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To cite this article: V Potapov *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **249** 012043

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Colloid silica in hydrothermal heat carrier: characteristics, technology of extraction, industrial applications

V Potapov¹, A Serdan², D Gorev¹, S Zubaha¹ and E Shunina¹

¹Research Geotechnological Center of Far East Division of Russian Academy of Sciences Severo-Vostochnoe shosse, 30. Petropavlovsk-Kamchatsky-City. Petropavlovsk-Kamchatsky, 683002. Russia

²Lomonosov Moscow State University. Chemistry Department. Lenin Hills, 1, build. 3. Moscow, 119991. Russia

vadim_p@inbox.ru

Abstract. Hydrothermal solution as one of new mineral source for silica production. We have developed methods for silica extraction from hydrothermal solution. Ultrafiltration membrane concentration was used to obtain silica sols. Ultrafiltration membranes have selectivity on colloid silica particles about 1.0 and low selectivity on silicic acid molecules and ions. Thus, ultrafiltration provides with a low content of impurities and stability of water sols up to the highest SiO₂ content (up to 62.5 %). Cryochemical vacuum sublimation of silica sols was used for production nanopowders with specific surface of particles up to 500 m²/g. Cryochemical vacuum sublimation of sols gave the possibility to reduce particles aggregation when silica was extracted from liquid phase. By extraction of silica purification of heat carrier can be achieved and the problem of solid scales formation in heat equipment of GeoPPs can be decided. Perspective ways of industrial applications for sols and nanopowders obtained from hydrothermal heat carrier such as building industry and agriculture were discussed.

Key words: hydrothermal solution, nanosilica, scales, particles diameters, nanosilica extraction, applications in building industry, agriculture.

Introduction

Currently the geothermal systems are one of the prospective and alternative sources of energy. In some cases it is possible to extract chemical compounds from geothermal fluid, which are of interest as the raw material for chemical production. Geothermal heat is widely used for the living accommodations and hot-houses heating. Extent of studying the geothermal systems is, to a considerable degree, explained by the economic and ecological advantages of the geothermal energy. However, in spite of the prospects of further development of this trend there are some problems that make it difficult to use widely similar resources.

Such problems include: prospecting of geothermal reservoirs, reserves evaluation, drilling in zones of high-temperature anomalies, conducting the logging activities in geothermal wells, prevention of corrosion of the heating technical equipment. Large difficulties concern also the multicomponent chemical composition of the geothermal heat carrier that contains dilute gases (hydrogen, carbon dioxide, hydrogen sulphide, nitrogen, methane), acids and mineral combinations. When temperature and pressure are decreasing then separation of dilute substances occurs in the course of the extraction



and heat-carrier exploitation that requires taking measures on speeding up, slowing down or prevention of this process.

Liquid phase (separate) of the steam-and-water mixture and geothermal gases (CO₂, H₂S) must be pumped backwards into the rocks of the field through the reinjected wells in order to maintain pressure in reservoir and decrease influence on the environment. Motion of separate in the heating equipment and reinjected well is often complicated by silica scaling from solution that decreases amount of obtained energy and leads to the additional expenses for hard material removal. In view of this the process of solids formation is of special importance for geothermal systems and needs to be studied and controlled.

Colloidal silica formed in hydrothermal solution in several stages. Primarily silicium enters the solution as molecules of silicic acids as the result of chemical interaction of water with aluminosilicate minerals of hydrothermal field rocks at a depth of 1.0-3.5 km in zones of thermal anomalies at increased temperature (up to 250-350°C) and pressure (4.0-20 MPa). Hydrothermal solution is multicomponent: Na, K, Si, Ca, Mg, Al, Fe, Cl, S, C, B, Li, As, Cu, Zn, Ag, Au and other compounds are present in it in ionic and molecular form.

