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Study of Colloidal Silica Formation and Precipitation in Solution of Mutnovskoe Hydrothermal Field (Kamchatka, Russia)

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ABSTRACT

Physical and chemical processes in hydrothermal solution in which colloidal silica took part were researched. The rate of nucleation of orthosilicic acid molecules H_4SiO_4 were calculated with the help of mathematical model. The order and constant of rate of silicic acid polymerization reaction were determined. The sizes and diffusion coefficients of colloidal silica particles were measured. Mechanism of coagulation and precipitation of colloidal silica particles by metal cations was investigated. In the experiments various types of metal cations were added to the solution: Ca^{2+}, Mg^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+}. Cations were added to the solution with slaked lime, calcium chloride, magnesium sulphate, cobalt sulphate, cupric sulphate, plumbous nitrate, nickel sulphate, aluminium sulphate, aluminium chloride, ferric chloride, sea water. Also cations were added by electrocoagulation on electrodes with soluble metals such as aluminium, ferric and cupric electrodes. The experiments on utilization of precipitated amorphous silica material were conducted. The technological scheme of silica precipitation from the separate of geothermal electric power station was developed.

INTRODUCTION

Colloidal silica formed in hydrothermal solution in several stages (Chukhrov F.V., 1955, Potapov V.V., 2003). Primarily silicium enters the solution as molecules of orthosilicic acid H_4SiO_4 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 (mg/kg) in water can be evaluated by α-quartz solubility (Crerar D.A., Anderson G.M. , 1971) :

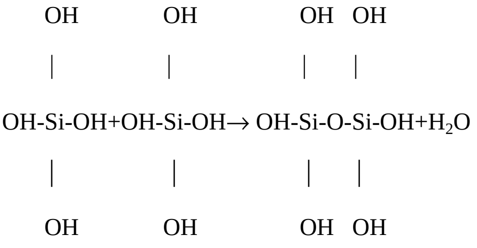
$$\log(C_t/60)= -1.468+252.9/T–3.217\cdot 10^5/T^2 \qquad (1)$$

Equation (1) gives the following values of quartz SiO_2 solubility (mg/kg): 25^{0}C – 3.46, 50^{0}C – 10.29, 100^{0}C – 47.6, 200^{0}C – 256.0, 250^{0}C – 415.6, 300^{0}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_t 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_e. According to the experimental data (Marshall W.L., 1980), value C_e(mg/kg) for pure water depends on absolute temperature T by the following way:

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

At the temperature of 200^{0}C C_e solubility is equal 940.8 mg/kg, at 150^{0}C - 651.8 mg/kg, at 100^{0}C - 405.3 mg/kg, at 25^{0}C - 130.8 mg/kg.

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 (Iler R., 1982):



$$\begin{matrix} OH & & OH & & OH\ \ OH \\ | & & | & & |\ \ \ \ | \\ OH\text{-}Si\text{-}OH & + & OH\text{-}Si\text{-}OH & \rightarrow & OH\text{-}Si\text{-}O\text{-}Si\text{-}OH+H_2O \\ | & & | & & |\ \ \ \ | \\ OH & & OH & & OH\ \ OH \end{matrix} \qquad (3)$$

$$Si_mO_{(m-1)}(OH)_{(2m+2)} + Si_nO_{(n-1)}(OH)_{(2n+2)} \rightarrow$$

$$Si_{(m+n)}O_{(m+n-1)}OH_{(2n+2m+2)} + H_2O \qquad (4)$$

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). 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, cement, concrete, sorbents, catalysts, and in chromatography and electronics also (Harper, R.T., Thain, I.A., Johnston, J.H., 1995; Harper R.T., Johnston J.H., Wiseman N., 1997).

1. MODELING STUDY OF NUCLEATION OF SILICIC ACID MOLECULES

As follows from the model (Weres 0., Yee A., Tsao L., 1980, 1981), worked out by Weres, Yee and Tsao on the basis of classical conceptions on nucleation (Abraham F.F., 1969), 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:

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

where ΔF_{cr} – is a change in free energy, connected with the formation of nucleus of critical radius 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, $g\cdot(cm^2\cdot min)^{-1}$, 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 =

