

PRECIPITATION OF COLLOIDAL SILICA IN HYDROTHERMAL SOLUTION BY METAL CATIONS (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 constants 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+} , Al^{3+} , Fe^{3+} . Cations were added to the solution with slaked lime, calcium chloride, magnesium sulphate, cobalt sulphate, cupric sulphate, plumbous nitrate, 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 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 silicic acids as the result of chemical interaction of water with aluminosilicate minerals of hydrothermal field rocks at a depth of 1.0-3.5 km in zones of thermal anomalies at increased temperature (up to 250-350°C) and pressure (4.0-20 MPa). Hydrothermal solution is multicomponent: Na, K, Si, Ca, Mg, Al, Fe, Cl, S, C, B, Li, As, Cu, Zn, Ag, Au and other compounds are present in it in ionic and molecular form.

At the temperature of 250-350°C, when solution has a contact with rock minerals, total content of silicium

C_t in water can be evaluated by α -quartz solubility (Crerar D.A., Anderson G.M., 1971):

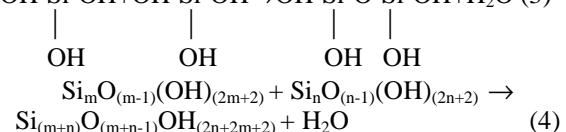
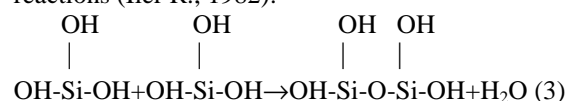
$$\log(C_t/60) = -1.468 + 252.9/T - 3.217 \cdot 10^5/T^2, \quad (1)$$

Equation (1) gives the following values of quartz SiO_2 solubility (mg/kg): 25°C – 3.46, 50°C – 10.29, 100°C – 47.6, 200°C – 256.0, 250°C – 415.6, 300°C – 592.5. At ascending filtration in the fissured-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 (Marshall W.L., 1980), value C_e for pure water depends on absolute temperature T by the following way:

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

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

Such a state of monomeric silicic acid in water solution is unstable. Oversaturation of the solution S_m , equal to the difference ($C_s - C_e$) of silicic acids concentration (monomeric silica) C_s and solubility C_e , is the driving 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):



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 и 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:

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

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, $A_{cr} = 4 \cdot \pi \cdot R_{cr}^2$, $\Delta F_{cr} = \sigma_{sw} \cdot A_{cr} / 3 = (16 \cdot \pi / 3) \cdot \sigma_{sw}^3 \cdot (M_{Si} / \rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N)$, σ_{sw} – coefficient of surface tension at the boundary silica-water, R_{md} – rate of molecular deposition of SiO_2 on the solid surface, $\Gamma \cdot (cm^2 \cdot min)^{-1}$, k_B – Boltzmann's constant, M_{Si} – molecular mass SiO_2 , N_A – Avogadro number, Q_{LP} – Loze-Paunde's factor, $Q_{LP} = 3.34 \cdot 10^{25} kg^{-1}$, 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 following equations (Weres 0., Yee A., Tsao L., 1980, 1981):

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

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

$$f_f = S_a^5, S_a < S_t \quad (8-1)$$

$$f_f = S_t^5 + 5 \cdot S_t^4 \cdot (S_a - S_t), S_a > S_t, \quad (8-2)$$

$$\log S_t = 0.0977 + 75.84/T, \quad (8-3)$$

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

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

$$\log f = pH - pK_i + \log [Na^+] \quad (9-3)$$

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

$$I = 0.119 \int_{-\infty}^{pH} F(pH', pH_{nom}(pH')) dpH', \quad (10-2)$$

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, $H_\sigma = 63.68 \cdot 10^{-3} J/m^2$, $S_\sigma = 0.049 \cdot 10^{-3} J/m^2 \cdot K$, $n_o = 6.84 nm^{-2}$.

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):

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

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:

$$\tau_{in} = 1.08 \cdot 10^{-6} \cdot (6 \cdot R_{md})^{-1} \cdot (Q_{LP} \cdot Z \cdot R_{cr}^2 \cdot \exp(-\Delta F_{cr}/k_B \cdot T))^{-0.25} \quad (12)$$

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 120-150⁰ C . So, for solution having pH = 8.7, $pH_{nom} = 7.86$, $C_t = 700 mg/kg$, at 20⁰C $S_N = 5.952$, $\sigma_{sw} = 24.46 \cdot 10^{-3} J/m^2$, $R_{cr} = 0.30 nm$, $\tau_{in} = 2.66 min$, $I_N = 2.00 \cdot 10^{21} nuclei/kg \cdot s$, $R_f = 0.44 nm$, $N_p = 5.76 \cdot 10^{15} cm^{-3}$; at 100⁰C - $S_N = 1.726$, $\sigma_{sw} = 13.84 \cdot 10^{-3} J/m^2$, $R_{cr} = 0.44 nm$, $\tau_{in} = 0.69 min$, $I_N = 6.40 \cdot 10^{21} nuclei/kg \cdot s$, $R_f = 0.65 nm$, $N_p = 1.25 \cdot 10^{15} cm^{-3}$; at 153⁰C - $S_N = 1.046$, $\sigma_{sw} = 6.91 \cdot 10^{-3} J/m^2$, $R_{cr} = 2.34 nm$, $\tau_{in} = 3966.8 min$, $I_N = 6.72 \cdot 10^9 nuclei/kg \cdot s$, $R_f = 7.00 nm$, $N_p = 5.20 \cdot 10^9 cm^{-3}$. 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 increases: at 20⁰C and pH = 7.0 $\sigma_{sw} = 46.79 \cdot 10^{-3} J/m^2$, $R_{cr} = 0.58 nm$, $\tau_{in} = 368.3 min$, $I_N = 3.99 \cdot 10^{14} nuclei/kg \cdot s$, $R_f = 0.89 nm$; at pH = 6.0 $\sigma_{sw} = 48.96 \cdot 10^{-3} J/m^2$, $R_{cr} = 0.61 nm$, $\tau_{in} = 3967.2 min$, $I_N = 6.05 \cdot 10^{12} nuclei/kg \cdot s$, $R_f = 1.20 nm$; at pH = 5.0 $\sigma_{sw} = 49.27 \cdot 10^{-3} J/m^2$, $R_{cr} = 0.61 nm$, $\tau_{in} = 39162.0 min$, $I_N = 4.67 \cdot 10^{11} nuclei/kg \cdot s$, $R_f = 1.26 nm$. 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 C_{trimer} trimers of silicic acid are