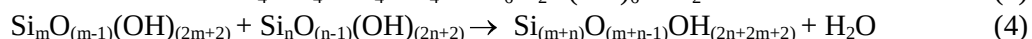
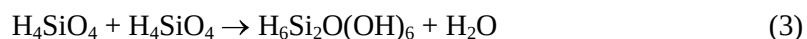
At the temperature of 250-350°C, when solution has a contact with rock minerals, total content of silicium C_t in water can be evaluated by α -quartz solubility on absolute temperature T [1]:

$$\lg \left(\frac{C_t}{60} \right) = \frac{-1.468 + 252.9}{T} - \frac{3.217 \cdot 10^5}{T^2} \quad (1)$$

At ascending filtration in the fissured-porous rocks or when moving in the productive wells of the geothermal electric- and heat electric power stations pressure and temperature of the solution decrease, and solution is divided into vapour and liquid phases. Total content of silica C_t in liquid phase can reach in this case 700-1500 mg/kg. Owing to this water solution becomes oversaturated with respect to the solubility of amorphous silica C_e . According to the experimental data, value C_e for pure water depends on absolute temperature T by the following way [2]:

$$\lg \left(\frac{C_e}{60} \right) = \frac{-0.1185 \cdot 1.126 \cdot 10^3}{T} + \frac{2.3305 \cdot 10^5}{T^2} - \frac{3.6784 \cdot 10^7}{T^3} \quad (2)$$

Such a state of monomeric silicic acid in water solution is unstable. Oversaturation of the solution S_m , equal to the difference ($C_s - C_e$) of silicic acids concentration (monomeric silica) C_s and solubility C_e , is the motive force for the processes of nucleation and silica acid molecules polymerization with condensation of silanol groups, formation of siloxane links and partial dehydration in the following reactions:



There is a problem of studying the physical-chemical properties of the colloid silica in hydrothermal solution. Results of the study are necessary for improvement of the model of hydrothermal system mineral formation, and also for working out technology of silica extraction and increasing the effectiveness of using hydrothermal heat-carrier of the geothermal heat electric power stations [3, 4, 5]. The material extracted from the heat-carrier depending upon its physical-chemical properties can be used in various spheres of industry for making paper, rubber, glue, glass, ceramics, brick, cement, concrete, sorbents, catalysts, and in chromatography and electronics also.

1. Parameters of the Verkhne-Mutnovsky geothermal electric power plant

Heat-and-power complex of the Verkhne-Mutnovsky geothermal electric power plant (GeoPP) with producing wells is located within eroded structure of volcano Zhirovsky that refers to the Mutnovsky volcanic region. This region is 70 km southward of Petropavlovsk-Kamchatsky city and on the whole it can serve as an example of relationships of various forms of current volcanic and hydrothermal activity. Fundamental section of the Mutnovskaya system includes two parts: the upper one with fresh cold waters and the lower consisting of the steam-and-condensate zone (in two-phase state) and zone

with prevalence of hot water. Temperature in the latter is 250-300°C; it contains the face part of many production wells.

Geothermal wells (048, 049i, 055) of the Verkhne-Mutnovsky geothermal electric power plant bring to the surface a heat-carrier as a steam-and-water mixture (SWM). Average steam content x of producing wells is 0.3 (Tabl. 1). (Index WP in Tabl. 1 concerns the water phase of the mixture and index SP concerns the steam phase.) Wells 024i, 043i and 054 are provided for reinjection. Typical well parameters are the following: 048 – depth is 1247 m, diameters of casing are 245 mm and 168 mm; 024i – depth is 1802 m, diameters are 245 mm and 168 mm.

Table 1. Discharge of the producing well 048 and chemical composition of the matter in geothermal solution (mg/kg).

Phase discharge, kg/s	pH	SiO ₂	Cl ⁻	SO ₄ ⁻²	HCO ₃ ⁻	Na ⁺ +K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
SWM, 64.5	9.2	841	293	163	26.7	285.4	1.66	1.18	1.0
WP, 44.5s	9.2	830	325	167	55	325.5	1.6	1.3	1.0
SP, 20.0	5.8	4	0.7	8.6	9.2	8.9	22.0	0.2	2.0

Thermal scheme of the geothermal electric power plant was worked out by the joint-stock companies «Nauka» and «Kaluzhsky turbine factory» and it included local schemes of the tie of producing wells, SWM transportation, double steam separation, turboaggregate tie, system of steam condensation, system of dissolution of undilute gases in condensate (system of ecological protection), system of steam obtaining from separate for ejectors, system of pumping condensate and separate, tie of injection wells. Working of three power modules with capacity of 4 MW each is planned. Turbine of the electric module designed by the joint-stock company «Kaluzhsky turbine factory» works on saturated steam with pressure of 0.8 MPa (8 bar) and with discharge of 8-9 kg/s per power module, that corresponds to the pumping of 48-50 kg/s of separate liquid into the reinjected wells. Pressure at the turbine outlet is 0.11 bar, mass portion of condensate is 12%, coefficient of efficiency is about 0.773.

