from the solution without the use of membrane concentration and cryochemical drying. The comparison showed that water removal in nanodispersed powder UF-20 takes place in another way: the curve of differential thermogravimetric analysis (DTG-curve) has got an atypical form for amorphous silica. On the DTG-curve of UF-20 powder there are three "fuzzy" maximums under temperatures about 200, 600 and 1000 ^{0}C in contrast to one "clear" maximum under 100-150 ^{0}C on the DTG-curve.

Data of X-ray phase analysis showed the amorphous structure of UF-20 powder. The powder turned in cristobalite after the heat treatment under 1000 ^{0}C.

Impurities content in nanopowders samples was brought up to 0.3 mass % (table 3). Table 3 presents data of chemical composition of one of the nanopowders obtained by the method of X-ray phase analysis on the spectrometer "S4 PIONEER". Such level of impurities concentration (0.3 mass %) is not minimum: before cryogranulation and sublimation silica sols can be diluted by distillate; membrane reconcentration can be done and thus impurities concentration can be reduced up to wishful level.

Table 3. Chemical composition of silica powder samples (mass %) extracted from silica sol.

SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO
99.72	<0.01	0.173	<0.01	<0.01
MnO	MgO	CaO	Na_2O	K_2O
<0.01	<0.01	0.034	0.034	0.069

Data of low-temperature nitrogen adsorption are given in table 3 (porometer ASAP-2010N Micromeritics). During different experiments we succeeded in obtaining powders with a high specific surface area within the range from 110-170 up to 300-400 m^2/g, and specific pores volume of 0.2-0.3 sm^3/g. The powders density was 0.035-0.010 g/sm^3. pH under which the ageing of the initial hydrothermal solution and further membrane sol concentration was made is one of the main factors influencing on the powder features. When pH reduced the particles sizes in sol increased before the cryochemical drying. Larger porous particles with an internal structure were formed. As a result after the sol cryochemical drying the specific surface of the powder increased. In accordance with a low-temperature nitrogen adsorption pH reducing caused the reducing of a mean pores diameter of the powder (table 3). When pH reduced the type of adsorption-desorption isotherm and hysteresis loop were changed (table 3). Mean pores diameters were within the range from 3.0 up to 7.1 nm.

Table 4. The characteristic of the silica powders obtained by cryochemical sols drying.

sample	Powder density, g/sm^3	The type of absorption-desorption isotherm (the type of hysteresis loop)	The area of the specific surface (S_{BET}), m^2/g	Mean pores diameter (d_p), nm	Summary pores volume (V_p), sm^3/g
UF17	0.035	II	166.53	6.22	0.259
UF18	0.010	II	115.04	7.11	0.204
UF19	0.010	II	118.30	7.78	0.230
UF20	0.016	IV	360.43	3.34	0.301

The least value of a mean diameter of powders pores obtained by drying of silica sols which had pH=4-5 was about 2.7 nm. The largest value of a mean pores diameter of 9.6 nm was obtained during drying of the sol with pH=9.0-9.2. When pH reduced the tendency to change the type of hysteresis loop on the adsorption-desorption isotherm took place: the IInd type turned in the IVth type.

POTENTIAL DIRECTIONS OF SOLS AND POWDERS USE

Obtained powders can be used in industry to produce the sorbents, catalysts, polymer composite materials, general mechanical rubber goods, varnish and paint. One of the tendencies of sols and powders use is their application as nanomodifiers to improve the characteristics of building materials: concrete, binding material (cement, gypsum, lime), glass, potting compounds, heat-insulating materials, etc. Silica colloidal particles inclusion in the cement composition by addition of silica sol or silica powder with SiO_2 concentration of 10^{-4}-10^{-3} mass percents increases compressive strength of cement samples in 28 days age up to 30-40 % and more. The characteristic of nanodispersed additions is a

nonhomogeneous strength dependence on mass percent of the addition. In contrast to traditional modifiers the curve strength-mass percent of nanoaddition has maximums and minimums.

CONCLUSIONS

Ultrafiltration membranes have selectivity on colloidal silica about 1.0 without preliminary addition any coagulants and low selectivity on silicic acid molecules and ions. Therefore it is possible to get by ultrafiltration the solution with high SiO_2 concentration and low concentration of impurity ions – Na^+, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+, 3+}$, Al^{3+}, SO_4^{2-}, Cl^- . Thus, ultrafiltration has got the advantages before other membrane processes when the problem of obtaining of silica concentrated water sols is solved. Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules.

The method of obtaining of the silica nanodispersed powders on basis of natural hydrothermal solutions was developed. This method is based on use of the following processes of solution molecules removing: a) membrane filtration; b) formation of cryogranules containing silica colloidal particles under an ultralow temperature in liquid nitrogen; c) sublimation of a solidified solution in vacuum. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest SiO_2 content. Use of ultralow temperatures and vacuum sublimation gives a minimum aggregation of colloidal particles. Both the parameters of cryogranulation, sublimation and the temperature and pH of water medium during the stage of orthosilicic acid polycondensation influence on the characteristics of powder pores – their diameter, area and volume. This method gives the possibility to obtain powders with particles size within the range of 10-100 nm, specific surface up to 400 m^2/g, mean pores diameters 3-10 nm.

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