$[-(\partial^2\Delta F_{cr}/\partial n_{cr}^2)/(2\cdot\pi\cdot k\cdot T)]^{0,5} = (2/3)\cdot[3\cdot M_{Si}/(4\cdot\pi\cdot\rho\cdot N_A\cdot n_{cr}^2)]^{1/3}\cdot \cdot(\sigma_{sw}/k\cdot T)^{0,5}$, 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 following equations (Weres 0., Yee A., Tsao L., 1980, 1981):

$$R_{md} = F(pH, pH_{nom})\cdot k_{OH}(T)\cdot f_f(S_a)\cdot(1 - S_N^{-1}) \qquad (6)$$

$$\log k_{OH}(T) = 3.1171 - 4296.6/T \qquad (7)$$

$$f_f = S_a^5,\ S_a < S_t \qquad (8\text{-}1)$$

$$f_f = S_t^5 + 5\cdot S_t^4\cdot(S_a - S_t),\ S_a > S_t, \qquad (8\text{-}2)$$

$$\log S_t = 0.0977 + 75.84/T, \qquad (8\text{-}3)$$

$$F(pH, pH_{nom}) = h_f\cdot f'(pH) + (1 - h_f)\cdot f'(pH_{nom}) \qquad (9\text{-}1)$$

$$f'(pH_{nom}) = f(pH_{nom})/f(7.0), \qquad (9\text{-}2)$$

$$\log f = pH - pK_i + \log [Na^+] \qquad (9\text{-}3)$$

$$\sigma_{sw} = H_\sigma - T\cdot S_\sigma - 2.302\cdot10^{-3}\cdot n_o\cdot k\cdot T\cdot I(pH, pH_{nom}) \qquad (10\text{-}1)$$

$$I = 0{,}119\int_{-\infty}^{pH} F(pH', pH_{nom}(pH'))dpH' \ , \qquad (10\text{-}2)$$

where $S_a = (1-\alpha_i)\cdot S_N$, α_i – fraction of silicic acid in ionized form, $pH_{nom} = pH + \log([Na^+]/0.069)$, $[Na^+]$ – ion activity $[Na^+]$, mol/kg, $pK_i = 6.4$, $f(7.0) = 0.119$, $h_f = 0.45$, H_σ, S_σ - enthalpy and entropy of silica surface in water, $H_\sigma = 63.68\cdot10^{-3}$ J/m^2, $S_\sigma = 0.049\cdot10^{-3}$ J/m$^2\cdot$K, $n_o = 6.84$ nm^{-2}.

Equation (5) expresses 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., 1981; Abraham F.F., 1969):

$$I_N(t) = I_N\cdot(1-e^{-t/\tau_{in}}), \qquad (11)$$

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:

$$\tau_{in} = 1.08\cdot10^{-6}\cdot(6\cdot R_{md})^{-1}\cdot(Q_{LP}\cdot Z\cdot R_{cr}^2\cdot\exp(-\Delta F_{cr}/k_B\cdot T))^{-0,25} \qquad (12)$$

Calculations by equations (1), (5)-(12) 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.

After completion of the polymerization process part of silicium remains as molecules of orthosilicic acid H_4SiO_4 which concentration is close to the solubility C_e in equilibrium with colloidal silica. Small quantity of ions of silicic acids ($H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSiO_3^-$, etc.) and macromolecules of polysilicic acids are present in the solution besides colloidal particles and molecules of silicic acids. As follows from the experimental data obtained by Rothbaum and Rohde (Rothbaum H.P., Rohde A.G., 1979), concentrations of C_{dimer} dimers and Ct_{rimer} trimers of silicic acid are approximated by equations (mole/kg) (Weres 0., Yee A., Tsao L., 1980):

$$\log C_{dimer} = -2.10 - 775/T, \qquad (13\text{-}1\ )$$

$$\log Ct_{rimer} = -3.22 - 919/T, \qquad (13\text{-}2\ )$$

Dependence of the constant of orthosilicic acid ionization of the 1-st - $K_1 = [H^+]\cdot[H_3SiO_4^-]/[H_4SiO_4]$ and 2-nd - $K_2 = [H^+]\cdot[H_2SiO_4^{2-}]/[H_3SiO_4^-]$ stages upon the temperature looks as follows (Arnorsson S., Sigurdsson S., Svavarsson H., 1982) :

$$\log K_1 = -2549/T - 15.36\cdot10^{-6}\cdot T^2, \qquad (14\text{-}1)$$

$$\log K_2 = 5.37 - 3320/T - 20\cdot10^{-3}\cdot T, \qquad (14\text{-}2)$$

Ions of metasilicic acid H_2SiO_3 are present in water solution except ions of orthosilicic acid. According to the equations (13-1), (13-2), at the temperature of 20-180^0 C and pH = 7.0-9.2 fraction of dimers with respect to the orthosilicic acid which concentration is close to the solubility $C_e(T)$ is not more than 1.0 %, fraction of trimers – 0.1 %, tetramers and low-molecular cyclic polymers (up to 6 units SiO_2) (Weres 0., Yee A., Tsao L., 1980) - < 0.1 %. Fraction of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ ions under these conditions is not more than 14.0 %.

