

## Silica Extraction from Hydrothermal Solution

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### ABSTRACT

Silica sols and powders extracted from hydrothermal solutions have been investigated. Hydrothermal heat carrier piped to the surface through production well of Mutnovsky geothermal electrical power station (GeoPP). Liquid phase of heat carrier contain the colloidal silica of about 0.5 g/dm<sup>3</sup> forming as a result of polycondensation of the molecules of orthosilicic acid. Formation of the amorphous silica solid scales in wells, separators, pipes and heat exchangers is the essential problem that makes difficult wide usage of hydrothermal system resources. Via ultrafiltration membrane concentration of hydrothermal solutions, silica sols with SiO<sub>2</sub> contents up to 940 g/dm<sup>3</sup> (62.2 wt %) and particle diameters of 5-100 nm are obtained. The silica powders with the specific surface of 50-500 m<sup>2</sup>/g, average pore diameter of 2-15 nm, and pore volume of 0.2-0.3 cm<sup>3</sup>/g are obtained via cryochemical vacuum-sublimation drying of sols with the use of liquid nitrogen. Samples of silica sols and powders were characterized by Dynamic Light Scattering, Scanning and Tunneling Electron Microscope, X-Ray Diffraction, BET Surface Area. In particular, it was shown that diameters of SiO<sub>2</sub> nanoparticles in sols and nanopowders were in the range of 5-100 nm. The possibility of obtained silica use as a modifying additive for concrete strength increase was substantiated. The test results on concrete compressive strength rise using nanosilica additive extracted from hydrothermal solution are presented. Silica sols and powders were used as additives for rising concrete compressive strength.

Keywords: hydrothermal solution, orthosilicic acid, membrane concentration, silica sol, silica nanopowders, concrete

### 1. INTRODUCTION

Colloidal silica formed in hydrothermal solution in several stages. Primarily silicium enters the solution as molecules of orthosilicic acid H<sub>4</sub>SiO<sub>4</sub> 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<sub>t</sub> (mg/kg) in water can be evaluated by α-quartz solubility (Crerar D.A., Anderson G.M., 1971) :

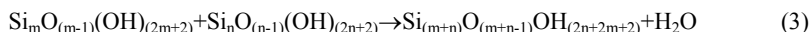
$$\lg(C_t/60) = -1.468 + 252.9/T - 3.217 \cdot 10^5/T^2 \quad (1)$$

Equation (1) gives the following values of quartz SiO<sub>2</sub> solubility (mg/kg): 25°C – 3.46, 50°C – 10.29, 100°C – 47.6, 200°C – 256.0, 250°C – 415.6, 300°C – 592.5. At ascending filtration in the fissured or porous rocks or when moving in the productive wells of the geothermal electric- power stations pressure and temperature of the solution decrease, and a part of solution is evaporated. Total content of silica C<sub>t</sub> in liquid phase after coming solution to the surface 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<sub>e</sub>. According to the experimental data (Marshall W.L., 1980) value C<sub>e</sub>(mg/kg) for pure water depends on absolute temperature T by the following way:

$$\lg(C_e/60) = -0.1185 - 1.126 \cdot 10^3/T + 2.3305 \cdot 10^5/T^2 - 3.6784 \cdot 10^7/T^3, \quad (2)$$

At the temperature of 200°C C<sub>e</sub> solubility is equal 940.8 mg/kg, at 150°C - 651.8 mg/kg, at 100°C - 405.3 mg/kg, at 25°C - 130.8 mg/kg.

Such a state of monomeric silicic acid in water solution is unstable. Oversaturation of the solution S<sub>m</sub>, equal to the difference (C<sub>s</sub> - C<sub>e</sub>) of silicic acids concentration (monomeric silica) C<sub>s</sub> and solubility C<sub>e</sub>, 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:



1. There is a problem of studying the physical-chemical properties of the colloidal 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 efficiency of using hydrothermal heat carrier of the geothermal heat electric power stations (Harper R.T., Thain I.A., Johnston J.H., 1992; Harper, R.T., Thain, I.A., Johnston, J.H., 1995). Amorphous 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, concrete, sorbents, catalysts, and in chromatography and electronics also (Kim L.V. et al., 2013).

Russian Federation has reserves of high-temperature hydrothermal resources in areas of the active volcanism. The potential for SiO<sub>2</sub> production reaches 3-5 thousand tons per year at the flow rate of 1,100-1,200 ton/h of the heat carrier aqueous phase of fluid production wells of the geothermal power station with capacity of 50-60 MWt and the SiO<sub>2</sub> content in the original aqueous medium (650-800 mg/kg).

