SILICA POWDERS PRODUCTION FROM HYDROTHERMAL SOLUTIONS

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Key words: hydrothermal solution, silica sol, membrane concentration, cryochemical vacuum-sublimation drying, silica nanopowders.

ABSTRACT

Obtaining of nanodispersed silica powders from natural hydrothermal solutions is described. Hydrothermal solutions contain the colloidal silica forming as a result of polycondensation of the molecules of orthosilicic acid. Via ultrafiltration membrane concentration of hydrothermal solutions, silica sols with SiO_2 contents up to 940 g/dm^3 (62.2 wt %) and particle radii of 29 - 135 nm are obtained. The silica powders with the specific surface of 110 - 400 m^2/g, average pore diameter of 3 - 10 nm, and pore volume of 0.2 - 0.3 cm^3/g are obtained via cryochemical vacuum-sublimation drying of sols with the use of liquid nitrogen. The particle size in the powders is in the range from 10 to 100 nm.

INTRODUCTION

The search for new sources of silica is caused by an increase in consumption of amorphous silica by modern industry involving high-tech branches associated with production of nanostructured materials. Economical purposefulness of extraction of silica from hydrothermal solutions is caused by the complex use of these solutions in power-mineral production. Deep removal of colloid silica from the solution increases the efficiency of the use of the power potential of heat carrier, gives the additional amount of electrical and heat power due to a decrease in the temperature of reverse pumping of the solution, and simultaneously provides obtaining the mineral raw material in a form of amorphous nanodispersed silica (Frolov Yu.G. et al., 1979).

Hydrothermal solutions are an unconventional source of mineral raw materials including amorphous silica. Silica is formed in the natural solution from the molecules of orthosilicic acid (OCA) as a result of its chemical interaction with alumosilicate minerals of rocks in the depths of hydrothermal deposits. As the solution lifts on the surface along the productive wells and the temperature decreases, the solution becomes supersaturated, and polycondensation and nucleation of OCA molecules occur in them, which leads to the formation of spherical silica nanoparticles with radii of 5-100 nm. Other components are also in the initial solution in addition to silica; their concentration is shown in table 1.

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$_3$BO$_3$	SiO$_2$	Cl$^-$
Concentration, mg/l	251.8	220.9	45.2	61.8	91.8	780	251.8

OBTAINED THE AQUEOUS SILICA SOLS

It is noteworthy that silica in the solution is situated in two states, namely, solid and liquid, the concentration of which is 200 mg/l.

There is the technological approach to extraction of useful components of hydrothermal solutions based on their baro-membrane concentration. As a result of the baro-membrane concentration, stable aqueous silica sols are obtained.

The concentrated aqueous silica sols were obtained from the liquid phase of hydrothermal heat carriers (separates) of the wells of Mutnovskie geothermal electric power stations (GeoES). The liquid phase was separated from the vapor phase of the two-phase flow in separators of the GeoES. The range of the values of pH of the starting separate is 4.5-9.4, the silica concentration Ct = 400-800 mg/kg, and the solution temperature is from 20 to 90°C.

The installation for membrane concentration of the hydrothermal solution involved a cartridge (cartridges) with membrane filters, pump, rotameters, manometers, lock and control valves; and capacities for the starting solution, concentrate, and filtrate. In the experiments, the possibilities of the use of main

membrane processes, mainly, microfiltration, ultrafiltration, nanofiltration, and reverse osmosis for concentration of hydrothermal solutions were studied. The experiments with membranes showed the advantage of ultrafiltration during obtaining the concentrated silica sols (Potapov V.V. et al., 2008). Therefore, to accumulate considerable volumes of sols, in most cases, ultrafiltration or combination of ultrafiltration and microfiltration were used.

We used ultrafiltration membranes of the capillary type. The starting medium is supplied into long capillary tubes, the walls of which constitute the membrane layer. During motion inside the tube, the medium is partially filtered outside into the radial direction; it is accumulated in the body of the cartridge-filter in the space between the tubes (filtrate). The part of medium, which passed over the entire length of the tube, being not filtered through the membrane walls (concentrate), is supplied into the concentrate collector and is led out of the cartridge in the axial direction. The filtrate is led out of the body of the cartridge-filter in the side direction.