2. STABILITY OF COLLOIDAL SILICA AND SOLID DEPOSITION FORMATION

As the result of nucleation and polymerization particles of the colloid-sized hydrated silica are formed in the solution. Part of the silanol groups SiOH on the particle surface dissociates with the detachment of H^+ proton, and the particle surface gets negative electric charge. The negative surface charge leads to the electrostatic repulsion of particles, and potential energy $U = U_e + U_m$ of interaction between silica particles of radius R has two components: U_m – molecular attraction, U_e - electrostatic repulsion (Deriagin B.V., Churaev N.V., Muller V.M., 1985; Deriagin B.V., 1986):

$$U_e = \varepsilon \cdot \varphi_0^2 \cdot R \cdot \ln(1 + \exp(-\tau \cdot s)), \qquad (15\text{-}1)$$

$$U_m = -(A/12) \cdot (1/s + 2 \cdot \beta \cdot \ln s), \qquad (15\text{-}2)$$

where $s = h/R$, h – the shortest distance between the particles, $\tau = \delta/R$, δ - Debye's depth of ionic layer, A – Hamaker's constant, ε - dielectric permittivity of the solution, φ_0 – electrostatic potential of the particle surface.

Electrostatic repulsion gives lowering in effectiveness α_c of coagulation of the particles in Brownian motion and, therefore, kinetic stability of colloidal silica in hydrothermal solution which is determined by the form of curve U(h) (Deriagin B.V., 1986) :

$$W = 2 \cdot R \cdot \int_{2R}^{\infty} e^{U(l)/kT} \frac{dl}{l^2} \qquad (15\text{-}3)$$

where $\alpha_c = 1/W$, $l = 2 \cdot R + h$.

Unstability of colloidal silica in narrow layer near the surface of the conducting channel leads to the formation of solid deposits from hydrothermal solution flow in fissured or porous medium of rock and on the inner surface of thermal equipment and wells of the geothermal electric- and heat electric power stations (Potapov V.V., 2003; Potapov V.V., Cerdan A.A., 2002; Potapov V.V., Povarov K.O., Podverbny V.M., 2003).

3. KINETICS OF POLYMERIZATION OF SILICIC ACID

Kinetics of colloidal silica polymerization reaction was studied at 20^0C 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 20^0C and 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., 1986) :

$$dS_m/dt_p = -k_p \cdot S_m^{n_p}, \qquad (16)$$

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. This showed that $n_p = 1$ and function $S_m(t_p)$ was exponential:

$$\ln S_m(t_p) = \ln S_0 - t_p/\tau_p, \qquad (17)$$

$$S_m(t_p) = S_0 \cdot \exp(-t_p/\tau_p), \qquad (18)$$

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 (17), based on which constants τ_p и k_p were found. At 20^0C 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 experimental data polymerization reaction is the first order in 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 colloidal particles (Fleming B.A., 1986) :

$$dC_s/dt_p = -k_f \cdot A_s \cdot (C_s - C_e) \cdot C_{SiO}, \qquad (19)$$

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):

$$k_f = k_{f0} \cdot \exp((A_{DH} \cdot I_s^{0,5})/(A_F + I_s^{0,5})), \qquad (20)$$

temperature dependence follows the Arrenius' equation (Fleming B.A., 1986) :

$$\ln k_{f0} = 22.1 - E_p/R_gT \pm 2.0, \qquad (21)$$

where E_p – is activation energy of polymerization reaction, $E_p = 54836.6$ J/mole (Fleming B.A., 1986), R_g – gas constant, $R_g = 8.31$ J/mole·K, A_{DH} – Debye-Huckel's constant, $A_{DH} = 1.238$, $A_F = 1.0$ $(\text{mole/kg})^{0,5}$.

According to Fleming's thermodynamic model concentration C_{SiO} of ionized groups on the silica particle surface follows equation (Fleming B.A., 1986) :

$$\frac{a_H}{K_0} = \frac{(n_{OH} - C_{SiO})}{C_{SiO} \cdot (C_{PB} \cdot C_{SiO} + (1 + C_{PB}{}^2 \cdot C_{SiO}{}^2)^{0.5})^2}, \qquad (22)$$

where a_H – is activity of hydrogen H^+ ions in basic mass of the solution at the large distance from the surface of colloidal silica particles, K_0 – constant of the ionization reaction of the surface silanol groups SiOH ($\equiv SiOH \leftrightarrow \equiv SiO^- + H^+$), equal $(5.13 \pm 1.59) \cdot 10^{-8}$, n_{OH} – concentration of SiOH groups on the surface of particles which are able to ionize with detachment of H^+ proton, $n_{OH} = (1.34 \pm 0.24)$ nm^{-2}; C_{PB} – constant in approximate solution of Puasson-Boltzmann's equation for electric potential φ in the solution which has a boundary with a solid phase, that is Debye-Huckel's approximation for spherical particles (Fleming B.A., 1986):

