

## Silica Extraction from Hydrothermal Solutions by Membrane Filters

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### ABSTRACT

The experiments on concentration of hydrothermal solutions by membrane filters for silica sols production were carried out. Three types of membranes were tested. The first type was ceramic membrane filters with diameters of pores 0.1-0.3 microns. The second type was filters with pores sizes in the range of ultrafiltration – 0.01-0.001 microns. The third one was filter with reverse osmosis membrane with diameters of pores in the range 0.001-0.0001 mm. Temperature of solution varied from 20 to 90 °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<sub>2</sub> content up to 600 g/dm<sup>3</sup> (43,0 mass %) and particles radii of 29-135 nm were obtained by the ultrafiltration. Silica powders with the specific surface of 110-400 m<sup>2</sup>/g, mean pores diameter of 3-10 nm, pores volume of 0.2-0.3 cm<sup>3</sup>/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.

### 1. INTRODUCTION

Searching of new silica sources is provided by increasing of amorphous silica utilization in current industry including high-tech branches connected with nanostructured material production. Hydrothermal solutions are untraditional source of mineral including amorphous silica (Potapov V.V., Serdan A.A., 2002; Potapov V.V. et al., 2003). A possibility of extraction of silica-containing material with different physical and chemical characteristics from hydrothermal solutions of considerable volumes was shown in a number of works. An extraction can be carried out by addition of coagulants, flocculants, by electrochemical coagulation and other methods (Potapov V.V., Serdan A.A., 2002; Potapov V.V. et al., 2003). There is an approach to extract of silica on basis of their membrane concentration. Stable monodisperse water silica sols are one of the products of membrane concentration.

Economic expediency of the projects of silica extraction from hydrothermal solutions is provided by multiple use of these solutions for energy and mineral production. Solution purification of colloidal silica must give an additional quantity of electric and thermal energy due to reduction of reinjection temperature and production of mineral as amorphous silica at the same time. There are large reserves of high-temperature hydrothermal resources in Russia. Total power potential of Mutnovsky field (the South Kamchatka) is 300 MW. During using of this potential the flow of separated water heat carrier of the Mutnovskaya GeoPP will be about 300 liter/s with average silica content 700 mg/liter.

When extraction rate is 45-60 % the volume of amorphous silica will be about 3-5 thousand tons per year.

Silica comes into natural solution as molecules of orthosilicic acid (OSA) as a result of its chemical interaction with aluminosilicate minerals of the rocks of hydrothermal fields. When the solution raises to the surface along producing wells and the temperature reduces the solution becomes supersaturated and polycondensation and nucleation of OSA molecules take place and they cause to the forming of silica spherical nanoparticles with radii 5-100 nm.

To develop of the technology of membrane silica concentration the main stages must be worked out. The stages are the following: nucleation and polycondensation of orthosilicic acid (OSA), sol filtering in membrane facilities and sol cleaning from electrolytes, sol stabilization (addition of stabilizing additives).

### 2. EXPERIMENTS ON MEMBRANE CONCENTRATION

The experiments on obtaining of concentrated water silica hydrosols were carried out with the separate of wells of the Mutnovskaya Geothermal power plants (GeoPP). Measurement range pH of the initial separate was 8,0-9,4, silica concentration was C<sub>i</sub>=500-1000 mg/kg, solution temperature varied from 20 to 90 °C. Concentrations of the main components of initial separate solution have values (mg/liter): Na<sup>+</sup> - 282, K<sup>+</sup> - 48,1, Li<sup>+</sup> - 1,5, Ca<sup>2+</sup> - 2,8, Mg<sup>2+</sup> - 4,7, Fe<sup>2+, 3+</sup> - <0,1, Al<sup>3+</sup> - <0,1, Cl<sup>-</sup> - 251,8, SO<sub>4</sub><sup>2-</sup> - 220,9, HCO<sub>3</sub><sup>-</sup> - 45,2, CO<sub>3</sub><sup>2-</sup> - 61,8, H<sub>3</sub>BO<sub>3</sub> - 91,8, SiO<sub>2</sub> - 780, SiO<sub>2</sub> - 200.