2. Chemical composition and mineral components of the samples of silica scales formed at the Mutnovskoe hydrothermal field

In conditions of the Mutnovskaya geothermal system several types of amorphous silica scales were distinguished: 1. white fine-dispersed silicate powder (specific volume of pores is about 3.0 cm³/gr); 2. solid hard thin coating on the rock surface (is formed when pouring steam-and-water mixture into the surface); 3. glass-like solid hard scales; 4. pinkish fragile uneven scales (two last on the inner surface of the pipes of the heat-exchangers and separators). In most of samples dioxide of silicium is up to 85 weight percents. Composition of the first type scales is the following (wt. %): SiO₂ – 85.02, TiO₂ – 0.08, Al₂O₃ – 1.37, Fe₂O₃ – 0.53, FeO – 0.06, MnO – 0.04, MgO – 0.09, CaO – 0.40, Na₂O – 0.27, K₂O – 0.75, H₂O (physically bound water) – 5.63, ignition losses – 5.15.

Salts deposition on the blades and inner surface of the Mutnovskaya turbine K-0.4 body represents separate group. Weight content of silica in them is in average lower – 70-80 wt. %, iron content is higher – 3-7 wt. %.

The fact that amorphous form of silicium combinations precipitates in the heating technical equipment is proved by the X-ray diffraction analysis of the material samples formed on the pipes of the heat exchanger and after pouring hot water on the surface.

3. Experiments on sols and nanopowders production

After the completion of orthosilicic acid polycondensation in hydrothermal solution and formation of silica colloid particles of given sizes the water removal was made to obtain nanodispersed powders. Water was removed in accordance with a two-stage scheme: the 1st stage is filtering through the membrane filters; the 2nd stage is cryochemical vacuum sublimation with liquid nitrogen use.

During the first stage hydrothermal mediums were filtered through the ultrafiltration membrane units. Under ultrafiltration silica colloid 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. Colloid particles were concentrated in aqueous medium, at the same time SiO₂ 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 SiO₂ were subjected to cryochemical sublimation 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 colloid particles and they can't be effective during the initial concentration stages under a low SiO₂ content. So ultrafiltration 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: SiO₂ content from 3 up to 10 g/dm³ was obtained during the first stage, during the second stage it was 10-30 g/dm³, during the third stage - 100-940 g/dm³ (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/dm³, the dynamic viscosity was 1-150 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

($p = 610 \text{ Pa}$) and the temperature is ($T = 0,0076 \text{ }^{\circ}\text{C}$). 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 shows the image of powder structures after water solution sublimation under the increasing in 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. If the influence was light the residual structures were destroyed forming the flakes of 0,1-0,2 micron thick.