We used the membranes made of polyethersulfone or polyacrylonitrile. The diameters of the pores of the membrane layer are distributed in the range of 20-100 nm. The characteristics of ultrafiltration membranes and cartridge-filters used in experiments are presented in Table 2.

Table 2. The parameters of the ultrafiltration membrane filters.

The characteristic of ultrafiltration membrane filter	Small standard size	Mean standard size	Large standard size	
			One-cartridge module	Two-cartridge module
The outer diameter of fiber	0.6	1.6	2.0	1.6
The inner diameter of fiber	0.4	1.0	1.2	1.0
The material of capillary fibers	polyether sulfone	polyacrylo nitrile	polyether sulfone	polyacrylo nitrile
A number of hollow fibers, pieces.	1150	1500	2520	3000
An area of the membrane layer of one fiber, m^2	0.00027	0.00166	0.0056	0.00333
Summary area of the membrane layer, m^2	0.31	2.5	15.0	10.0
Module size	315x65 mm	550x100 mm	1500x220 mm	1260x90 mm

Concentration was performed in three stages. At the first stage, the contents of SiO_2 of 3-10 g/dm^3 were attained; at the second stage, 10-30 g/dm^3; and at the third stage, 100-940 g/dm^3 (10-62.5 wt %).

At the first stage, we used the large-size filters; at the second stage, average-size ones; and at the third stage, small ones.

It is established that the ultrafiltration membranes have selectivity by the colloidal silica about 1.0 without preliminary addition of coagulants and low selectivity by molecules of silicic acid and ions. Therefore, using ultrafiltration, we can obtain the solution with a high SiO_2 content and low concentration of impurity ions Na^+, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+,3+}$, Al^{3+}, SO_2^{-4}, and Cl^-. Using dilution of sol and repeated ultrafiltration concentration, we can attain a decrease in the concentration of impurity ions. Therefore, ultrafiltration has advantages over other membrane processes when solving the problem of obtaining stable concentrated aqueous silica sols with a low content of impurities. To concentrate the sols with large diameters of the particles (40-70 nm and larger), microfiltration can be applied.

The SiO_2 content in silica sols with the use of ultrafiltration membranes was brought up to 100-940 g/dm^3. The density of sols was in the limits 999-1550 g/dm^3, the dynamic viscosity was 1-150 mPa s, the radii of silica particles were 5-135 nm, and the zeta-potential of the particles was (-32.4- -42.5) mV.

Taking into account the obtained experimental data, the main stages of the baro-membrane concentration are the following:

1. aging of the starting hydrothermal solution in a definite temperature mode, nucleation and polycondensation of orthosilicic acid, and the growth of silica nanoparticles;

2. introduction of the stabilizer to prevent aggregation of nanoparticles;

3. filtering of the solution through membrane cartridge-filters with the goal of concentration performed in several stages (2-3 stages);

4. removal of ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+,3+}$, Al^{3+}, SO_2^{-4}, and Cl^-) from the obtained sol via the ion exchange (ion-exchange columns, filters) to increase the chemical purity of the sol and its stabilization, or dilution of the sol and its repeated concentration.

OBTAINED THE LOW-AGGREGATED NANODISPERSED POWDERS

The concentrated aqueous silica sols were used to obtain the low-aggregated nanodispersed powders. To isolate the solid phase from aqueous sols, coagulation (flocculation), sol-gel transition, and cryochemical technology were applied (Generalov, M.B., 2006; Shabanova, N.A., Sarkisov, P.D., 2004).

The cryochemical technology, which is based on the combination of low-temperature and high-temperature impacts on the processed materials, provides wide possibilities for obtaining the nanodispersed materials particularly from sols and

suspensions (Brazhnikov, S.M., Generalov, M.B., Trutnev, N.S., 2004).

The process flowsheet of cryochemical involves the following sequence of main production phases of the manufacture:
- preparation of the concentrated aqueous silica sol;
- dispersing of the sol and cryocrystallization of the drops of the dispersed medium;
- sublimation removal of the solvent from the cryogranulate obtained at the previous stage;
- utilization (desublimation) of the solvent.