$$C_{PB} = \frac{z \cdot e \cdot R}{2 \cdot \varepsilon_0 \cdot \varepsilon \cdot k_B \cdot T \cdot (1 + \delta^{-1} \cdot R)}, \qquad (23)$$

where e – is an elementary charge, $1.60 \cdot 10^{-19}$ C, k_B – Boltzmann's constant , z – ion charge, R – particle radius, ε_0 – electric constant, $\varepsilon_0 = 8.854 \cdot 10^{-12}$ $C^2/m^2 \cdot H$, ε - dielectric permittivity of the solution, δ - Debye's parameter which characterizes depth of ionic layer in the solution near the charged spherical particle, $\delta = ((\varepsilon_0 \cdot \varepsilon \cdot k_B \cdot T)/(2 \cdot e^2 \cdot N_A \cdot I_s))^{0,5}$ at T = 293 K, $I_s = 0.0141$ mole/kg, ε = 81 - δ = 2.57 nm.

Calculations by equations (17)-(23) showed the following values of constants k_p and τ_p at increased temperatures: at

50^0C - τ_p = 36.01 min, k_p= 1.666 h^{-1}; 75^0C - τ_p = 20.91 min, k_p= 2.869 h^{-1}; 100^0C - τ_p = 8.3 min, k_p = 7.221 h^{-1}. At pH = 7.0 dependence $S_m(t_p)$ considerably changed. At t_p from 0 to 6 h derivative dS_m/dt_p was 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.

Photon correlation spectroscopy measurements showed that average radius of polymerized silica particles ranged from 7.0 to 20.0 nm, main fraction of particles had radius R within the range from 1.0 to 50.0 nm. Measurements were conducted at a temperature of 20^0C, in all samples light scattering angle had the fixed value 90^0 and laser light wave length was 633.3 nm. Diffusion coefficient D was calculated from Stocks-Einstein equation:

$$D=k_B \cdot T/6 \cdot \pi \cdot \mu \cdot R, \qquad (24)$$

where μ- the dynamic viscosity of solution. Average value of diffusion coefficient was about $2.9 \cdot 10^{-7}$ cm^2/s.

4. EXPERIMENTS ON COAGULATION AND PRECIPITATION OF COLLOIDAL SILICA

Experiments on colloidal silica particles precipitation were carried out with the probes of hydrothermal solution from the productive wells of Mutnovskoe hydrothermal field. Metal cations were introduced to solution with addition of lime CaO, calcium chloride $CaCl_2$, magnesium sulphate $MgSO_4 \cdot 7H_2O$ and hydrolyzed salts: aluminium sulphate $Al_2(SO_4) \cdot 18H_2O$, aluminium chloride $AlCl_3 \cdot 6H_2O$, ferric chloride $FeCl_3 \cdot 6H_2O$, copper $CuSO_4 \cdot 5H_2O$, cobalt $CoSO_4 \cdot 7H_2O$ and nickel $NiSO_4 \cdot 7H_2O$ sulphates, plumbous nitrate $Pb(NO_3)_2$. In the experiments residual concentrations of colloidal and monomeric silica, coagulating cations, pH value were determined, critical concentration of coagulants and coagulating cations was found. In precipitated material content of Ca, Mg, Al, Fe, Cu, Co and Pb was determined, and material was studied by methods of X-ray and thermochemical analyses, infra-red spectroscopy. The experiments with coagulants were carried out at 20^0C and 96^0C.

Concentrations of basic components in the solution before treatment had the following values (mg/kg): Na^+ - 239.4, K^+ - 42.0, NH_4^+ - 1.1, Ca^{2+} - 1.6, Mg^{2+} - 0.72, Li^+ - 0.71, Fe^{2+} - 0.1, Al^{3+} - 0.27, Cl^- - 198.5, SO_4^{2-} - 192.1, HS^- - 5.0, HCO_3^- -81.0, CO_3^{2-} - 19.9, H_3BO_3 – 106.9, SiO_2 – 680.0, pH = 9.2, M_h = 1638.9 mg/kg, I_s = 14.22 mmole/kg.

Table 1 contains data on critical concentration of each coagulant and coagulating cation. It was established, that silica coagulation and precipitation occurred according to the following mechanism: 1) injection into the solution of a critical amount 50-120 mg/kg of Ca^{2+}, Mg^{2+}, Cu^{2+}, Co^{2+}, Pb^{2+}, Ni^{2+}, Al^{3+}, Fe^{3+} cations (individual or in a combination); 2) sorption of a part of those cations (5-20 mg/kg) or their hydrated polycation complexes by the particle surface until the neutralization of the particles negative surface charge; 3) formation of bridge-bonds between the particle surfaces involving coagulant-cations, coagulation and precipitation of colloidal silica.

Table 1 Data on the mechanism of colloidal silica coagulation and precipitation in hydrothermal solution by metal cations, temperature 20^0C.