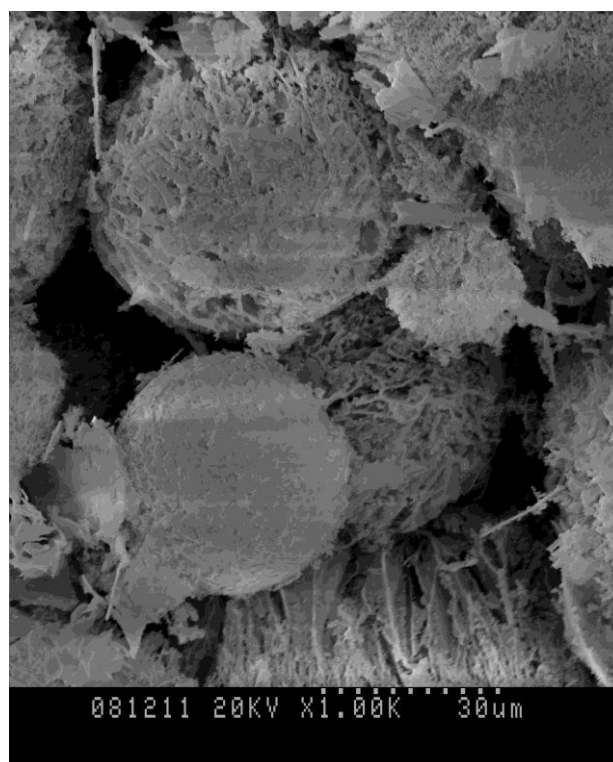


Fig. 1. Structures images from the particles of silica powder formed from cryogranules after water solution sublimation. Magnification factors on the scanning electron microscope 1000.

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 kD and the temperature was $20 \text{ }^{\circ}\text{C}$ power consumption for membrane concentration was $0.32 - 0.18 \text{ kW}\cdot\text{h/kg}$, when pores size was 10 kD specific consumption reduced considerably: up to $0.3 - 0.025 \text{ kW}\cdot\text{h/kg}$. 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 $14.0 \text{ kW}\cdot\text{h/kg}$, when SiO_2 content is 45 mass % (600 g/dm^3) power consumption is $7.0 \text{ kW}\cdot\text{h/kg}$. Thus, total power consumption for obtaining of silica powder is $E_m = 14.32 - 7.18 \text{ kW}\cdot\text{h/kg}$.

When SiO₂ 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 SiO₂ content is 25 mass % (300 g/dm³) in a sol the specific nitrogen consumption is 16.66 kg/kg, when SiO₂ content is 62.25 mass % (940 g/dm³) nitrogen rate is 8.33 kg/kg.

4. Measuring of colloid silica particles sizes

Silica colloid 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 colloid particles on basis of an analysis of dynamic fluctuations of scattered light intensity; these fluctuations 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.

The results of measurement of the sizes and zeta-potential of silica colloid 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 °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 °C. The separate for UF18 and UF19 sols aged in two-phase ageing: first it was made under 72-70 °C, then the cooling up to 50 and 30 °C was made. Separate cooling influenced on particles sizes little because the particles mainly formed under a high temperature 72-70 °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.

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 colloid particles surface in water sols.

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, mV
	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

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 10⁴ up to 10⁵, 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 colloid particles images in the sols and powders were obtained on a scanning and tunnel electron microscope (Fig, 2, 3).

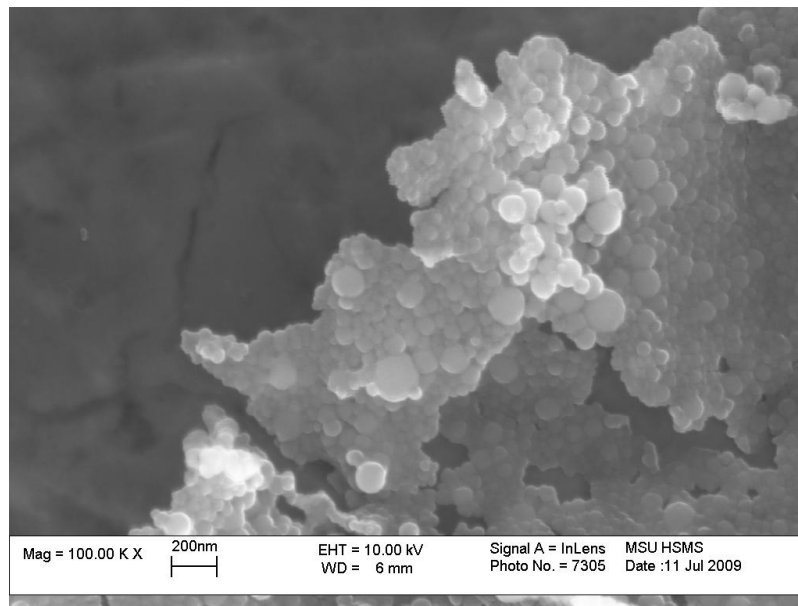


Fig. 2. Silica powder images obtained on the scanning electron microscope.