Dispersing of aqueous sols into separate drops is applied to form the developed interphase surfaces providing a high cooling rate during the contact with liquid nitrogen. Such cooling rate is necessary to exclude segregation of silica nanoparticles that are contained in the starting sol.

The main goal of the crystallization process is to retain high chemical and granulometric uniformity inherent to the dispersed sol. The possibility to retain high chemical uniformity is determined by different conditions including the size of the frozen drops of the solution, its temperature, physicochemical nature, and temperature of the cooling agent. The granulometric uniformity of the product is characterized by the sizes of both cryogranules themselves and dispersed crystallites formed at the stage of aging of the starting hydrothermal solution.

The feature of cryogranulation is in that the crystallization process of the aqueous sol is performed at temperatures substantially lower than the freezing temperature of water. Such a decrease in temperature is necessary to increase the freezing rate, which allows us to exclude the aggregation and to fix the uniformly distributed silica nanoparticles situating in the sol in the solid state. Further, during the sublimation removal of water, the low-aggregated silica powder remains with dispersity corresponding to dispersity of silica in the aqueous sol.

The sublimation stage of ice is performed at a pressure lower than the pressure corresponding to the triple point of water, for which these parameters are the following: pressure ($p = 610$ Pa) and temperature ($T = 0.0076^{\circ}$C). This allows us to minimize agglomeration of silica particles formed at the stage of freezing due to exclusion of appearance of fragments of dropped moisture.

At the sublimation stage, the heat consumed to evaporation of ice is supplied to the product by the conductive heat transfer (by thermal conductivity). The specific heat of sublimation q_{sub} approximately equals to the sum of their specific heats of melting q_m and evaporation q_{ev}. For water, the value of q_{sub} reaches approximately 3 MJ/kg, while q_m is only 0.34 MJ/kg.

Sublimation drying of cryogranules of the silica sol was performed on an experimental installation. The main parts of the experimental installation are an autonomous sublimation chamber (or sublimator) with a heat-leading facility, desublimator, and vacuum-pump system. The main process of sublimation drying, during which the process of transfer of ice from the crystalline state into gaseous state omitting the liquid phase is performed, proceeds in the sublimation chamber. This chamber is equipped with a system of heat supply to the product and devices for monitoring and controlling the process. The heat-leading facility, which is performed on a base of plate heat exchanger, serves to provide the power supply to the layer of the frozen granulated material subjected to sublimation drying. The temperature mode varied in the range from 20 to 200°C. Condensation in the solid state on a cooled surface of the sublimed vapor under a pressure below the triple point takes place in a desublimator, which is arranged in a separate case. The sublimator and desublimator are connected by branch pipes of a large cross section, into which vacuum valves are placed.

The evacuation system is intended to holding of the specified level of the residual pressure during the whole drying process. The system consists of a vacuum pump, PMT-3 manometric thermocouple transformer, and detecting device (VT-3 thermocouple vacuummeter).

The installation operates in the following manner. Tray with frozen cryogranules of the starting concentrated silica sol is placed into sublimation chamber on heating plate. The door of the chamber is closed, and vacuum pump is switched on. The degree of rarefaction is measured by vacuummeter, which operates with thermoelectron sensor. The sublimed vapors of the solvent enter desublimator, where they are deposited on a cooled surface of a flask filled with liquid nitrogen. Uncondensed gases are removed into atmosphere through a filter using vacuum-pump. Upon reaching the rarefaction in the chamber (2-1 Pa), the supply is led to the heating plate. The temperature of the heating plate is monitored using electron thermometer; it is controlled using universal voltage controller. Under these conditions, the drying process is prolonged for several hours. After finishing the drying process, the installation is switched off of the main, rarefaction in the installation is dropped, and the tray with a dried material is extracted.

THE CHARACTERISTICS OF THE SILICA POWDERS OBTAINED BY CRYOCHEMICAL DRYING

The characteristics of the sols and powders obtained in one of the series of experiments are shown in Table 3a,b.