Coagulant	Coagulating cation	Critical coagulant concentration, mg/kg	Critical cation concentration	
			mg/kg	mmol/kg
CaO	Ca^{2+}	80.0	57.1	1.424
$CaCl_2$	Ca^{2+}	500.0	180.18	4.495
$CuSO_4 \cdot 5H_2O$	Cu^{2+}	200.0	50.9	0.801
$CoSO_4 \cdot 5H_2O$	Co^{2+}	400.0	83.88	1.423
$Pb(NO_3)_2$	Pb^{2+}	150.0	93.6	0.451
$NiSO_4 \cdot 7H_2O$	Ni^{2+}	225.0	47.0	0.801
$Al_2(SO_4) \cdot 18H_2O$	Al^{3+}	250.0	20.2	0.748
$AlCl_3 \cdot 6H_2O$	Al^{3+}	150.0	16.65	0.617
$FeCl_3 \cdot 6H_2O$	Fe^{3+}	250.0	55.66	0.996

Evaluation of density of the surface charge σ_s of colloidal silica particles was done according to the calcium concentration in the material precipitated with addition of CaO and $CaCl_2$ at the concentrations close to the critical one. In this case amount of sorbed cations Ca^{2+} was determined by the condition of neutralization of the surface charge (Iler R.K., 1975). The following values were obtained: pH = 8.5 - σ_s = 0.66 nm^{-2} = 10.62 $\mu C/cm^2$, pH = 9.3 - σ_s = 1.39 nm^{-2} = 22.26 $\mu C/cm^2$, pH = 10.0 - σ_s = 1.495 nm^{-2} = 23.92 $\mu C/cm^2$.

Table 2 Results of separate treatment with addition of slaked lime (*C_t* - residual total content of silica, *C_s* - residual concentration of monomeric silica, Ca^{2+} - amount of calcium cations injected into solution with lime).

CaO mg/kg	Ca^{2+}, mg/kg	20^0C			96^0C		
		pH	C_t, mg/kg	C_s, mg/kg	pH	C_t, mg/kg	C_s, mg/kg
0	0	9.29	697.0	150.3	9.26	718.8	135.0
100	71.4	10.10	158.1	158.1	9.73	344.9	244.4
150	107.1	10.48	158.0	158.0	n.d.	n.d.	n.d.
200	142.8	10.82	158.0	158.0	9.76	329.8	273.0
300	214.2	11.42	153.0	153.0	9.88	315.0	275.0
400	285.6	11.68	137.5	131.9	10.32	345.0	322.5
500	357.0	11.6	75.6	73.8	10.1	339.0	334.4
600	428.4	12.07	75.0	71.3	10.16	307.8	307.8
700	499.8	12.12	69.0	67.0	10.48	260.9	260.9
800	571.2	12.16	41.3	36.3	10.92	229.7	217.2
1000	714.0	12.25	24.0	24.0	11.16	203.1	203.1
1500	1071.4	12.25	1.6	1.6	12.24	6.3	6.3

In treatment by the slaked lime pH of the solution reached the value of 10-12. Precipitation of both colloidal and monomeric silica took place, however stability of monomeric silica was much higher than the colloidal

(Table. 2). Practically all colloidal silica precipitated already at CaO concentration of 80-100 mg/kg, which was critical at 20^0-96^0C. Monomeric silica concentration started decreasing at CaO concentration over 400 mg/kg at 20^0C, and over 700 mg/kg at 96^0C. Decrease of the total content C_t of silica at 94-96^0C because of the higher content of monomeric silica occured slower than at 20^0C. At high lime CaO concentrations (1000 and 1500 mg/kg) total silica SiO_2 amount reduced to 24 and 1.6 mg/kg correspondingly.

A series of experiments on treatment by slaked lime with seawater injection were conducted. Seawater showed pH level of 8.3 and concentrations of cations Ca^{2+} = 210 mg/kg and Mg^{2+} = 699 mg/kg. Treatment was carried out at lime concentration lower than the critical one CaO = 70-40 mg/kg, seawater concentration amounted 15-100 cm^3/kg. For stable precipitation of silica it was necessary to inject the following volumes of seawater: 15-20 cm^3/kg of seawater – at CaO concentration of 70 mg/kg, 25-30 cm^3/kg of seawater – at CaO concentration of 60 mg/kg, and about 40 cm^3/kg of seawater – at lime concentration of 40-50 mg/kg. Total content of SiO_2 reduced to 140-190 mg/kg, which corresponded to almost complete precipitation of colloidal silica. The smallest value of CaO/SiO_2 ratio 0.006 was obtained in the sample precipitated at lime CaO concentration of 40 mg/kg and seawater discharge of 40 cm^3/kg. Mg/Ca ratio in this sample being 2.513. At such a treatment regime about 65 mg/kg of cations Ca^{2+} and Mg^{2+} was injected into the solution. Thus, additional intake of seawater allows to reduce lime consumption and obtain the material with a smaller calcium amount.

