EXPERIMENTS ON SILICATES AND GELS PRODUCTION WITH USING OF SILICA EXTRACTED FROM HYDROTHERMAL SOLUTION

[1]Kashpura V.N., [2]Potapov V.V., [2]Turina N.N., [2]Zubaha S.V , [2]Gorbach V.A.,

[1]Kamchatka State Technical University, 683003, Petropavlovsk-Kamchatsky, Russia, Kluchevskaya street, 35
[2]Research Geotechnological Center, Far East Branch of Russian Academy of Sciences (RGC FEB RAS), Petropavlovsk-Kamchatsky, Russia, 683003, Severo-Vostochnoe shosse, 30, P.O. Box 56,

ABSTRACT

Experiments on production of water polysilicates and gels with using colloidal silica extracted from hydrothermal solution were carried out. Silica was concentrated by reverse osmosis to content SiO_2 5-27 g/liter. Than alkali NaOH was added for rising pH to 12.5, colloidal silica dissolution and production of polysilicate. After developing of reaction with silicate production HCl was added for solution neutralisation to pH 7-8 and gel formation. The physical and chemical characteristics of gels producted on the base of geothermal silica were investigated.

INTRODUCTION

Colloidal silica formed in hydrothermal solution in several stages (Weres 0., Yee A., Tsao L., 1980, 1981; Potapov V.V., 2003). Primarily silicium enters the solution as molecules of silicic acids as the result of chemical interaction of water with alumosilicate 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^{0}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^{0}C, when solution has a contact with rock minerals, total content of silicium C_t in water can be evaluated by α-quartz solubility 3. (Crerar D.A., Anderson G.M., 1971):

$$\lg(C_t/60)=-1.468+252.9/T-3.217\cdot10^5/T^2, \quad (1)$$

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 (Marshall W.L., 1980):

$$\lg (C_e/60) = -0.1185 - 1.126\cdot10^3/T + 2.3305\cdot10^5/T^2 - 3.6784\cdot10^7/T^3, \quad (2)$$

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 siilica) 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 (Iler R., 1982):

$$H_4SiO_4 + H_4SiO_4 \rightarrow H_6Si_2O(OH)_6 + H_2O \quad (3)$$

$$Si_mO_{(m-1)}(OH)_{(2m+2)} + Si_nO_{(n-1)}(OH)_{(2n+2)} \rightarrow Si_{(m+n)}O_{(m+n-1)}OH_{(2n+2m+2)} + H_2O \quad (4)$$

There is a problem of working out technology of silica extraction and increasing the effectiveness of using hydrothermal heat-carrier of the geothermal heat electric power stations. 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.

MODELING STUDY OF NUCLEATION OF SILICIC ACID MOLECULES

As follows from the model, worked out by Weres, Yee and Tsao (1980, 1981) on the basis of classical conceptions on nucleation, oversaturation $S_N(T)$, equal C_s/C_e, and pH are basic factors determining rate of silicic acid nucleation I_N in water solution:

$I_N=Q_{LP}\cdot Z\cdot(R_{md}\cdot A_{cr}\cdot N_A\cdot M_{Si}^{-1})\cdot\exp(-\Delta F_{cr}/k_B\cdot T)$ (5)