Table 3a. The characteristics of the silica powders obtained by cryochemical sols drying.

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, mB
	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

Table 3b. The characteristics of the silica powders obtained by cryochemical sols drying.

sample	Powder density, g/sm^3	The type of absorption-desorptionis otherm (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

Aging of the separate before the baro-membrane concentration was performed at different temperatures (72-30°C) and values of pH (9.2-4.2). Four samples of aqueous sols are obtained at different temperatures of aging and values of pH. The sol corresponding to UF1 sample is obtained by concentration of the separate that passed aging at 72°C. The separate for sols UF18 and UF19 passed the two-stage aging, initially at 72-70°C, and then cooling to 50 and 30°C. Cooling of the separate weakly affected the particle size since the particles were mainly formed at an elevated temperature of 72-70°C. However, as a result, the particles in sol UF19 are coarser than in sols UF17 and UF18 (see Table 3). This is explained by the fact that sol UF19 was obtained by the dead-end filtration flow chart, when the output for the concentrate was blocked, while the concentrated medium recycled multiply, which caused the aggregation of the silica particles. The particle sizes in the sol UF20 are coarser than in other sols, which is caused by the lower value of pH at the aging stage of the separate.

Using the method of correlation spectroscopy (dynamic scattering of light), we determined the radii of the particles in sols: 29.5, 29.55, 55.5, and 135 nm.

The ζ-potential of nanoparticles was determined by the electrophoresis method: (-39.5 - 56.0) mV.

The samples of silica powders UF17, UF18, UF19, and UF20 were obtained by the subsequent cryochemical vacuum-sublimation drying. By the data of the electron spectroscopy at magnifications of 100 - 7000, as a result of vacuum-sublimation drying of sol drops, spherical cryogranules of 60-100 μm in size with a porous-network structure and a void in the central part were formed (Fig. 1). Under easy impact, the cryogranules are destructed forming the flakes of about 0.1-0.2 μm in size. Using electron microscopy at magnifications of 10 000-100 000, it is established that the particle sizes of the powders are in the range of 10-100 nm.

The data on the low-temperature adsorption of nitrogen are presented in Figs. 3 and 4 and in Table 3.
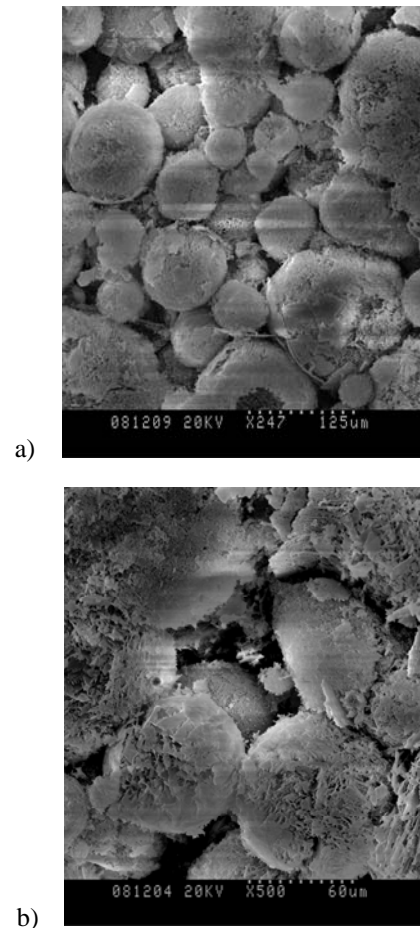

a)

b)