Results of the experiments on silica precipitation with addition of seawater have showed that seawater acted as a coagulant. Colloidal silica precipitation and reducing of C_t concentration to the values of 160-190 mg/kg occured already after addition of 100 cm^3/kg.

Concentration of hydrolyzed salts of calcium, magnesium, copper, cobalt, nickel, plumbum, aluminium and ferrum varied within 0-10000 mg/kg. pH of the solution decreased because of hydrolysis of metal cations injected into solution during salt treatment. Hydrolysis is accompanied by the formation of colloidal particles of metal hydroxides. Low-soluble hydroxide molecules form the aggregates on the surface of which ions adsorb from the solution and form electrically charged micelle nucleus which pulls up ions of opposite charge from the solution. Multicharge colloidal particles of hydrated metal cations or their macrocomplexes as flake are sorbed by the surface of colloidal silica particles. This resulted in colloidal silica coagulation and precipitation from the solution.

Experiments on silica precipitation by electrocoagulation are carried out in the regime of direct current and represented in the paper of Potapov V.V. and Serdan A.A., 2002. Experiments on silica precipitation by electrocoagulation were carried out in regime of direct current. Electrodes of aluminium, copper and ferrum were used. In this case coagulant added to the solution as a result of metal anode dissolution and following hydrolysis of metal cations. Silica precipitation by electrocoagulation had its peculiarities. Colloidal and monomeric silica precipitated by electrocoagulation simultaneously and gradually. Decrease of the total silica content at electrocoagulation on aluminium electrodes passed three stages. Colloidal silica in hydrothermal solution was more stable with respect to the gradual coagulant addition than to the quick one, as at the treatment by $Al_2(SO_4)_3{\cdot}18H_2O$.

Electric power consumption for treatment reduced while temperature increased because the specific conductivity σ of hydrothermal solution increased: at I=1.0 A and 20^0C- $\sigma=1.28{\cdot}10^{-3}$ $S{\cdot}cm^{-1}$, at 99^0C- $\sigma= 2.92{\cdot}10^{-3}$ $S{\cdot}cm^{-1}$, at 130^0C- $\sigma= 3.85{\cdot}10^{-3}$ $S{\cdot}cm^{-1}$. Ions contributed to the conductivity of the solution most of all are Na^+-33.24%, K^+-6.82%, Cl^--39.85%, SO_4^{2-}-13.23%, HCO_3^- - 2.04%, CO_3^{2-} - 2.73%. At current density j=30-200 A/m^2 and current strength I=0.5-1.5 A per 1 kg of water solution, distance between electrodes h_{el}=8-10 mm, treatment duration t_{et}=10-40 min consumption of electric energy per 1 kg of treated solution accounted for Q_{EL}=0.0009-0.0033 kW·h/kg and per 1 kg of precipitated silica - Q_{Si}=1.8-6.0 kW·h/kg.

After treatment by calcium chloride pH of the solution reduced to the value of 8.2 (Table 3). Negative electric charge of the colloidal particles decreased, sorption capacity of the surface became worse with respect to metal cations and, as the result, rate of coagulation processes, flake-formation and silica precipitation at high $CaCl_2$ concentrations decreased.

Table 3 Results of the hydrothermal solution probe treatment by hydrolyzed salts at 20^0C (CC – coagulant concentration, Ca, Al, Fe – quantity of Ca^{2+}, Al^{3+}, Fe^{3+} cations introduced to solution by addition of calcium chloride $CaCl_2$, aluminium sulphate $Al_2(SO_4)_3{\cdot}18H_2O$, ferric chloride $FeCl_3{\cdot}6H_2O$ correspondingly).

CC, mg/kg	$CaCl_2$			$Al_2(SO_4)_3{\cdot}18H_2O$			$FeCl_3{\cdot}6H_2O$		
	Ca, mg/kg	pH	C_t, mg/kg	Al, mg/kg	pH	C_t, mg/kg	Fe, mg/kg	pH	C_t, mg/kg
0	0	8.90	687.5	0	9.22	725.0	0	9.45	725.0
250	n.d.	n.d.	n.d.	20.2	4.96	146.9	51.5	3.73	187.5
500	180.0	8.70	468.8	40.4	4.36	161.25	103.0	2.75	178.1
1000	360.0	8.54	131.25	80.8	4.02	153.1	206.0	2.36	665.6
2000	720.0	8.41	129.4	161.6	3.78	158.1	412.0	2.10	725.0
3000	1080.0	8.46	131.25	242.4	3.73	158.1	618.0	2.52	725.0
4000	1440.0	8.34	129.4	323.2	3.72	153.1	814.0	2.08	725.0
5000	1800.0	8.37	135.6	404.0	3.70	156.0	1030.0	2.17	725.0
6000	2162.1	8.36	135.6	484.8	3.66	151.8	1236.0	2.14	725.0
10000	3600.0	8.29	130.6	808.0	3.56	128.1	2060.0	1.98	728.1