Tables 1 a,b show the characteristic of membrane processes: pore diameters of membrane layer d<sub>p</sub>, volume density of membrane surface D<sub>MS</sub> in filters, penetrability of membrane layer - G, selectivity of membrane layer on colloidal silica φ<sub>cs</sub> and ions of dissolved salts φ<sub>TDS</sub>, pressure drop on membrane layer ΔP (transmembrane pressure), electric power consumption for silica concentration: per unit mass SiO<sub>2</sub> in water sol E<sub>SM</sub> and per unit sol volume E<sub>SV</sub>.

Total charge of electric power A (kW·h) was estimated according to pressure drop ΔP on membrane layer and filtrate volume V<sub>f</sub> passed through membrane layer:

$$A = \Delta P \cdot V_f \quad (1)$$

Specific consumption of electric power E<sub>SM</sub> (kW·h/kg) and E<sub>SV</sub> (kW·h/l) was estimated by division of total consumption A by silica mass m<sub>s</sub> in obtained sol or by sol volume V<sub>s</sub>:

$$E_{SM} = \frac{A}{m_s} \quad (2)$$

**Table 1a: The characteristic of membrane processes used for silica extraction from hydrothermal solution**

Type	$d_p, \mu m$	$\Delta P, MPa$	$D_{MS}, m^2/m^3$	$G, m^3/m^2 \cdot h \times 10^{-3}$	$\varphi_{cs}$	$\varphi_{TDS}$
MF	0,1-0,3	0,078	154,0	115,0-51,0	0,6-0,89	0,0
UF	0,01-0,001	0,18-0,22	20000-30000	1,35-1,53	1,0	0,0715
NF	0,0006-0,008	0,30	425,0	31,74-3,03	1,0	0,79-0,88
ROF	0,001-0,0001	0,45-0,55	425,0	11,6-1,0	1,0	0,83-0,94

MF means microfiltration on ceramic filters, UF means ultrafiltration, NF means nanofiltration, ROF means reverse osmosis filtering. The temperature is 20 °C.  $\varphi_{cs}$  is the selectivity on colloidal silica;  $\varphi_{TDS}$  is the selectivity on salts (electrolytes);  $G, m^3/m^2 \cdot h$  is membrane penetrability;  $D_{MS}, m^2/m^3$  is volume density of a placing of membrane surface;  $\Delta P$ , MPa is pressure drop;  $d_p$  is diameter of membrane pores, micrometer.

**Table 1b: Electric power rate to obtain silica water sols by membrane concentration for different membrane processes**

Type of membrane process	$K_C$	$E_{SM}, \text{kilowatt} \cdot \text{h/kg}$	$E_{SV}, \text{kilowatt} \cdot \text{h/liter}$
F	6,8	0,098	0,0005
UF	17,25	0,426	0,0055
	110,0	0,252	0,0208
NF	60,0	0,511	0,0132
RO	20,8	0,560	0,00875
	35,82	0,521	0,0140

$K_C$  is concentration rate that is equal the ratio of total silica in concentrated sol and initial hydrothermal solution.  $E_{SM}$  is electric power rate per mass unit of  $\text{SiO}_2$  in obtained sol;  $E_{SV}$  is electric power rate per volume unit of obtained sol.

$$E_{SV} = \frac{A}{V_s} \quad (3)$$

The rate of water flow  $Q_f (m^3/s)$  through membrane layer (filtrate charge) and membrane penetrability  $G$  at that pressure drop  $\Delta P$  are connected by:  
 $G = Q_{GW}/S_m$ , (4)

where  $S_m$  is a total surface of membrane layer in the cartridge,  $m^2$ .

The experiments with microfiltration membranes were carried out with simultaneous addition of cations-coagulants  $\text{Al}^{3+}$  to enlarge silica nanoparticles. Without coagulant addition the selectivity of membrane layer on silica nanoparticles was low.