Fig. 1.a,b Cryogranules of the powder obtained by vacuum-sublimation drying of silica sol, magnifications: a) 247; b) 500;
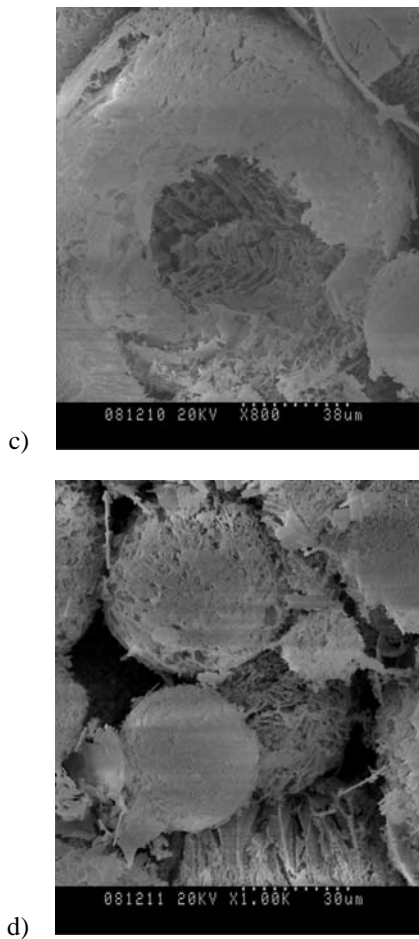
c)

d)

Fig. 1.c,d Cryogranules of the powder obtained by vacuum-sublimation drying of silica sol, magnifications: c) 600; d) 1000;

In different series of tests, we were able to obtain the powders with a high specific surface from 110-170 to 300-400 m^2/g and with the specific volume of the pores of 0.2-0.3 g/cm^3. The pH index, at which aging of the starting hydrothermal solution and subsequent membrane concentration of the sol were performed, is one of the main factors affecting the characteristics of the powder. A decrease in the value of pH had led to an increase in the particle sizes in the sol before the cryochemical drying. The coarser porous particles with the internal structure formed so that after the cryochemical drying, the specific surface of the powder increased. By the data of the low-temperature adsorption of nitrogen, a decrease in pH had also led to a decrease in the average diameter of the pores of the powder (see Table 3). At reduced pH, the type of the adsorption-desorption isotherm and hysteresis loop varied (see Table 3).

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.
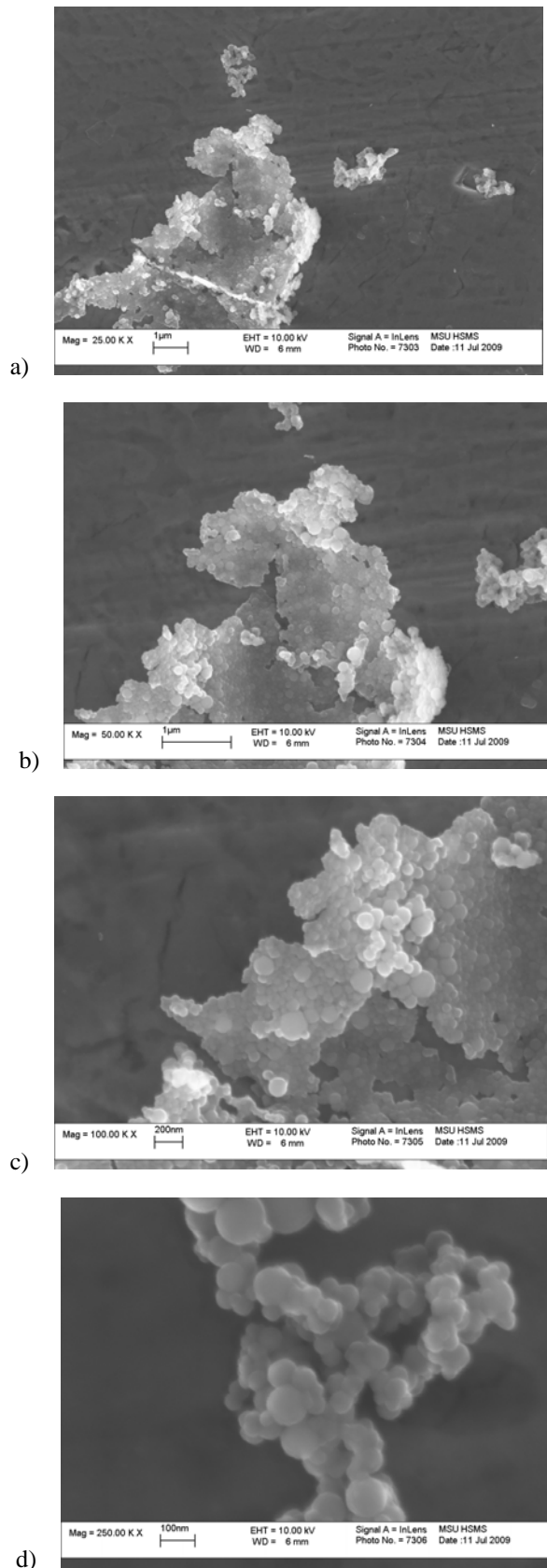

a)

b)

c)

d)

