PROCEEDINGS, 41st Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 22-24, 2016
SGP-TR-209

Research of Silica Extracted from Hydrothermal Solution

Vadim V. Potapov, Denis S. Gorev, Elena V. Shunina, Svetlana V. Zubaha

Research Geotechnological Center, Far East Branch of Russian Academy of Science

Petropavlovsk-Kamchatsky, Russia, 683002, Severo-Vostochnoe shosse, 30, e-mail: vadim_p@inbox.ru

Keywords: hydrothermal solution, silica, silica sols and powders, membrane concentration, silica utilization, concrete compressive strength rising

ABSTRACT

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 were obtained. Three types of membrane processes were cheked: microfiltration, ultrafiltration, reverse osmosis. Temperature of solution varied from 20 to 90 ^{0}C. Selectivity of membrane layers with respect to colloidal silica particles and molecules of orthosilicic acid was determined in the experiments. Silica sols with SiO_2 content up to 940 g/dm^3 (62.25 mass %) and particles diameters of 5-100 nm were obtained by the ultrafiltration. We determined silica particles sizes, surface square and concentration of impurities. Utilisation of silica sols produced from hydrothermal solutions for concrete compressive strength have been investigated.

1. INTRODUCTION

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

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

$$\begin{array}{ccccc} \mathrm{OH} & & \mathrm{OH} & & \mathrm{OH}\quad\mathrm{OH} \\ | & & | & & |\qquad | \\ \mathrm{OH\text{-}Si\text{-}OH} & + & \mathrm{OH\text{-}Si\text{-}OH} & \rightarrow & \mathrm{OH\text{-}Si\text{-}O\text{-}Si\text{-}OH} + H_2O \\ | & & | & & |\qquad | \\ \mathrm{OH} & & \mathrm{OH} & & \mathrm{OH}\quad\mathrm{OH} \end{array} \quad (1)$$

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

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

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

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

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

2.EXPERIMENTS ON MEMBRANE CONCENTRATION

After the completion of OSA polycondensation of hydrothermal solutions and formation of silica colloidal particles of given sizes the water removal was made by membrane filtration with a two-stage scheme discrybed in (Potapov V.V. et al., 2008; Generalov M.B., 2006; Brazhnikov S.M., Generalov M.B., Trutnev N.S., 2004; Generalov M.B., Trutnev N.S., 2006; Onopko K.D., Platov I.V., Trutnev N.S., 2008).

Under ultrafiltration silica colloidal particles were stopped by the membrane layer and water molecules and ions of dissolved salts passed through this layer. Thus, the electrolytes content reduces as silica was concentrated, it provided sols stability. Colloidal particles were concentrated in aqueous medium, at the same time SiO_2 content increased up to 10-62.2 mass %, and water content reduced up to 90-37.5 mass %.

The possibility of use of the main membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis for concentration of hydrothermal solutions were studied. The experiments with membranes showed the ultrafiltration advantage for the obtaining of stable concentrated silica sols. When nanofiltration and reverse osmosis were used both silica concentration and mean ions content increased, and the obtained sols were unstable. Microfiltrational membranes have a low selectivity on silica colloidal particles and they can't be effective during the initial concentration stages under a low SiO_2 content. So ultrafiltration or ultrafiltration with microfiltration were used to store a considerable sols volume. Ultrafiltration was used first, then during the later stages microfiltration was used. The ultrafiltration membranes of capillary type were used, the material of membrane layer was made of polyethersulfone and polyacrylonitrile. The diameters of the membrane layer pores were within the range of 2-100 nm. Ceramic microfiltration membranes were of tube type, mean pores size was 70 nm (0,07 micron). The concentration was made in three stages: SiO_2 content from 3 up to 10 g/dm^3 was obtained during the first stage, during the second stage it was 10-30 g/dm^3, during the third stage - 100-940 g/dm^3 (10.0-62.25 mass %). During the first stage the filters of a large standard size were used, during the second stage – the filters of a mean standard size, during the third stage – the filters of a small standard size. The sols density was in the range of 999-1510 g/dm^3, the dynamic viscosity was 1-150 mPa·s, diameters of silica particles were 5-100 nm, the particles zeta-potential was from -25,0 up to - 56,0 mV.