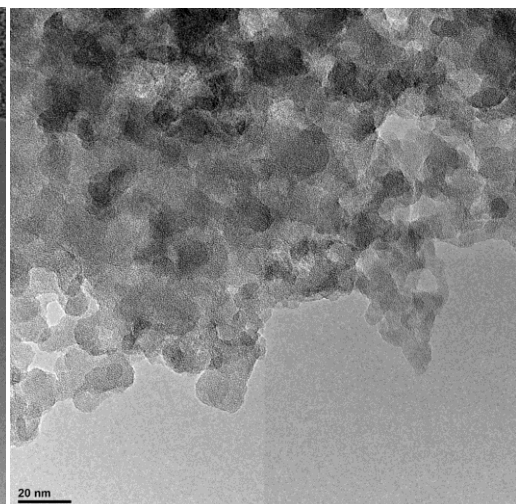
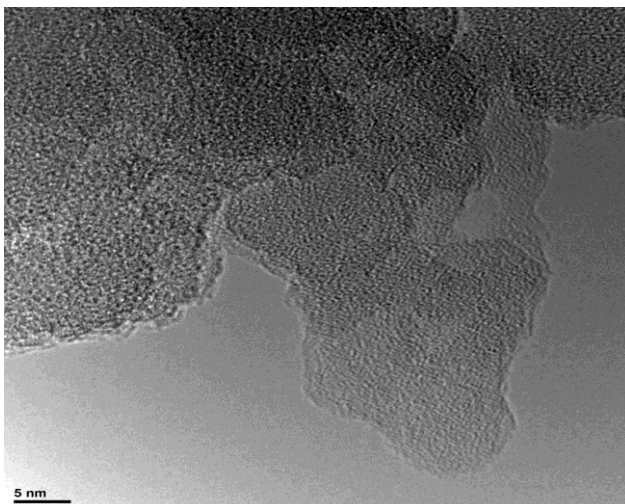
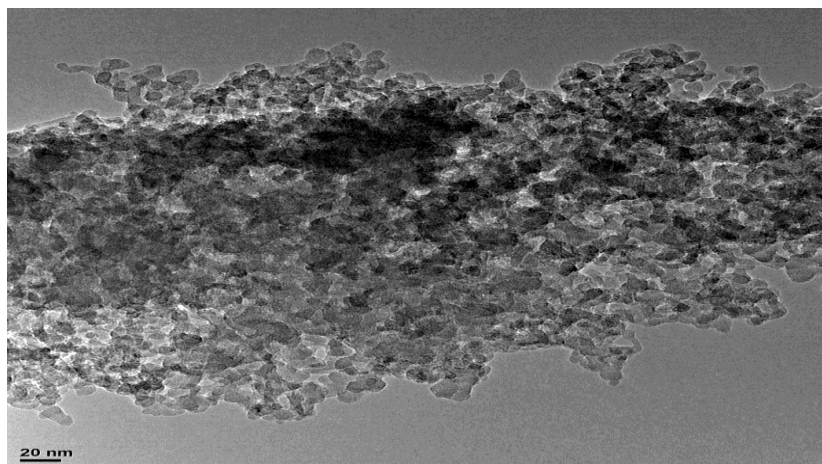


Fig. 3. Silica powder images obtained on the tunnel electron microscope.

Cryochemical vacuum sublimation of sols with using liquid nitrogen under 77 K 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 diameters of the main particles part of sols and powders are within the range of -100 nm.

5. The characteristic of silica powders obtained by cryochemical vacuum sublimation

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 °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 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 (mass %) extracted from silica sol.

SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO
99.72	<0.01	0.173	<0.01	<0.01
MnO	MgO	CaO	Na ₂ O	K ₂ O
<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 m²/g, and specific pores volume of 0.2-0.3 sm³/g. The powders density was 0.035-0.010 g/sm³. 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 4). When pH reduced the type of adsorption-desorption isotherm and hysteresis loop were changed (table 4). 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	166.5	6.2	0.259
UF18	0.010	II	115.0	7.1	0.204
UF19	0.010	II	118.3	7.7	0.230
UF20	0.016	IV	360.4	3.3	0.301

The least value of a mean diameter of powders pores obtained by sublimation 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.