The fraction of extracted silica  $\varphi_s$  in a filtrate, that is membrane selectivity on colloidal silica and silicic acid, calculated according to:

$$\varphi_s = \frac{C_t^0 - C_t^f}{C_t^0} \quad (5)$$

$C_t^0, C_t^f$  are total silica in initial solution and filtrate.

The fraction of extracted colloidal silica in a filtrate  $\varphi_{cs}$ , that is membrane selectivity on silica nanoparticles, calculated according to the equation:

$$\varphi_{cs} = \frac{C_{col}^0 - C_{col}^f}{C_{col}^0} \quad (6)$$

$C_{col}^0, C_{col}^f$  are the concentration of colloidal silica in initial solution and filtrate.

During various tests with microfiltration membranes  $\varphi_s$  at 20°C the selectivity on colloidal silica ranged from 0.20 to 0.97 at different concentrations of added  $\text{Al}^{3+}$  in the range 2-8 mg/kg. Silica selectivity was up to 0,726.

Reverse-osmosis membranes in addition to a high selectivity  $\varphi_{cs}$  on colloidal silica had considerable selectivity  $\varphi_{ms}$  on dissolved orthosilicic acid (OSA) reached up to 0,7-0,9. This result gives the possibility to change process flowsheet of concentration fundamentally, if the stage of ageing of initial hydrothermal solution is eliminated when nucleation of orthosilicic acid (OSA) and colloidal particles growth occur. Reverse-osmosis membranes give the possibility to concentrate molecules of OSA without their preliminary transformation in silica nanoparticles. Use reverse-osmosis provides with deeper cleaning of water heat carrier of GeoPP from silica, it increases the effectiveness of utilization of heat carrier power budget. The selectivity  $\varphi_{cs}$  on colloidal silica of nanofiltration membranes was close to 1,0; the selectivity on molecules of OSA was too much lower than reverse-osmosis membranes had. The imperfection of reverse osmosis concentration as well as nanofiltration concentration is salts accumulation in a concentrated medium due to this type of membranes have high selectivity on ions of dissolved salts: reverse-osmosis membranes have  $\varphi_{TDS} = 0,83-0,94$ , nanofiltration membranes have  $\varphi_{TDS} = 0,79-0,88$ .

The selectivity  $\varphi_{TDS}$  on ions of dissolved salts of ultrafiltration membranes is low. So electrolytes accumulation doesn't occur when  $\text{SiO}_2$  content increases in concentrated sols. It profitably distinguishes ultrafiltration membranes as a method of obtaining of stable water sols

with the highest  $\text{SiO}_2$  contents and low impurities concentration.

Silica content in filtrates after ultrafiltration can be reduced up to the values which correspond to amorphous silica solubility, i.e. colloidal phase in filtrates will be completely absent. At the same time metals' ions of the initial solution are weakly delayed by ultrafiltration membranes and come into filtrate in considerable quantity. If the filtrate is concentrated by reverse osmosis after ultrafiltration facilities water environments with high content of lithium, rubidium, caesium and other useful chemical compounds presenting in initial solution in ionic or molecular form will be obtained.

The experiments with membranes showed the ultrafiltration advantage under the obtaining of concentrated silica sols (Potapov V.V. et al., 2008). Ultrafiltration or microfiltration and ultrafiltration combination were used to accumulate significant sols volumes.

The ultrafiltration membranes of capillary type were used. An initial medium is supplied into long capillary pipes which walls are the membrane layer. During the moving inside the pipe a part of flow is filtrated outwards in a radial direction and accumulated in the case of element-filter in the space between the pipes (filtrate). The part of flow which has passed through the whole pipe length without filtration through the membrane walls (concentrate) enters the concentrate collector and come out the cartridge in an axial direction. Filtrate comes out the element-filter case in a lateral direction.

The membranes made of polyethersulfone or polyacrylonitrile were used. The diameters of the membrane layer pores are within the range 20-100 nm. The characteristics of the ultrafiltration membranes and element-filters using during the experiments are shown in table 2. The concentration was made in three stages:  $\text{SiO}_2$  content from 3-10 g/dm<sup>3</sup> was obtained during the first stage, during the second stage it was 10-30 g/dm<sup>3</sup>, during the third stage - 100-600 g/dm<sup>3</sup> (10-43,0 mass %). During the first stage the filters of a large standard size were used, during the second – the filters of a mean standard size, during the third – the filters of a small standard size.