where ΔF_{cr} – is a change in free energy, connected with the formation of critical radius nucleus R_{cr}, $R_{cr} = 2\cdot\sigma_{sw}\cdot M_{Si}/(\rho\cdot N_A\cdot k_B\cdot T\cdot \ln S_N)$, A_{cr} – surface area of critical nucleus, $A_{cr} = 4\cdot\pi\cdot R_{cr}^2$, $\Delta F_{cr} = \sigma_{sw}\cdot A_{cr}/3 = (16\cdot\pi/3)\cdot\sigma_{sw}^3(M_{SI}/\rho\cdot N_A\cdot k_B\cdot T\cdot \ln S_N)^2$, σ_{sw} – coefficient of surface tension at the boundary silica-water, R_{md} – rate of molecular deposition of SiO_2 on the solid surface, г·(см^2·min)$^{-1}$, k_B – Boltzmann's constant, M_{Si} – molecular mass SiO_2, N_A – Avogadro number, Q_{LP} – Loze-Paunde's factor, $Q_{LP} = 3.34\cdot10^{25}$ kg^{-1}, Z – Zeldovich's factor, $Z = [-(\partial^2\Delta F_{cr}/\partial n_{cr}^2)/(2\cdot\pi\cdot k\cdot T)]^{0,5} = (2/3)\cdot[3\cdot M_{Si}/(4\cdot\pi\cdot\rho\cdot N_A\cdot n_{cr}^2)]^{1/3}\cdot(\sigma_{sw}/k\cdot T)^{0,5}$, n_{cr} – quantity of molecules SiO_2 in nucleus of critical size, $n_{cr} = (4\cdot\pi/3)\cdot(\rho\cdot N_A/M_{Si})\cdot R_{cr}^3$. Dependence of functions R_{md} and σ_{sw} upon temperature and pH of the solution in the model is expressed by the equations presented in work of Weres 0., Yee A., Tsao L., 1980, 1981.

Equation (5) express maximum rate of nucleation I_N for particles having radius, which is somewhat higher than the critical one, and amount of molecules SiO_2, equal $N=N_{CR} + 0.5/Z$. Time dependence $I_N(T)$ looks as follows (Weres 0., Yee A., Tsao L., 1980, 1981):

$I_N(t) = I_N\cdot(1-e^{-t/\tau in})$, (6)

where τ_{in} – time of the induction required for the growth and formation of the stable population of particles having sizes close to the critical one: $\tau_{in}=1.08\cdot10^{-6}\cdot(6\cdot R_{md})^{-1}\cdot(Q_{LP}\cdot Z\cdot R_{cr}^2\cdot\exp(-\Delta F_{cr}/k_B\cdot T))^{-0,25}$

Calculations by equations (1), (5),(6) show that critical radius R_{cr} increases while the temperature rises because of lowering in oversaturation. As a result there is a tendency for decreasing the rate of nucleation I_N and increasing time of the induction τ_{in}. This leads to the decrease in concentration of the particles N_p and growth of the finite average radius of the particles R_f. Real time when hydrothermal solution is in wells and surface heat equipment of the geothermal electric power stations is not enough for the process of nucleation development at the temperature of 120-150^0 C . So, for solution having pH = 8.7, pH_{nom} = 7.86, C_t = 700 mg/kg, at 20^{0}C S_N = 5.952, $\sigma_{sw} = 24.46\cdot10^{-3}$ J/m^2, R_{cr} = 0.30 nm, τ_{in} = 2.66 min, $I_N = 2.00\cdot10^{21}$ nuclei/kg·s, R_f = 0.44 nm, $N_p = 5.76\cdot10^{15}$ cm^{-3}; at 100^{0}C - S_N = 1.726, $\sigma_{sw} = 13.84\cdot10^{-3}$ J/m^2, R_{cr} = 0.44 nm, τ_{in} = 0.69 min, $I_N = 6.40\cdot10^{21}$ nuclei/kg·s, R_f = 0.65 nm, $N_p = 1.25\cdot10^{15}$ cm^{-3}; at 153^{0}C - S_N = 1.046, $\sigma_{sw} = 6.91\cdot10^{-3}$ J/m^2, R_{cr} = 2.34 nm, τ_{in} = 3966.8 min, $I_N = 6.72\cdot10^9$ nuclei/kg·s, R_f = 7.00 nm, $N_p = 5.20\cdot10^9$ cm^{-3}. Decrease of pH leads to the growth of surface tension and lowering of the deposits growth rate. Therefore, at low pH values critical radius significantly increases, rate of nucleation lowers and time of the induction becomes large: at 20^{0}C and pH = 7.0 $\sigma_{sw} = 46.79\cdot10^{-3}$ J/m^2, R_{cr} = 0.58 nm, τ_{in} = 368.3 min, $I_N = 3.99\cdot10^{14}$ nuclei/kg·s, R_f = 0.89 nm; at pH = 6.0 $\sigma_{sw} = 48.96\cdot10^{-3}$ J/m^2, R_{cr} = 0.61 nm, τ_{in} = 3967.2 min, $I_N = 6.05\cdot10^{12}$ nuclei/kg·s, R_f = 1.20 nm; at pH = 5.0 $\sigma_{sw} = 49.27\cdot10^{-3}$ J/m^2, R_{cr} = 0.61 nm, τ_{in} = 39162.0 min, $I_N = 4.67\cdot10^{11}$ nuclei/kg·s, R_f = 1.26 nm. In common case the rate of the processes of nucleation and particle growth, finite size of the particles and their concentration depend upon temperature, pH of the solution and sizes and quantity of nuclei which were present in solution prior to the initiation of nucleation.