6. Development of methods of utilization of silica extracted from the hydrothermal solution in industry.

6.1 Utilization of silica as a sorbent for purification of water from oil products

We worked out an utilization method of silica for making sorbent which can be used for the purification of sewage of different fields of industry and polluted waters of natural reservoirs from oil products.

Capacity to absorb of organic liquids of silica precipitated from the hydrothermal solution in some cases is 1.5–2.0 times larger than capacity of synthetic amorphous dioxide of silicon obtained by another methods with expenses of reagents. Capacity of geothermal silica to absorb of petrols reaches 160 – 200 g/100g of silica, capacity to absorb of diesel fuel is 190 – 200 g/100g of silica.

6.2 Utilization silica in gas chromatography

Experiments were done on using silica nanopowder extracted from hydrothermal solution as a sorbent in chromatographic columns to separate mixtures of organic liquid and gaseous substances. Utilization of silica as a sorbent for gas chromatography makes it possible to use sorption properties of precipitated silica surface. That extends fields of utilization of silica material, increases its cost and makes use of hydrothermal heat-carrier more effective. This very method excludes costs of expensive reagents on production of traditional synthetic dispersive amorphous silicas which serve as the initial material for making sorbents for chromatography.

Experiments were done on separating the components of mixture of organic compounds in two chromatographic columns. One column was filled with silica precipitated from the hydrothermal solution and another one – with commercially produced sorbent silochrome C-80. Sizes of fraction of silochrome C-80 particles was within 0.315 – 0.5 mm, specific powder surface – 80.0 m²/g, average pore diameter – 40.0 – 50.0 nm, specific pore volume – 1.3 cm³/g. Both columns had the same preparation and worked simultaneously. The length of columns was 1.8 m, inner diameter – 2.0 mm, mass of sorbent in the column filled with silochrome C-80 was 4.67 g, in the column filled with geothermal silica – 1.45 g. Analyzed components were eluted through the columns by gas-carrier – helium. Helium consumption through each column was 0.2 ml/s. Temperature of the experiments was 130°C. To register chromatographic peaks flame-ionization detector was used. Consumption of hydrogen in detector was 0.5 ml/s, air consumption was 5.0 ml/s.

Table 5. Comparative time of retainment of different components in the columns (length of columns – 1.8 m, diameter – 2.0 mm) filled with silica, precipitated from the hydrothermal solution, and silochrome C-80.

Component	Volume of sample, microliters	Time of retainment, t _R	
		Silochrome C-80	Geothermal silica
Isobutan	200.0	44.0 s	53.7 s
Hexane	0.1	1 min 11.0 s	1 min 30.2 s
Heptane	0.1	1 min 43.0 s	2 min 13.0 s
Benzene	0.1	1 min 22.5 s	3 min 22.3 s
Toluene	0.1	2 min 26.0 s	6 min 33.5 s
O-xylol	0.1	4 min 36.9 s	13 min 08.7 s

Table 5 contains experimental results on obtaining the chromatograph peaks of isobutan and vapours of organic liquids: hexane, heptane, benzene, toluene, o-xylol. The evaporator temperature at which vapours of liquids were obtained was 200°C. As it can be seen from the Table 4, time of retainment t_R of each component is larger in the column filled with hydrothermal silica. The experiments with mixture of these components also showed larger time of retainment of the components for the column with silica precipitated from the hydrothermal solution. That indicated better adsorption activity of hydrothermal silica surface in comparison with silochrome C-80.

6.3 Utilization of silica for liquid glass production

The samples of finely dispersive powder were obtained with large weight fraction of dioxide of silicon from 95 to 99 %, amorphous structure, high density of surface hydroxyl groups – 4.9 OH/nm² at 200 °C, high reflectivity of light by the surface – up to 91 – 95 %, oil absorption capacity – up to (159 - 218) g/100g and low Ca, Al, Fe. Concentrations of Ca, Al, Fe are totally not more than 0.6 weight %.