It was determined that the ultrafiltration membranes selectivity is close to 1,0 on a colloidal silica without a preliminary coagulants adding and low selectivity on the molecules of silicic acid and ions. So it is possible to obtain the solution with a high  $\text{SiO}_2$  content and low concentration of impurity ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+,3+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  due to ultrafiltration. The concentration of impurity ions will be reduced if the sol is diluted and the ultrafiltration concentration is repeated. Thus, ultrafiltration has advantages in comparison with other membrane processes to obtain stable concentrated water sols of silica with a low content of impurities. Microfiltration can be used to concentrate sols with large particles diameters (40-70 nm and more).

$\text{SiO}_2$  content in silica sols was made up to 100-600 g/dm<sup>3</sup> using ultrafiltration membranes. The sols density was in the range 999-1325 g/dm<sup>3</sup>, the dynamic viscosity was 1-150 mPa·s, the radii of silica particles were 5-135 nm, particles zeta-potential was from -32,4 to 42,5 mV.

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

- 1) Ageing of the initial hydrothermal solution under the definite temperature regime, nucleation and polycondensation of orthosilicic acid, silica nanoparticles growth;
- 2) Stabilizer adding to prevent nanoparticles aggregation;
- 3) Filtration solution through the membrane element filters for concentration; the filtration was made in several stages (2-3 stages);
- 4) Ions removal (ions  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+,3+}$ ,  $\text{Al}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) out off the obtained sol using the method of ion exchange (ion-exchange columns, filters) to increase chemical sol purity and its stabilization or to dilute the sol and concentrate it once more

**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	<u>polyethersulfone</u>	<u>polyacrylonitrile</u>	<u>polyethersulfone</u>	<u>polyacrylonitrile</u>
A number of hollow fibers, pieces.	1150	1500	2520	3000
An area of the membrane layer of one fiber, m <sup>2</sup>	0,00027	0,00166	0,0056	0,00333
Summary area of the membrane layer, m <sup>2</sup>	0,31	2,5	15,0	10,0
Module size	315x65 mm	550x100 mm	1500x220 mm	1260x90 mm

### 3. SOL'S DRYING AND SILICA POWDER PRODUCTION

The concentrated water sols of silica were used to obtain low-aggregated nanodispersed powders. Coagulation (flocculation), sol-gel transition, cryochemical technology (Generalov M.B., 2006; Shabanova N.A., Sarkisov P.D. 2004) are used to extract of solid phase from water sols. Cryochemical technology based on the combination of low and high temperature effects on the process material gives multifold possibilities to obtain nanodispersed material including from sols and suspensions (Brazhnikov S.M. et al., 2004).

Process flowsheet of cryochemical nanotechnology includes the following order of the main technological stage of the production:

- Preparing of the concentrated water sol of silica;
- Sol dispersing and cryocrystallizing of the dispersion medium drops;
- 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. The possibility to keep a high chemical uniformity is determined by different conditions including the size of freezable solution drops, solution temperature, physical-chemical characteristics and refrigerant temperature. Granulometric uniformity is defined by the sizes of both the cryogranules and dispersed crystalline particles formed during the ageing stage of the initial hydrothermal solution.

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 is 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 ( $p = 610$  Pa) and the temperature

is ( $T = 0,0076$  °C). It gives 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 is supplied to the material using conductive heat transfer (heat conductivity). The specific heat of substance sublimation  $q_{\text{sub}}$  is approximately equal to the sum of their specific fusion heat  $q_{\text{fus}}$  and evaporation heat  $q_{\text{evap}}$ . The value of  $q_{\text{sub}}$  for water reaches approximately 3 MJ/kg, and  $q_{\text{fus}}$  is equal to 0,34 MJ/kg approximately.