## 2. SILICA EXTRACTION FROM HYDROTHERMAL SOLUTION

The main part of the experiments in the membrane concentration of the separate was carried out at the Mutnovskoye field of steam-hydrotherm: at sites of existing stations – Mutnovskaya GeoPP (electric power of 50 MW) and Verkhne-Mutnovskaya GeoPP (electric power of 12 MW).

Productive wells of geothermal power plants take out to the surface the heat carrier in the form of vapor-water mixture (VWM) with the mass vapor content of 0.2 - 0.3. In the manifold, wherein takes place mixing of heat-carrier flows of different wells. In separators of the first and second lines at the pressure of 0.8 MPa and the temperature of 170.4 °C, VWM is divided into the vapor phase, which is fed to turbines and the liquid phase (separate). The separate enters the expander tank, wherein the pressure is about 0.4 MPa, and the temperature is about 143.6 °C.

From the separator at the pressure of 0.4 MPa it is pumped through two reinjection wells back into rocks of the hydrothermal deposit. There are restrictions on reducing the temperature of the water pumped into wells after separators and expander tanks, because of the risk of formation of solid deposits in the heat engineering equipment, pipes and wells of the separate injecting. The total content of SiO<sub>2</sub> in the separate is 650-820 mg/kg. To extract silica, the separate through the intermediate expander tank with the pressure of 0.1 MPa is fed into heat exchangers, wherein the temperature is brought up to 20-70 °C, then transferred into a tank for aging and growth of SiO<sub>2</sub> particles.

Concentrated aqueous silica sols were obtained from the liquid phase of hydrothermal heat carriers (separate) in wells of the Mutnovsky geothermal power stations (GeoPP). The division (separation) of the liquid phase from the vapor phase of the two-phase flow was carried out in separators of the geothermal power plant. Concentrations of the main compounds in the combined separate of the Mutnovsky GeoPP wells are shown in Table 1. The total content of silica (the sum of contents of colloidal silica and dissolved silicic acid) in separates of the Mutnovsky GeoPP productive wells is C<sub>i</sub> = 400-800 mg/kg.

Table 1. The concentration of main components of the initial hydrothermal solution (the separate of productive wells of MutnovskyGeoPP).

Component	Na <sup>+</sup>	K <sup>+</sup>	Li <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Fe <sup>2+</sup> , Fe <sup>3+</sup>	Al <sup>3+</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub> <sup>2-</sup>	H <sub>3</sub> BO <sub>3</sub>	SiO <sub>2</sub>
Concentration, mg/dm <sup>3</sup>	282	48.1	1.5	2.8	4.7	<0.1	<0.1	251.8	220.9	45.2	61.8	91.8	780

In order to accumulate significant amounts of sols, the ultrafiltration was used in most cases, or a combination of ultrafiltration and microfiltration. The scheme of the baromembrane installation for concentrating nanosilica in the hydrothermal solution included tanks with the initial medium and for the accumulation of the concentrate and the filtrate, shut-off and regulating valves, water flow meters, manometers and filter cartridges.

On the site of the geothermal power plant, the enlarged baromembrane module with ultrafiltration membranes with the productivity by SiO<sub>2</sub> - from 3.0-33.3 kg/day (100 to 1,000 kg/month) was installed and tested. Aquaflex HP SXL55 ultrafiltration cartridges (the internal diameter of capillaries of 0.8 mm, the filter surface area made of the hydrophilic membrane based on a mixture of polyvinylpyrrolidone and polyether sulfone, 55 m<sup>2</sup>/piece, the nominal pore diameter of 20 nm, the parameter of the minimum mass weight cut of particles MWCO = 50 kDa, the length of the filter cartridge of 1,537 mm, the body diameter of 220 mm) operated as a part of the enlarged installation.

Thus, with the help of the ultrafiltration it is possible to obtain the concentrate with a high SiO<sub>2</sub> content and a low concentration of impurity ions - Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2,3+</sup>, Al<sup>3+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>. The ultrafiltration has advantages over other membrane processes in obtaining stable concentrated high-purity aqueous sols on the basis of the hydrothermal solution: SiO<sub>2</sub> particles are retained by the membrane layer, while impurity ions pass through membrane pores. As a consequence, the salt content and the relative electrical conductivity in sols, concentrated with ultrafiltration membranes, increased insignificantly as compared to the SiO<sub>2</sub> content.

The installation for cryochemical vacuum sublimation UVS-2L included nozzles for dispersion of sols, vessels with the liquid nitrogen, the sublimation chamber with troughs having heating, desublimator, vacuum pump, thermocouple pressure transducer, vacuum meter, electronic thermometer, automated control.

Table 2. Physical and chemical characteristics of aqueous silica sols, obtained by the ultrafiltration membrane concentration.