By the method of low-temperature nitrogen adsorption pore characteristics of samples of nanosilica precipitated by freezing out the hydrothermal solution were measured. Isotherms of adsorption-desorption of nitrogen of IV-type were obtained for the samples of silica powder. Silica samples are characterized by high specific surface area – from 50 to 300 m²/g, porosity – up to 1.1 cm³/g, average values of pore diameters d_p = 12.7 – 16.6 nm, low fraction of area (9 – 10.7 %) and volume (0.5 – 0.856%) of micropore. The largest part of the pores of hydrothermal silica is concentrated in a rather small range of diameters: 60.9 % of total area and 79.8 % of total pore volume were in the the pores with diameters d_p from 5.18 to 26.47 nm.

Using silica precipitated from solution the samples of liquid sodium silicate glass were produced by autoclave method with heat supply from the waste hydrothermal heat-carrier. Amorphous structure and large specific surface of silica provided its rapid and homogeneous dissolution and reaction acceleration with formation of sodium silicate. That reduced duration of the process and energy expenses for its conducting. Different technical characteristics of glass, such as density, concentrations of combinations, silicate magnitude up to 4.0, satisfying norms for high-quality glass were obtained. Rather low content of calcium, ferrum and aluminium in initial silica provided necessary low contents of these impurities in the final product.

6.4 Application of nanosilica to improve concrete strength

The experiments were carried out to study the effect of silica nanoparticles on the compressive strength of concretes (cement-sand-water-crushed stone): the introduction of a silica sol with average particle diameters in the range of 10-100 nm and a specific surface of 100-500 m²/g.

Portland cement (PC) of Korean production of 42.5R class, which meets the standards of Russia for Portland cements was used as a binder. According to GOST (State Standart) 31108-2003 it is classified as a type of CEM-I based on clinker with the content $C_3S=55-58\%$, $C_3A=8.2-8.5\%$ and conventional chemical-mineralogical clinker quality indicators (lime saturation coefficient $KH=90-91\%$, alumina module $p=1.7$, silicate module $n=2.3$). Physical-mechanical characteristics (brand, rest on a sieve No. 008, setting time, compressive strength) are within the requirements of the standard for the fast-hardening Portland cement of PC 500-D0 brand of 42.5B class. The fillers were crushed stone of diorite fraction from 5 to 20 mm according to GOST 8267 –State standard of Russian Federation (bulk density is 1300 kg/m³, density is 2.73 g/cm³) and quartz-feldspar sand according to GOST 8736 ($M_{kr}=3.4$ and 2.9, density is 2.62 g/cm³) in a mixture with standard quartz monofractional sand. The additive/addition is a superplasticizer from a series of highly effective water-reducing ability of polycarboxylates (PCX). The density of the aqueous solution of PCX was 1082 g/dm³, the solids content was 412 mg/g.

The effectiveness of the silica sol addition was determined by the concrete strength. The water-cement ratio was within the limits of $W/C=0.61-0.71$, the sediment of the standard cone is $CS=12-19$ sm, the SiO_2 content is 2.0 % of the cement mass, the addition of the solution is $PKK=2.2-2.6$ % of the mass of cement. Concrete tests were carried out according to GOST 30459-2003, item 7. The

consumption of materials (kg/m^3) is as follows: cement (PC 550) - 345 ± 5 ; sand quartz-feldspar - 400; sand standard quartz - 400; crushed stone fraction 5-20 mm - 1060. The dosage of the sol was calculated taking into account the fact that there are 3500 g of cement and 2250 g of water in a batch of 10 liters in addition to crushed stone and sand.

Sol volume was calculated by the Equation:

$$V_3 = \frac{C \cdot \text{SiO}_2}{100 \cdot K_3} \quad (6)$$

where C is the cement consumption, g; SiO_2 – silica concentration, %; K_3 is SiO_2 content in the sol, g/dm^3 .