Sublimation drying of cryogranules of silica sol was made in the experimental setup. The main parts of the experimental setup are self-contained sublimation chamber (sublimator) with heat-supplying unit, desublimator and vacuum pumping system. The main process namely the sublimation drying takes place in sublimation chamber; during the sublimation drying the ice transition from crystalline state into gaseous state without liquid phase happens. The chamber has the system of heat supply to the material, the instruments of process control. Heat-supplying unit made on basis of plate-type heat exchanger provides with power supply to the layer of frozen granulated material subjecting to the sublimation drying. The temperature conditions varied within the range from 20 °C up to 200 °C. The desublimator is located in a separate case. The condensation of a sublimation steam in a solid state on the cooling surface when the pressure is lower than triple point takes place in it. Sublimator and desublimator are connected by the pipes of a large section; vacuum valves were placed on the pipes.

The vacuumization system is intended for maintaining of the given level of residual pressure during the whole drying process. The system consists of the vacuum pump, suction connection (vacuum line) with stop valves, manometric thermocouple transformer (transducer) TMT-2 and register (thermocouple vacuum gage VT-3).

The unit works in the following way: trough with frozen cryogranules of the initial concentrated sol of silica is placed in sublimation chamber on the heating stove. The chamber door is closed and vacuum pump is switched on. The vacuum level is measured by vacuumometer working with thermoelectronic sensor 6. Sublimation water solution steam enters desublimator where it settles on the cooled surface of flask filled with a liquid nitrogen. Residual gases are removed by vacuum pump and enter the atmosphere through the filter. When vacuum ( $2 - 1$  Pa) appears in the chamber the power is supplied to the heating stove. The temperature of the heating stove is controlled by electronic thermometer and all-purpose voltage controller (APVC). The drying process lasts several hours in such conditions. After the drying process ending the unit is switched off, vacuum is thrown off the unit and the trough with dried material is taken out.

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

Sample	The conditions of separate ageing before the membrane concentration		Mean radius of the particles in silica sol before the cryochemical drying, nm	Zeta potential of the particles surface, mB
	Temperature, °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 <sup>3</sup>	The type of absorption-desorption isotherm (the type of hysteresis loop)	The area of the specific surface (S <sub>BET</sub> ), m <sup>2</sup> /g	Mean pores diameter (d <sub>p</sub> ), nm	Summary pores volume (V <sub>p</sub> ), sm <sup>3</sup> /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

Table 3 a,b shows the characteristics of sols and powders obtained during one of these experiments. Separate ageing before the membrane concentration was made under different temperatures (72-30 °C) and pH (9,2-4,5). Four samples of water sols were obtained under different ageing temperatures and pH. The sol corresponding to UF17 was obtained by the separate concentration after the ageing under 72 °C. The separate for UF18 and UF19 sols aged in two-phases: first it was made under 72-70 °C, then cooling up to 50 and 30 °C was made. Separate cooling influenced on particles size little because the particles mainly formed under higher temperature 72-70 °C. However as a result the particles of UF19 sol are larger than in UF17 and UF18 sols (table 3). 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.

Particles radii in sols were determined by the method of photon correlation spectroscopy (dynamic light scattering). They were 29,5 nm, 29,55 nm, 55,5 nm, 135 nm. Zeta-potential of nanoparticles was determined by electrophoretic technique: from -39,5 to -56,0 mV.

The samples of silica powders UF17, UF18, UF19 and UF20 were obtained by the following cryochemical vacuum-sublimation drying of sols. In accordance with the electron microscopy under the increase in 100-7000 times using vacuum-sublimation drying of sol drops the spherical cryogranules of 60-100 µm which have porous-net structure and cavity in a central part were formed. Under a light influence the cryogranules are destroyed and form the flakes of 0,1-0,2 µm thick. It was determined that the sizes of powders particles are within the range 10-100 nm; it was made using the electron microscopy under the increase in 10000-100000 times.