Characteristics	Values
pH	8.0-9.2
total SiO <sub>2</sub> content, g/dm <sup>3</sup>	3.0-600.0
sol density $\rho$ , g/dm <sup>3</sup>	1001-1325
nanoparticles mean diameters, nm	5-100
salinity TDS, mg/dm <sup>3</sup>	800-2,000
specific electrical conductivity, mS/cm (20°C)	0.8-1.56
average Zeta-potential of nanoparticle surface, mV	25.0...-56.0
dynamic viscosity $\eta$ , mPa·s (20°C)	1.0-120.0
SiO <sub>2</sub> content in the material, precipitated from sol, wt.%	up to 99.72

To obtain nanopowders, silica sols were dispersed before sublimation in the vacuum chamber, droplets were solidified in the liquid nitrogen at the temperature of 77 K and cryogranules were obtained. Technological parameters of the vacuum sublimation were ascertained: time dependences of pressure and temperature in different parts of the vacuum chamber.

During cryogranulation, the size of sol droplets was 30-100  $\mu\text{m}$ , the cooling rate of droplets was 125 K/s, the crystallization rate was 0.26 mm/s. The vacuum sublimation was carried out at the pressure of 0.02-0.05 mm Hg and the temperature range from -80 up to + 25 °C. Such parameters provided the absence of coalescence of particles: particle sizes in powders did not exceed the particle sizes in sols. The capacity of the UVS-2L installation at the power of 3-5 kWt was 0.15-0.20 l/h. Dispersion of solutions on individual drops is used to create developed interphase surfaces, which ensure the high intensity of heat and mass transfer processes, accompanying technological phases of cryocrystallization and sublimation.

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

Silica colloidal particles images in the sols were obtained on a scanning electron microscope JEM-100CX (JEOL, Japan) under the magnification factors from 10000 up to 500000. Particles images of silica powder obtained on a scanning electron microscope under a magnification factor in sequence in 25000, 50000, 100000 and 250000 times are presented on fig. 1.

a)

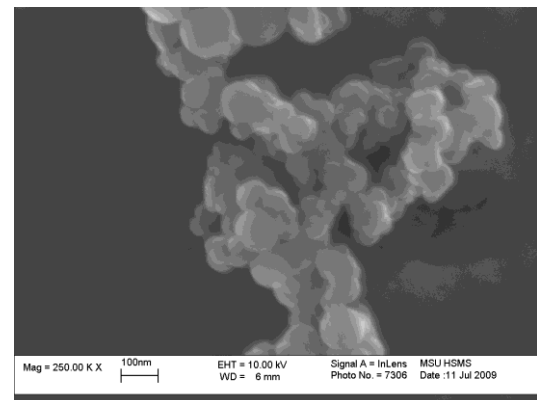
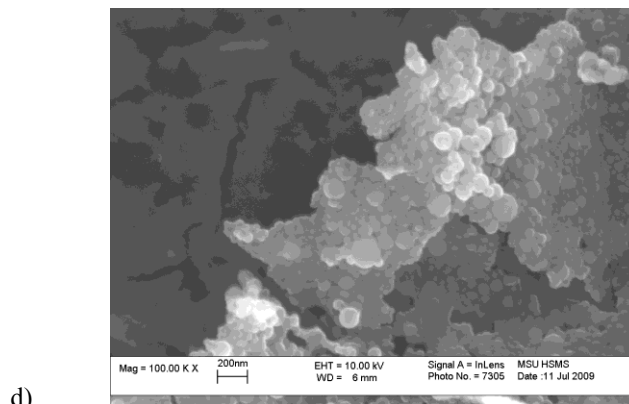
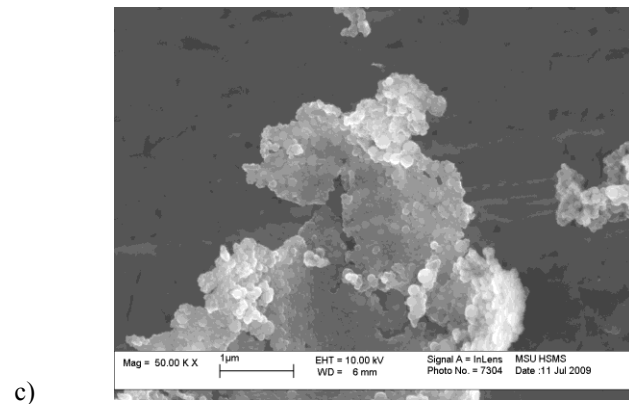
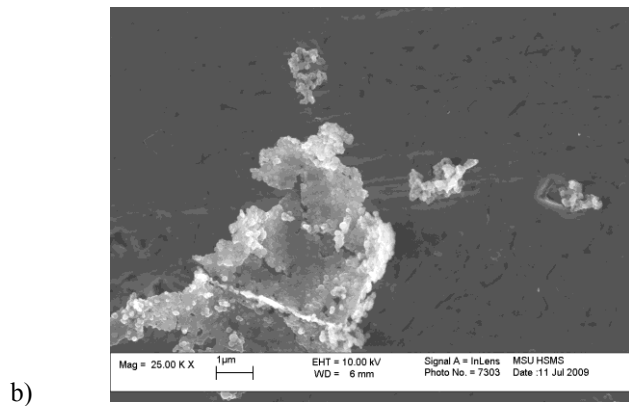


Figure 1: Silica powder pictures obtained on the scanning electron microscope. Magnification was in: a) 10000; b) 50000; c) 100000; d) 250000 times.