During the hydrothermal solution treatment by easily hydrolyzed salts decrease of pH is more considerable. After treatment $Al_2(SO_4){\cdot}18H_2O$ pH reduced to 3.5-4.0, after treatment $AlCl_3{\cdot}6H_2O$ to pH = 3.6, $CuSO_4{\cdot}5H_2O$ - to pH = 4.6, $CoSO_4{\cdot}7H_2O$ - to pH = 5.0, $Pb(NO_3)_2$ - to pH = 5.12. The largest decrease of pH was observed at solution treatment by ferric chloride $FeCl_3{\cdot}6H_2O$: in this case pH reduced to 1.96. In a result, not only the sorption capacity of silica particles surface became worse, but also the solubility of hydrated charged complexes of metal cations increased. Aluminium hydroxide stopped to precipitate at pH = 4.0, $Cu(OH)_2$ - at pH = 6.2, $Fe(OH)_2$ - at pH = 2.3, $Co(OH)_2$ - at pH = 7.6, $Pb(NO_3)_2$ - at pH = 7.4. Therefore, at acidification of the solution up to the pH values less than mentioned above formation of charged cation complexes was difficult. Precipitation of complexes and coprecipitation colloidal silica became worse, coagulation slowed down. After treatment by hydrolyzed salts monomeric silica did not precipitate even at the highest coagulant concentration up to 10000 mg/kg.

Because of the pH decrease and sorption capacity of the silica surface being worse the fraction of total mass of metals in the material precipitated by injection of hydrolyzed salts was not large. Thus, in calcium chloride treatment CaO/SiO_2 ratio increased from 0.0163 at $CaCl_2$ concentration of 1500 mg/kg to 0.0755 at $CaCl_2$ concentration of 10000 mg/kg. In the material precipitated by aluminium sulphate injection Al/SiO_2 ratio was within a range from 0.0412 to 0.0285 and decreased when coagulant concentration increased to 10000 mg/kg. During lime treatment pH, on the contrary, increased, therefore, CaO/SiO_2 ratio in the precipitated material increased from 0.0196 at CaO concentration 80 mg/kg to 1.50 at CaO concentration 1500 mg/kg.

The series of experiments with addition of hydrolyzed salts and simultaneous alkalization of hydrothermal solution by alkali was carried out to improve coagulation and silica precipitation and reduce coagulant consumption. Alkalization allowed: 1) to precipitate silica with coagulant concentration less than the critical one; 2) to speed up coagulation and precipitation processes; 3) to increase quantity of precipitated colloidal and monomeric silica; 4) to vary concentration of metal in the precipitated material.

In experiments the regime of treatment was developed that allowed to obtain a precipitate which passed into silicates of metals after thermal treatment at 900-1000^{0}C. Precipitation in this regime was carried out by introducing metal cations and simultaneous increase of pH to the value of 10-12 and higher. Under such conditions a sufficient quantity of $H_3SiO_4^-$ and $HSiO_3^-$ ions appeared in the solution which were able to form low-soluble compounds with metal cations. Thus, cobalt, magnesium and calcium silicates (Co_2SiO_4, Mg_2SiO_4 и $CaSiO_3$) were obtained. Metal silicates can be used in ceramics, glass, paint and anticorrosion material production.

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

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

We worked out an utilization method of silica precipitated by freezing out dispersed hydrothermal solution 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 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 petrols reaches 160 – 200 g/100g of silica, capacity to absorb 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 at the boundary with silica and add hydrophobic properties to the surface. At the same time coefficient of surface tension of organic liquids at 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 dispersed hydrothermal solution. Silica was modified according to the method presented in the work of Il'inskii V.V., Komarova T.I., Koronelli T.V., Lisichkin G.V. and Serdan A.A. (1993). 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.

5.2. Utilization of 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 were 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 4 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 4 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.

5.3. Addition of silica to cement for increasing of concrete 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 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 %.

5.4. 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 – 218.0) g/100g and low Ca, Al, Fe concentrations. 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 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. TECHNOLOGICAL SCHEME OF SILICA PRECIPITATION FROM THE HYDROTHERMAL SEPARATE

The experiments allowed to reveal physical-chemical properties of the solution which influenced the process of colloidal particle coagulation and determined the technology of silica precipitation: 1) total content SiO_2 C_t = 300-1500 mg/kg; 2) average radius of colloidal silica particles R = 3.0-16.0 nm and specific area of particle surface A_s = 500-2000 cm^2/cm^3 (30-300 m^2/g); 3) density of the surface electric charge of silica particles σ_s = 10.62-23.92 $\mu C/cm^2$; 4) solution pH before treatment - from 9.4 to 7.0; 5) mineralization M_h = 1000-2500 mg/kg; 6) ionic strength of the solution I_s = 10-20 mmole/kg; 7) a ratio between the concentrations of basic cations (Na^+/K^+) and anions (Cl^-/SO_4^{2-}).