Electric power consumption E_m to obtain mass unit of silica consists of power consumption for pumps drive of membrane unit for sol concentration Power consumption for sol membrane concentration depends on selectivity of ultrafiltration membranes and process temperature. Power consumption for ultrafiltration membrane concentration was 0.18 - 1.0 kW·h/kg.

3. THE MEASURING OF COLLOIDAL SILICA PARTICLES SIZES

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

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

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

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

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

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

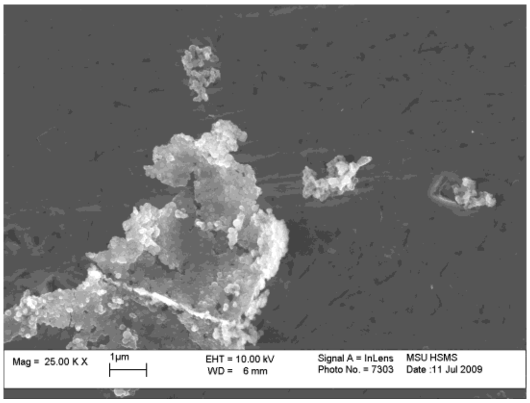
where k_B is the Boltzmann's constant; T is an absolute temperature; μ is the dynamic medium viscosity where the particles of radius R are suspended.

The results of measurement of the sizes and zeta-potential of silica colloidal particles were the follows: diameters of silica particles were 5-100 nm, the particles zeta-potential was from -25,0 up to - 56,0 mV.

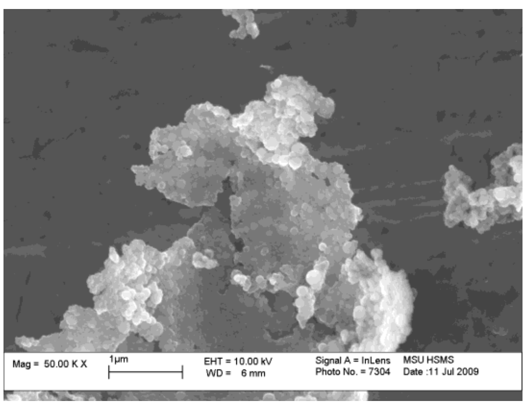
The method of scanning electron microscopy was also used to measure the size, form, structure of particles in the sols. Sols samples were prepared for electron microscopy by cryochemical vacuum-sublimation drying.

Silica colloidal particles images in the sols were obtained on a scanning electon microscope JEM-100CX (JEOL, Japan) under the magnification factors from 10000 up to 500000. 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. 1.

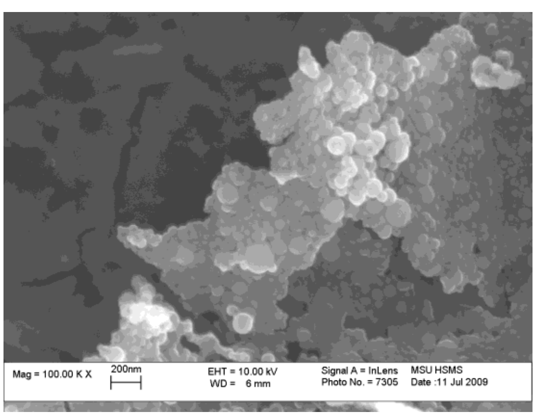
a)



b)



c)



d)

e)

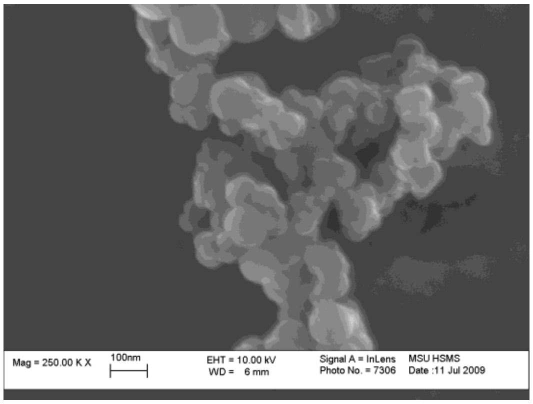


Figure 1: Silica powder pictures obtained on the scanning electron microscope. Magnification was in: a) 10000; b) 50000; c) 100000; d) 250000 times.