KINETICS OF POLYMERIZATION OF SILICIC ACID

Kinetics of colloidal silica polymerization reaction was studied at 20^{0}C and pH from 5.0 to 9.4. All the curves of oversaturation $S_m(t_p) = C_s - C_e$ obtained from the series of measurements at 20^{0}C and natural pH from 8.0 to 9.4 had the same form with concavity and were characterized by close values of the derivative dS_m/dt_p.

The function S_m follows the differential equation (Fleming B.A.б 1986):

$dS_m/dt_p = -k_p\cdot S_m^{np}$, (7)

where k_p – is a constant of polymerization reaction rate which depends upon temperature, pH, ionic strength of the solution, n_p – order of polymerization reaction. Dependence $\ln S_m(t_p)$ in the time period t_p from 0 to 6 h was close to linear, which pointed to exponential character of the function $S_m(t_p)$ at $n_p = 1$:

$\ln S_m(t_p) = \ln S_0 - t_p/\tau_p$, (8)

$S_m(t_p) = S_0\cdot\exp(-t_p/\tau_p)$, (9)

where τ_p – characteristic time of the polymerization reaction, $\tau_p = 1/k_p$.

Experimental dependence $\ln S_m(t_p)$ was approximated by equation (8), based on which constants τ_p и k_p were found. At 20^{0}C and pH = 8.0-9.4 average value of τ_p was 2.04 h, k_p = 0.485 h^{-1}. According to Fleming's model

polymerization reaction is the first order reaction regarding both the difference (C_s - C_e), and surface concentration C_{SiO} of ionized hydroxyl groups SiO^-, that is the surface charge σ_s of colloid particles (Fleming B.A.б 1986):

$dC_s/dt_p = -k_f \cdot A_s \cdot (C_s - C_e) \cdot C_{SiO}$, (10)

where A_s – is a specific surface area of the particles. Rate constant k_f depends upon the absolute temperature T and ionic strength of the solution I_s (Fleming B.A., 1986).

Calculations by equations (7)-(10) showed the following values of constants k_p and τ_p at increased temperatures: at 50^0C - τ_p = 36.01 min; 75^0C - τ_p = 20.91 min; 100^0C - k_p = 7.221 h^{-1}, τ_p = 0.138 h = 8.3 min. At pH = 7.0 dependence $S_m(t_p)$ considerably changed, at t_p from 0 to 6 h curve $S_m(t_p)$ convex derivative dS_m/dt_p went noticeably lower than in the solution with pH = 8.9-9.4: silicic acid concentration started to reduce actively at t_p = 3.0 h. At pH = 5.0 inhibition of polymerization reaction was observed, and considerable changes in concentration C_s occurred only in 5-7 days after reaction has started.

DEVELOPMENT OF METHODS OF UTILIZATION OF SILICA PRECIPITATED FROM THE HYDROTHERMAL SOLUTION IN INDUSTRY

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

We worked out an utilization method of silica precipitation by freezing out dispersed hydrothermal solution for making sorbent wich 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.