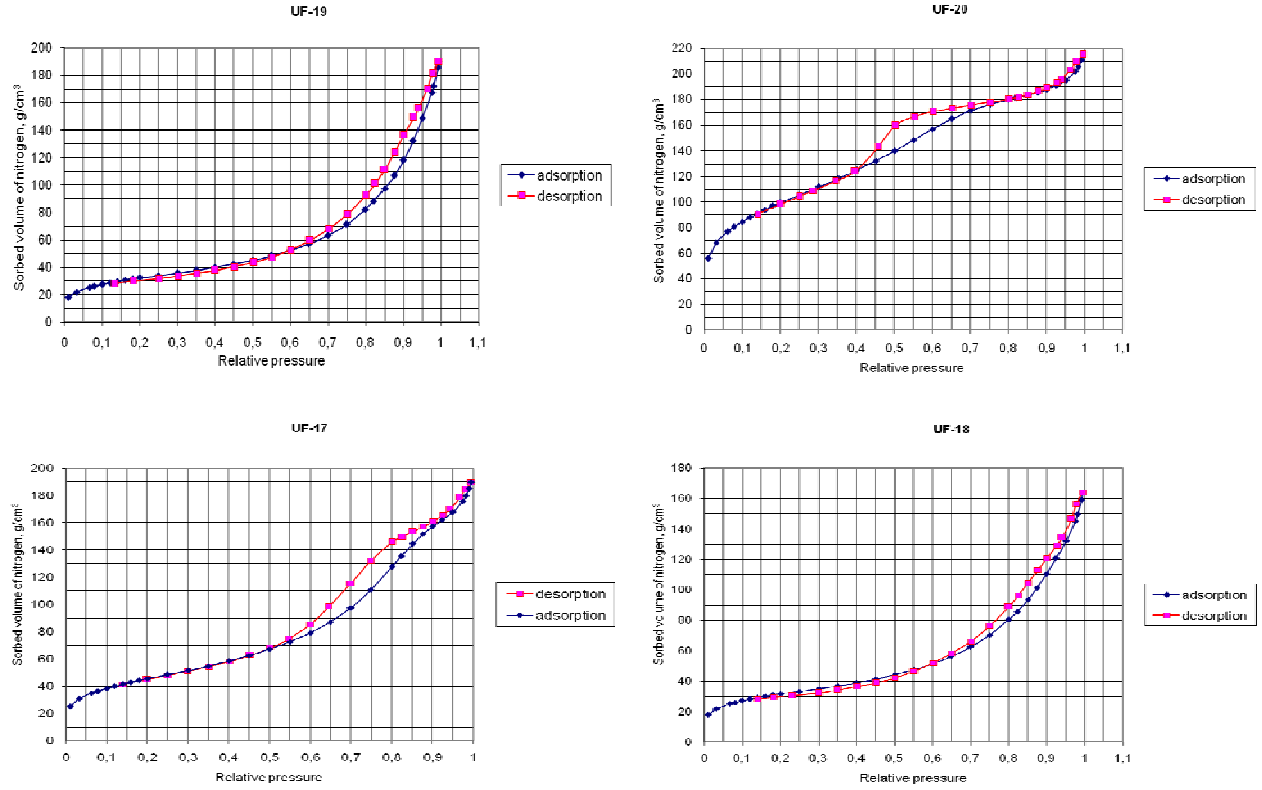Fig. 2. Silica powder pictures obtained on the scanning electron microscope.