Technological scheme of colloidal and monomeric silica precipitation at a temperature from 20 to 140–160^o C from hydrothermal solution was developed based on the experiment results. It included the following stages: (1)

monomeric silica polymerization with the formation of colloidal particles; (2) addition of precipitant (coagulants, flocculants, primary colloidal particles) in a certain moment of polymerization process to form a microstructure of the silica particle complexes without silica precipitation from the solution; (3) injection of a precipitant or mixture of precipitants (coagulants, flocculants, recirculation of precipitated sludge or solution with polymerized silica) for silica coagulation and precipitation; (4) adjusting pH of the solution by adding reagents on the stage of silica coagulation and precipitation to control kinetics of the process and Ca, Mg, Al, Fe content in the precipitated material; (5) separation of flakes of precipitated material and clarification of the solution; (6) dehydration and drying of precipitated material. Dispersity of precipitated material was adjusted by the temperature of solution during the process of silica nucleation and polymerization and also by a composition, amount and time of precipitant(s) addition during polymerization and precipitation processes.

Increasing the efficiency of using hydrothermal heat carrier is determined by a number of factors including elimination of downtime at the geothermal electric power stations, obtaining of additional heat and electric energy in binary cycle with organic liquid having low-boiling temperature and extraction of minerals as amorphous silica.

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. Critical radius of nucleus in hydrothermal solution is about 0.3-0.6 nm. Critical radius increases while the temperature rises because of lowering in oversaturation. As a result there is a tendency for decreasing the rate of nucleation and increasing time of the induction. This leads to the decrease in concentration of the particles and growth of the finite average radius of the particles. Decrease of pH leads to the growth of surface tension and lowering of the deposits growth rate. Therefore, at low pH critical radius significantly increases, rate of nucleation lowers and time of the induction becomes large.

2. The experiments showed that the kinetics of the reaction of monomeric silica polymerization in hydrothermal solution is first-order in the supersaturation S_m. Polymerization rate constant $k_p = 0.485$ h^{-1} and time of reaction $\tau_p = 123.6$ min at 20^{0}C were determined. Rate constant k_p increases with temperature rising. Acidification of solution and pH decreasing led to decreasing the constants of the reaction rate and inhibition of polymerization.

3. 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 were about $D = 2.9 \cdot 10^{-7}$ cm^2/s.

4. Colloidal silica coagulation took place after addition to the solution of a critical quantity of these cations (from 60 up to 120 mg/kg), alone or in combination. Only a part of added cations 5-20 mg/kg adsorbed by the surface of silica and neutralized of negative charge of colloidal particles. Colloidal silica coagulated because of formation of bridge bounds between particle surfaces. In the average 20-60 SiO_2 molecules corresponded to 1 metal cation in this reactions.

5. The value of pH is the basic factor determining kinetics of colloidal silica coagulation and precipitation in hydrothermal solution. Negative electric charge of colloidal particle surface and surface sorption of metal cations depend upon pH value. The solubility of metal hydroxides and complexes of metal cations and silicate-ions also depends upon pH.

6. Physical-chemical properties of hydrothermal solution essential for the process of coagulation and silica precipitation technology were revealed: 1) total content C_t of silica in the solution; 2) average radius, surface area of colloidal silica particles; 3) electric charge of particle surface; 4) concentration of basic cations (Na^+, K^+) and anions (Cl^-, SO_4^{2-}); 5) pH ; 6) mineralization of the solution M_h; 7) ionic strength I_s.

7. Physical and chemical characteristics of silica precipitated from the hydrothermal solution were determined: area and volume of silica pores, density of surface hydroxyl groups, concentration of impurities, oil absorption capacity. According to these charateristics precipitated silica can be utilized in the following industries: a) production of sorbent for water purification from oil products; b) production of sorbent for gas chromatografy; c) addition to the portland cement for increasing of concrete strength; d) for liquid glass production.

8. Factors on which increasing of efficiency of hydrothermal heat carrier using based are the follows: 1) elimination of downtime at the geothermal electric power stations; 2) obtaining of additional heat and electric energy in binary cycle with organic low-boiling liquid; 3) precipitation of amorphous silica material which can be utilized in industry; 4) extraction of valuable minerals such as compounds of Li, B, As which can not be successful with out preliminary precipitation of silica.

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