Material precipitated by freezing out after drying turned into dispersive powder, surface of which was modified using silicic organic modificators in such a way, that to change coefficient of surface tension of water on the boundary with silica and add hydrophobic properties to the surface. At the same time coefficient of surface tension of organic liquids on the boundary with silica after modification provided moistening of silica surface and absorption of liquid by powder. One of the oil products (petrol, diesel fuel, etc.), or mixture of several oil products with any ratios of mixing can be tested as organic liquid. Modified silica can be used to eliminate consequences of oil products spilling to the natural reservoirs, including extraction of undissolved filmy formations on the water surface. To remove dissolved oil products, volume of water is filtered through the layer of modified sorbent. Amount of sorbent required for removing oil products from the given volume of polluted water is determined from the condition of saturation of modified silica with organic liquid in accordance with the capacity of sorbent to absorb this liquid.

Experiments were done on extraction of oil products from water using silica precipitated by freezing out of dispersed hydrothermal solution. Silica was modified according to the method presented in the work Il'inskii V.V., Komarova T.I., Koronelli T.V., Lisichkin G.V., Serdan A.A. (1998). At the first stage silica was dried in toluene. Dry distilled morpholine and then modificator gexadethildimethylchlorsilan $C_{16}H_{33}Si(CH_3)_2Cl$ were added to SiO_2 dried at the first stage. Mixture was boiled during 8 hours. Then mixture was washed in the following order: 1) with toluene in filtering vessels twice; 2) with acetone (or isopropanol); 3) with mixture acetone-water-acetic acid with the ratio 2:1:1 according to the volume twice; 4) with mixture acetone-water with the ratio 1:2 three times; 5) with acetone twice. Mixture was dried to powder state, when drying temperature was slowly increased from 70°C up to 120°C.

After modification experiments were done on silica use for purification of distilled water from impurity of petrol A-76 with density 0.758 g/cm^3 and diesel fuel with density 0.817 g/cm^3. Amount of oil product added to the water before purification was from 4 to 20 ml/l. Consumption of sorbent to remove undissolved oil products was 100 g/(195 - 211)g of petrol and diesel fuel. During the experiments on removal of dissolved oil products volume of distilled water was filled up with diesel fuel up to the concentration 10 microliters/l (less than 1 weight part per 100000). Then, volume of polluted water was filtered through the layer of sorbent modified by the indicated method. Residual total concentration of oil products in the filtered water was 0.19 microliters/l = 0.16 mg/l, that is 98 % of oil products dissolved in water was removed.

Utilization silica in gas chromatography

Experiments were done on using silica precipitated by freezing out the 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 m^2/g, average pore diameter – 40.0 – 50.0 nm, specific pore volume – 1.3 cm^3/g. Both columns had the same preparation and worked simultaneously. The length of columns was 1.8 m, inner diameter – 2.0 m, 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 1. 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 1 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 geothermal 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 geothermal silica surface in comparison with silochrome C-80.

Addition of silica to cement for increasing of concreat strength

Experiments were done on studying the influence of small silica addition to cement on strength of the concrete product made on the basis of cement. Silica was added to portland cement of the allitic type. Tests were carried out according to the following method. Slurry of normal thickness was prepared from 200 g of cement. It was laid with rodding in two metal forms, each of them had six cells to make bricks with the size 20x20x20 mm. Each brick was rodded ten times, then forms were placed on the shaking table. Forms were shaked 25 times and closed with screwing up lids. Then form was placed in the bath with hydraulic back-pressure valve at the temperature 20 ± 2°C. Samples were subjected to compression by the press to determine concrete strength after 7 and 28 days.

Experiments showed, that addition of silica precipitated from the hydrothermal solution to cement leaded to the increase in concrete strength. A method of utilization of silica precipitated by lime addition in order to increase concrete strength was proposed. Precipitation is carried out after ageing of the solution and completion of polymerization and formation of the colloidal silica particles. CaO consumption must be within a range of 100 – 1000 mg/kg. Weight fraction of silica with respect to cement must be within a range from 1 to 6-7 %, water-cement ratio – from 0.25 to 0.38. In other regime the silica precipitated by freezing out the dispersed hydrothermal solution is added to the cement. In this case quantity of silica added to cement must not be more than 5 weight %.

Utilization of silica for liquid glass production

By freezing out the hydrothermal solution 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/nm^2 at 200 ^0C, 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 dispersive silica 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 m^2/g, porosity – up to 1.1 cm^3/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 geothermal 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.