4. EXPERIMENTS ON USING OF SILICA FOR CONCRETE COMPRESSIVE STRENGTH RISING

The aqueous medium containing orthosilicic acid H_4SiO_4 in concentration range of 600-800 mg/dm^3, was guided from the separators of geothermal power plant in reinforced concrete tank (cooler), where at a temperature 63°C occur a polycondensation of H_4SiO_4 with the formation of the silica particles. After cooling the separat was filed in baromembrane installation for concentration and to obtain a stable aqueous silica sol. Initial separat had the following characteristics: salinity - 702 mg/dm^3; pH = 9,73; the total content of SiO_2 C_t = 716 mg/dm^3;

Table 2. Characteristics of sol.

Appearance		Opalescent liquid
Density, g/dm^3		1072
Content of SiO_2, g/dm^3		115
pH		9,1
Material composition		Amorphous silica
Chemical composition, mass %	SiO_2	94
	CaO	0,9
	Na_2O	0,13
	Al_2O_3	0,5
	Loss on ignition	4,2
Content of the aqueous solution, g/dm^3		957

Characteristics of the silica sol are shown in table 2. The pressure difference across the membrane layer was 0.14 MPa, flow rate of solution passing through the membrane installation - 1.2 m^3/h. At the first stage of concentration was obtained silica sol with a density of 1015-1022 g/dm^3, C = 28-40 g/dm^3. In the second stage the density of sol increased to 1070 g/dm^3, and a - up to 115 g/dm^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.

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

Additive was polycarboxylate (PCX) superplasticizer with high efficient water-reducing ability, the density of the aqueous solution of 1082 g/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 WCR=0.61-0.71, slump of standard cone CS=12-19 cm, content of SiO_2 = 2.0 mass % of the weight of cement and content of additives PCX = 2.2-2.6% of cement mass.

Material consumption, kg/m^3 was following: cement (PC 550) - 345±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 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. Other important conclusions:

Thus, the additive of silica sol at the dosage of 2% by weight of cement in combination with PCX for concretescan 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_2 concentration and low concentration of impurity ions – Na^+, K^+, Ca^{2+}, Mg^{2+}, $Fe^{2+, 3+}$, Al^{3+}, SO_4^{2-}, Cl^- . Thus, ultrafiltration has got the advantages before other membrane processes when the problem of obtaining of silica concentrated water sols is solved. Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules. Ultrafiltration provides with a low content of impurities and stability of silica water sols up to the highest SiO_2 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.

REFERENCES

Potapov V.V., Allakhverdov G.R., Serdan A.A., Min G.M., Kashutina I.A. (2008), "Obtaining of silica water sols by membrane concentration of the hydrothermal solutions", *Chemical technology*, № 6, pp. 14-22.

Generalov M.B. (2006) Cryochemical technology, 325 p.

Brazhnikov S.M., Generalov M.B., Trutnev N.S. (2004), "Vacuum-sublimate method of the obtaining of ultradispersed powders of inorganic salts" *Chemical engineering,* № 12. pp. 12-15.

Generalov M.B., Trutnev N.S. (2006) "Freezing of the drops of salts solutions in cryogenic granulators" *Chemical engineering*. № 1. pp. 13-16.

Onopko K.D., Platov I.V., Trutnev N.S. (2008) "Heat exchange during nitrogen film boiling on the surface of the solution drops", *Chemical engineering*, № 3. pp. 19-21.