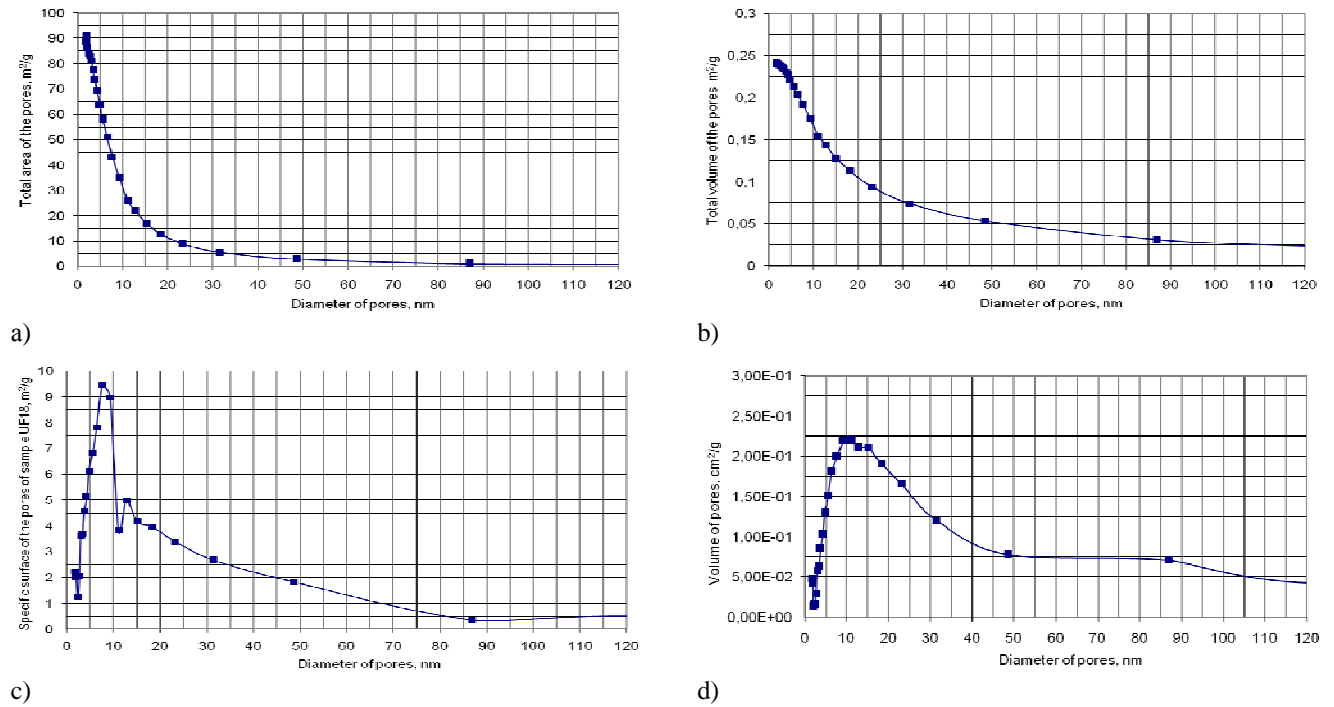Fig. 3. Adsorption-desorption curves of the silica powders.

Fig. 4. Data on the low-temperature adsorption of nitrogen for sample UF18: (a) integral curve of the area by diameters of pores, (b) integral curve of volumes by diameters of pores, (c) differential curve of area by diameters of pores, and (d) differential curve of volume by diameters of pores.

The obtained powders are promising for the industrial use in production of sorbents, catalysts, polymer composites, rubber, and paints.

CONCLUSIONS

The method of obtaining the nanodispersed silica powders on the basis of natural hydrothermal solutions is developed. Hydrothermal solutions are concentrated by using ultrafiltration membranes. Ultrafiltration provides a rather low content of impurities and stability of aqueous silica sols up to highest SiO_2 contents. The solvent (water) remaining in the sols is removed using the cryochemical technology via crystallization of sol drops in liquid nitrogen with the subsequent sublimation of solid ice in vacuum. The method provides obtaining of powders with the particle size in the range of 10-100 nm, specific surface up to 400 m^2/g, and average diameters of pores of 3-10 nm.

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