EXPERIMENTS ON SILICA EXTRACTION BY REVERSE OSMOSIS

The experiments on silica extraction by reverse osmosis (RO) were carried out in the laboratory at 20 ^0C and in Mutnovsky GeoPP at 50-80 ^0C. RO plant included cartridge with RO membrane filter, pump RO-900 with the pressure up to 1.0 MPa, device for automatic regulation of flow rate of pumped water, adapter for transformation of electric voltage to constant 24 V, manometer, vessels for hydrothermal solution, filtrate and concentrate. RO membrane made of thin film of composite material was rolled in the cartridge in spiral form. The total surface of membrane was 0.3 m^2, diameters of pores of membrane layer were in the range of 0.001-0.0001 μm = 1.0 - 0.1 nm. Density of membrane surface in the cartridge volume was D_{MS} = 425 m^2/m^3.

At the laboratory experiments carried out at 20 ^0C filtrate rate was 3.5-4.5 liters per hour, concentrate rate – 20 l/h, pressure drop on membrane layer ΔP = 0.45-0.55 MPa. RO membrane penetrability was G = 0.0116-0.0115 m^3/m^2·hour. Membrane selectivity on total silica φ_S was 0.96, membrane selectivity on colloidal silica φ_{CS} – 1.0, selectivity on cations and anions retained by RO membrane - φ_{TDS} = 0.89. The experiments on second stage filtration at 20 ^0C shown that molecules of silicic acid were extracted by RO membrane. RO membrane selectivity on silicic acid was φ_S = 0.78-0.90, fraction of cations and anions - φ_{TDS} = 0.83-0.94. Thus reverse osmosis can be used for extraction of silicic acid molecules when nucleation and polymerisation of silicic acid is not over and silica colloidal particles are not formed.

In the experiments with recirculation of concentrate solutions were received with silica content SiO_2 15600-27300 mg/kg, that is 20-36 times higher than in the initial hydrothermal separate.

During the experiments at Mutnovsky GeoPP the vessel for filtrate was put into the thermos to get a little decline of the filtrate temperature at the second stage of filtration. Two experiments with hot solution were carried out.

At the first experiment the temperature of filtrate on the 1-st stage was 62 ^0C, on the 2-nd - 55 ^0C. Filtrate flow rate was 10.19 l/h, pressure drop ΔP = 0.32-0.34 MPa, RO membrane penetrability G=0.0339 m^3/m^2·hour. Silica content SiO_2 in the initial hydrothermal separate was C_t = 718.75 mg/kg, C_s = 200.0 mg/kg, total dissolved salts TDS= 750 mg/kg. Silica content in the filtrate of the 1-st stage was C_t = 156.25 mg/kg, C_s = 150.0 mg/kg, TDS = 110 mg/kg. Only soluble silicic acid was in filtrate after 1-st stage of filtration, all colloidal silica was retained by RO membrane. Silica content in the filtrate of the 2-st stage was C_t = 50 mg/kg, C_s = 50.0 mg/kg, TDS = 30 mg/kg. Thus the characteristics of RO membrane on the 1-st stage of filtration were: φ_s = 0.782, φ_{TDS} = 0.853. On the 2-nd stage of filtration φ_s = 0.720, φ_{TDS} = 0.727.

Table 2. Chemical composition of filtrates and concentrates obtained by reverse osmosis in the second experiment. HS – initial hydrothermal solution, K1, K2 – concentrates of the 1-st and 2-nd stage of filtration; F1, F2 – filtrates of the 1-st and 2-nd stage of filtration. n.d. – not determined.