Table 3 present data of low-temperature nitrogen adsorption. 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<sup>2</sup>/g, and specific pores volume of 0,2-0,3 sm<sup>3</sup>/g. The powders density was 0,035-0,010 g/sm<sup>3</sup>. pH under which the ageing of the initial hydrothermal solution and following 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 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 absorption pH reducing caused the reducing of a mean pores diameter of the powder (table 7). When pH was reduced the type of absorption-desorption isotherm and hysteresis loop were changed.

The obtained powders can be used in industry to produce the sorbents, catalysts, polymers, rubber, paint.

#### 4. ECONOMIC BENEFIT OF SOL'S PRODUCTION

Sols production by membrane concentration of hydrothermal solutions is characterized by low expenses of chemical reagents in comparison with traditional sols production. For instance, sols production on the base of water solution of liquid glass (alkali silicate) needs the expenses of sodium silicate, cationite to purify initial water solution from sodium, and the expenses of electric energy for membrane concentration. Suggested technology deletes the expense of liquid glass and high expense of H-cationite.

The cost of water sols depending to their physical and chemical characteristics reaches \$1000-4000 per a ton. The cost of silica mass unit in nanodispersed condition in water sol is higher than silica powders' cost.

Silica water sol can be used to produce the materials with a controlled structure and defined properties. On basis of sol-gel method a large quantity of catalysts and adsorbents, zeolites, glasses, thermo-and-antidrumming compounds, porous materials, ceramics, composite and paintwork material, drilling fluids, etc. (Hench L.L., West J.K., 1990; Ulrich D.R., 1988; Sychoy M.M., 1990; Shabanova N.A., Sarkisov P.D., 2004) are produced. Sol-gel technology allows to carry out the process in optimal conditions with respect to management efficiency of properties of a final product, expenses of energy and process productivity. Sols transformation in gels is the base of the latest nanotechnologies to obtain optical conductors, ceramic ultrafiltration membranes, anticorrosive coats, photomaterials, fibres, high-dispersed abrasives and other materials. Thanks to binding properties colloidal silica is successfully used as inorganic binder in materials with different filling material: inorganic powders, fibres, polymers, metals, etc. The character of such materials is their durability and heat resistance. Ceramic forms obtaining during the founding on smelted models, the production of refractory ceramics, insulating material can be the example of it.

#### 5. CONCLUSIONS

- 1) 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<sub>2</sub> concentration and low concentration of impurity ions – Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, <sup>3+</sup>, Al<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>. Thus, ultrafiltration has got the advantages before other membrane processes when the problem of obtaining of silica concentrated water sols is solved.
- 2) Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules. Thus, reverse osmosis can

be used for extraction of silicic acid molecules without solution ageing when nucleation and polymerization of silicic acid are not over and colloidal silica particles are not formed. Moreover reverse osmosis can be used to obtain metal salts concentrates and other commercial chemical compounds from filtrates purified from silica in ultrafiltration facilities.

- 3) For economic substantiation of process flowsheet of membrane concentration of hydrothermal solution it is necessary to consider the following factors:
  - a. principal cost of membrane facilities that includes the cost of membrane surface taking into account definite quantity of cycles of membranes regeneration till their degradation, the cost of pumps, fittings, armature, storage tanks, control equipment, automated mechanisms
  - b. the cost of electric power for membrane filtering of hydrothermal solution and periodical reverse cleaning of membranest
  - c. the cost of cations and anionites in ion-exchange columns and solutions cost for their periodical regeneration
  - d. the cost of a final product namely concentrated water sol utilized in different industrial branches.
- 4) The method of obtaining of the silica nanodispersed powders on basis of natural hydrothermal solutions was developed. Hydrothermal solutions are concentrated by bar-membrane filtration with ultrafiltration membranes use. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest  $\text{SiO}_2$  content. The water solution that remained in sols is eliminated using cryochemical technology. Sol drops in liquid nitrogen are cryocrystallized by sublimation under the vacuum of a solid ice. This method gives the possibility to obtain powders with particles size within the range of 10-100 nm, specific surface up to 400  $\text{m}^2/\text{g}$ , mean pores diameters 3-10 nm.

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