Thus, the sol volume per 10 liters of batch is:

$$V_3 = 3500 \cdot 2 / 100 \cdot 115 = 0.609 \text{ dm}^3.$$

This volume of sol contains $0.609 [\text{dm}^3] \times 15 [\text{g/dm}^3] = 9.135 \text{ g SiO}_2$. The mobility of concrete mixtures was provided by means of an appropriate dosage of PCX. Technological and structural parameters of the quality of mixtures and concrete were determined according to the following standards: mobility, density of concrete mixture - GOST 10181; concrete density - GOST 12730.0; concrete compressive strength at the age of 1, 2 and 28 days of normal storage and after steam treatment (ST) in accordance with GOST 10180. The efficiency criteria were calculated by the Equation 2 GOST 30459-2003:

$$\Delta R_t = 100 \cdot \frac{(R_t^R - R_t^b)}{R_t^R} \quad (7)$$

where R_t^b is concrete strength of basic composition in the equivalent age, MPa; R_t^R – concrete strength of the control composition in the equivalent age, MPa. The results of concretes tests with the addition/additive of silica sol in a combination with PCX are presented in Table 3.

According to the results obtained SiO_2 nanoadditives are applicable: first, to accelerate the strength of concrete (more than twofold increase in strength after the first day of hardening); secondly, to increase strength at the age of 28 days - up to 40%. At $W/C=0.52-0.55$ the silica sol introduction resulted in an increase of compressive strength of concrete at the age of 28 days at the cement SiO_2 consumption: 0.5% - (+28%), 1% - (+43%), 2% - (48%), 3% - (58.5%).

Table 6. Concrete test results with the addition(additive) of silica sol (№ 66 and № 69 compositions are control, criterion of efficiency is within the brackets). HWT –heat water treatment. CS – cone sedimentation.

Set	Composition number	SiO_2 , % from C	SVC	W/C	CS, sm	Mixture density, kg/m^3	Compression strength, MPa			
			5New, % from C				1 day	2 days	28 days	HWT
1	66	–	–	0.643	13	2345	6.8	12.0	26.6	–
	67	2	2.33	0.715	10	2322	12.7 (+86%)	19.8 (+65%)	33.6 (+26%)	–
	68	2	2.58	0.643	18–20	2320	15.5 (+128%)	–	36.4 (+37%)	–
2	69	–	–	0.62	16	2322	10.1	–	28.5	19.7
	70	2	2.23	0.61	18	2335	19.2 (+90%)	–	39.9 (+40%)	26.6 (+35%)

6.5 Results of application of nanosilica in agriculture

We used hydrothermal nanosilica for rising characteristics of agricultural animals and plants - cows:

- increasing of calves mass - 3-9.2 % ;
- regulation Ca/P metabolism in blood;
- pigs:
 - increasing bones tensile strength of piggies - 17 %;
 - piggies vitality– 20 %;
- fowl:
 - increasing of eggs production – 3.0 – 7.9 %;
 - vitality –2.5-3.2 %;
 - thickness of eggs shell– 5.7 %;
- bees:
 - increasing of honey production – 62.9 %;
 - wax production - 62.5 %;
 - pollen production – 350 %
- potatos: increasing of production – 30 %.

Conclusions

1. Hydrothermal solution is one of new mineral source for silica production. Silica formed in hydrothermal solution as the result of orthosilicic acid polycondensation. Temperature and pH of solution are main factors influenced the sizes of silica particles.
2. Ultrafiltration membranes have selectivity on colloid silica particles about 1.0 and low selectivity on silicic acid molecules and ions. Therefore it is possible to get by ultrafiltration solution with high SiO₂ concentration (up to 62,5 mas. %) and low concentration of impurity ions – Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe^{2+, 3+}, Al³⁺, SO₄²⁻, Cl⁻. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest SiO₂ content.
3. Cryochemical vacuum sublimation of silica sols can be used for production nanopowders with specific surface of particles up to 500 m²/g. Cryochemical vacuum sublimation of sols with using liquid nitrogen under temperature 77 K gave the possibility to reduce particles aggregation when silica was extracted from liquid phase. 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.
4. By extraction of silica purification of heat carrier can be achieved and the problem of solid scales formation in heat equipment of GeoPPs can be decided.
5. Perspective ways of industrial applications for sols and nanopowders obtained from hydrothermal heat carrier are building industry and agriculture.

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