Parameters	HS mg/kg	K1 mg/kg 72 ^{0}C	K2 mg/kg 58 ^{0}C	F1 mg/kg 72 ^{0}C	F2 mg/kg 58 ^{0}C
pH	9.33	9.34	9.25	8.61	7.93
Na^+	279.7	362.5	82.9	53.7	20.4
K^+	50.2	94.2	22.9	9.2	3.84
Li^+	n.d.	n.d.	n.d.	n.d.	n.d.
Ca^{2+}	2.0	2.2	<0.4	0.4	<0.4
Mg^{2+}	0.6	1.2	0.36	0.1	0.9
NH_4^+	n.d.	n.d.	n.d.	n.d.	n.d.
Fe^{3+}	<1.0	<1.0	<1.0	<1.0	<1.0
Fe^{2+}	<1.0	<1.0	<1.0	<1.0	<1.0
Al^{3+}	<0.5	<0.5	<0.5	<0.5	<0.5
Cl^-	228.7	310.3	56.0	278.4	4.3
F^-	n.d.	n.d.	n.d.	n.d.	n.d.
SO_4^{2-}	196.9	288.2	28.8	<0.5	2.4
HCO_3^-	59.2	59.2	53.1	87.3	57.4
CO_3^{2-}	42.9	48.6	36.6	7.5	n.d.
SiO_2 (silicic acid)	200.0	208.75	246.9	186.9	59.4
SiO_2 (total silica)	781.25	1000.0	307.8	192.2	60.0
H_3BO_3	95.5	94.4	104.1	97.2	76.1

At the second experiment the temperature of filtrate on the 1-st stage was 72.0-68.8 ^{0}C, on the 2-nd - 58 ^{0}C (Table 2). Filtrate flow rate was 8.18-7.49 l/h, pressure drop ΔP = 0.30-0.34 MPa, RO membrane penetrability G=0.272-0.249 m^3/m^2·hour. Silica content SiO_2 in the initial hydrothermal separate was C_t = 781.25 mg/kg, C_s = 200.0 mg/kg, total dissolved salts TDS= 750 mg/kg. Silica content in the filtrate of the 1-st stage was C_t = 192.2 mg/kg, C_s = 186.9 mg/kg, TDS = 130 mg/kg. Silica content in the filtrate of the 2-st stage was C_t = 60.0 mg/kg, C_s = 59.4 mg/kg, TDS = 30 mg/kg. Thus the characteristics of RO membrane on the 1-st stage of filtration were: φ_s = 0.753, φ_{TDS} = 0.826. On the 2-nd stage of filtration φ_s = 0.687, φ_{TDS} = 0.769.

KINETICS OF WATER SILICATES FORMATION

For water silicates production alkali was added to the silica sol. After alkali added to sol the process of depolymerisation of molecules of polisilicic acids on the surface of silica particles took begun. Parameter m= SiO_2:Na_2O or SiO_2:K_2O was in the range from 6:1 to 1:1. In the Tables 3 a, b, c, d experimental results on kinetics of silica depolymerisation at different values of parameter m are presented. Total SiO_2 content in sol used for the experiments was 15600 mg/kg.

Table 3a. Kinetics of silica depolymerisation. SiO_2:Na_2O = 6:1, pH = 11.24, temperature – 20 ^{0}C. C_s – soluable orthosilicic acid concentration, mg/kg; t_{ps}- time of silica depolymerisation,minutes.

$t_{ps,}$	0	10	120	150	180	240	300	360	420	720
C_s	415	609	625	628	628	671	687	662	659	668

Table 3b. Kinetics of silica depolymerisation. SiO_2:Na_2O = 4:1, pH = 11.89, temperature – 20 ^{0}C. C_s – soluable orthosilicic acid concentration, mg/kg; t_{ps}- time of silica depolymerisation,minutes.

t_{ps}	0	10	20	30	40	50	60	80
C_s	312	392	468	578	743	793	868	993
t_{ps}	102	120	150	180	210	240	300	360
C_s	1093	1181	1231	1231	1237	1237	1237	1237

Table 3c. Kinetics of silica depolymerisation. SiO_2:Na_2O = 2:1, pH = 12.2, temperature – 20 ^{0}C. C_s – soluable orthosilicic acid concentration, mg/kg; t_{ps}- time of silica depolymerisation,minutes.

t_{ps}	0	10	20	30	40	50	60	80	100	120
C_s	376	484	672	753	872	956	1041	1412	1612	1953
t_{ps}	140	160	180	210	240	270	300	360	1320	1380
C_s	2125	2265	2469	2516	2531	2516	2531	2656	2937	3031

Table 3d. Kinetics of silica depolymerisation. SiO_2:Na_2O = 1:1, pH = 12.6, temperature – 20 ^{0}C. C_s – soluable orthosilicic acid concentration, mg/kg; t_{ps}- time of silica depolymerisation,minutes.