The developed technological mode provides obtaining of powders, having the specific surface area of up to  $500 \text{ m}^2/\text{g}$ , pores volume – 0.20 up to  $0.30 \text{ cm}^3/\text{g}$ , average pore diameter of the powder – 2 up to 15 nm, average particle diameters – 5 up to 100 nm, the density of the surface silanol groups – up to  $4.9 \text{ nm}^{-2}$ , the residual moisture – up to 0.2 wt.%, and the bulk density –  $0.035\text{-}0.30 \text{ kg}/\text{dm}^3$ .

### 3. EXPERIMENTS ON USING OF SILICA FOR CONCRETE COMPRESSIVE STRENGTH RISING.

Characteristics of the silica sol used in experiments are shown in table 3. As a binder used South Korean Portland cement (PC) of 42,5 R class, corresponding to the Russian standards for ordinary Portland cement. Physico-mechanical characteristics (brand, residue on sieve No.008, setting time, compressive strength) are within the requirements of the standard for rapid hardening Portland cement PC 500-D0, class 42,5 B.

Table 3. Characteristics of sol used for rising concrete strength.

Appearance		Opalescent liquid
Density, $\text{g}/\text{dm}^3$		1072
Content of $\text{SiO}_2$ , $\text{g}/\text{dm}^3$		115
pH		9.1
Material composition		Amorphous silica
Chemical composition, mass %	$\text{SiO}_2$	94
	CaO	0.9
	$\text{Na}_2\text{O}$	0,13
	$\text{Al}_2\text{O}_3$	0,5
	Loss on ignition	4.2
Content of the aqueous solution, $\text{g}/\text{dm}^3$		957

As fillers were used diorite rubble of fraction from 5 to 20 mm according to GOST 8267 (bulk density of  $1300 \text{ kg}/\text{m}^3$ , true density of  $2,73 \text{ g}/\text{cm}^3$ ) and quartz- feldspar sand in a mixture with standard quartz monofunctional sand.

Additive was polycarboxylate (PCX) superplasticizer with high efficient water-reducing ability, the density of the aqueous solution of  $1082 \text{ g}/\text{dm}^3$  and the dry matter content of 412 mg/g.

The effectiveness of silica sol additive was determined by the strength of concretes with water/cement ratio  $\text{WCR}=0.61\text{-}0.71$ , slump of standard cone  $\text{CS}=12\text{-}19 \text{ cm}$ , content of  $\text{SiO}_2 = 2.0 \text{ mass \%}$  of the weight of cement and content of additives  $\text{PCX} = 2.2\text{-}2.6\%$  of cement mass.

Material consumption,  $\text{kg}/\text{m}^3$  was following: cement (PC 550) -  $345\pm 5$ ; quartz-feldspar sand - 400; standard quartz sand - 400; diorite rubble - 1060.

The mobility of the concrete was controlled by means of an appropriate dosage of PCX.

Technological and structural parameters of quality of mixes and concrete were determined according to the methods of the following standards: compressive strength of concrete at the age of 1 day, 2 days and 28 days of normal storage and after heat- moisture treatment (HMT).

Despite the higher value of WCR, the strength of the composition with the addition of silica sol is significantly higher than the strength of the control composition with a smaller WCR.

The addition of sol in conjunction with the PCX significantly increases the strength of concrete in all periods and in all modes of hardening. For example, the effectiveness of strength after 28 days of hardening was 37-40% compared to

Potapov et al.

compounds without additives, while in the initial stages of hardening (1 day) this indicator reaches 90-128 %. It can be associated with presumably very high pozzolanic activity of silica sol in the cement, probably many times higher than the activity of microsilica sol. Thus, the additive of silica sol at the dosage of 2% by weight of cement in combination with PCX for concretes can be used for: the hardening accelerator; additive that increases durability.

## 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<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+, 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. Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest SiO<sub>2</sub> content.

One of the tendencies of silica sols use is their application as modifiers to improve the characteristics of building materials: concrete, binding material (cement, gypsum, lime), glass, potting compounds, heat-insulating materials, etc.

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