$t_{ps,}$	0	10	20	30	40	50	60	80	100
C_s	493	609	671	750	871	937	1028	1325	1575
t_{ps}	120	140	230	260	290	350	410	470	720
C_s	1731	2125	3156	3437	3594	3984	4390	5031	5406

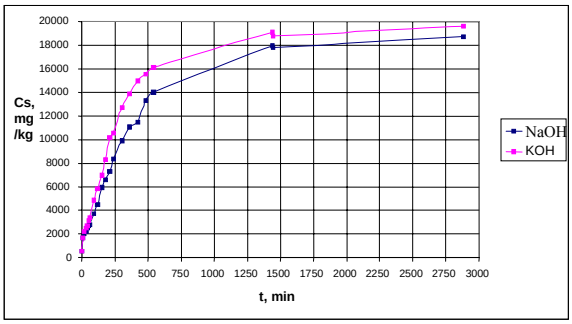

Fig. 1. Kinetics of silica depolymerisation. 1- KOH, 2- NaOH added to silica sol.

On the Fig. 1 experimental results $C_s(t_{ps})$ are shown. Total SiO_2 content in sol used for the experiment was 20000 mg/kg. Two types of alkali was added to sol: Na_2O and K_2O. The value of parameter m was 1.0. As one can see from Fig. 1 the process of silica dissolution went faster in sol in which KOH was added.

KINETICS OF GEL's FORMATION

We investigated the process of gel's formation in two types of solutions: 1. silica soles concentrated by reverse osmosis; 2. water solutions of Na-silicate produced from the silica precipitated from hydrothermal solution.

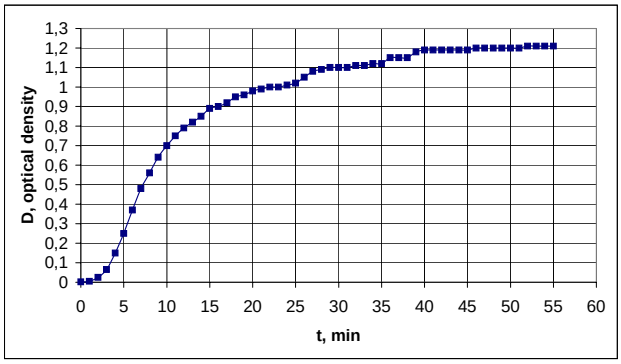

Fig. 2. Optical density D versus time t during of gel's formation. The length of light wave is 540 nm.

On Fig. 2 time dependence of optical density D(t) of Na-silicate solution is presented. SiO_2 content in solution was 52.5 g/l. Gel's formation was begun at pH=10.7 after solution neutralisation by HCl acid.

There was three regions on the curve that corresponded to three stages of the process: 1 – t = 0-3 min; 2 – 3-25 min; 3 – 25-60 min. The most rate of optical density increasing was observed on the 2-nd stage at t=3-25 min.

CONCLUSIONS

1. It was shown, that nucleation and polymerization of silicic acid molecules in hydrothermal solution actively developed at the temperature lower 120-150^{0}C. The order n_p of silicic acid polymerization reaction in hydrothermal solution equaled 1.0. Polymerization rate constants k_p = 0.485 h^{-1} and τ_p = 123.6 min at 20^{0}C were determined, values of these constants at increased temperature were calculated. Radii of colloidal silica particles measured by photon correlation spectroscopy were distributed within 1.0-50.0 nm, average radius R = 7.0-20.0 nm, diffusion coefficients $D = 2.9 \cdot 10^{-7}$ cm^2/s.

2. Experiments showed the possibility of utilization of silica material precipitated from the hydrothermal heat carrier in the following industries: 1. as mineral raw material for production of sorbent for purification of water from oil products; 2. for production of sorbent for gas chromatografy; 3. for addition to portland cement for increasing concreat strength; 4. for liquid glass production; 5. for sols and gels production.

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