approximated by equations (mol/kg) (Weres O., Yee A., Tsao L., 1980):

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

$$\log C_{\text{trimer}} = -3.22 - 919/T, \quad (13-2)$$

Constant dependence of the orthosilicic acid ionization of the 1-st - $K_1 = [\text{H}^+]\cdot[\text{H}_3\text{SiO}_4^-]/[\text{H}_4\text{SiO}_4]$ and 2-nd - $K_2 = [\text{H}^+]\cdot[\text{H}_2\text{SiO}_4^{2-}]/[\text{H}_3\text{SiO}_4^-]$ stages upon the temperature looks as follows (Arnorsson S., Sigurdsson S., Svavarsson H., 1982) :

$$\log K_1 = -2549/T - 15.36\cdot 10^{-6}\cdot T^2, \quad (14-1)$$

$$\log K_2 = 5.37 - 3320/T - 20\cdot 10^{-3}\cdot T, \quad (14-2)$$

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^o 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 O., Yee A., Tsao L., 1980) - < 0.1 %. Fraction of H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$ ions under these conditions is not more than 14.0 %.

STABILITY OF COLLOIDAL SILICA AND SOLID DEPOSITION FORMATION

As the result of nucleation and polymerization particles of the colloid-sized hydrated silica $n\text{SiO}_2\cdot m\text{H}_2\text{O}$ 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):

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

$$U_m = -(A/12)\cdot(1/s + 2\cdot\beta\cdot\ln s), \quad (15-2)$$

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) :

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

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-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). As the result there is a problem of studying the physical-chemical properties of the colloidal silica dispersion in hydrothermal solution. Results of the study are necessary for improvement of the model of hydrothermal system mineral formation, and also for working out technology of silica extraction and increasing the effectiveness of using hydrothermal heat-carrier of the geothermal heat electric power stations. 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.

KINETICS OF POLYMERIZATION OF SILICIC ACID

Kinetics of colloidal silica polymerization reaction was studied at 20^oC 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^oC and natural pH from 8.0 to 9.4 were of the same shape with convexity and characterized by close values of the derivative dS_m/dt_p .

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

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

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, which pointed to exponential character of the function $S_m(t_p)$ at $n_p = 1$:

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

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

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^oC and pH = 8.0-9.4 average value of τ_p was 2.04 h, $k_p = 0.485 \text{ h}^{-1}$. 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., 1986) :

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

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) :

$$k_f = k_{f0} \cdot \exp((A_{DH} \cdot I_s^{0.5}) / (A_F + I_s^{0.5})), \quad (20)$$

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

$$\ln k_{f0} = 22.1 - E_p / R_g T \pm 2.0, \quad (21)$$

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/mol·K, A_{DH} – Debye-Huckel's constant, $A_{DH} = 1.238$, $A_F = 1.0$ (mol/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) :

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

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 Poisson-Boltzmann's equation for electric potential ϕ in the solution which has a boundary with a solid phase (Debye-Huckel's approximation for spherical particles) (Fleming B.A., 1986) :

$$C_{PB} = \frac{z \cdot e \cdot R}{2 \cdot \epsilon_0 \cdot \epsilon \cdot k_B \cdot T \cdot (1 + \delta^{-1} \cdot R)}, \quad (23)$$

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, $\epsilon_0 = 8.854 \cdot 10^{-12}$ C²/m²·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, $\delta = ((\epsilon_0 \cdot \epsilon \cdot k_B \cdot T) / (2 \cdot e^2 \cdot N_A \cdot I_s))^{0.5}$ (at $T = 293$ K, $I_s = 0.0141$ mol/kg, $\epsilon = 81$ - $\delta = 2.57$ nm).

Calculations by equations (4)-(10) showed the following values of constants k_p and τ_p at increased temperatures: at 50°C - $\tau_p = 36.01$ min; 75°C - $\tau_p = 20.91$ min; 100°C - $k_p = 7.221$ h⁻¹, $\tau_p = 0.138$ 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.

Primary silica particles in unpolymerized solution are sized within the limits of 0.5-1.5 nm (Potapov V.V., Cerdan A.A., 2002). Photon correlation spectroscopy measurements showed that average radius of polymerized silica particles ranged from 7.0 to 16.0 nm, particle radii are distributed within a range from 1.0 to 30.0 nm.

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 Mutnovskoye hydrothermal field. Metal cations were introduced to solution with addition of lime CaO, calcium chloride CaCl₂, magnesium sulphate MgSO₄·7H₂O and hydrolyzed salts: aluminium sulphate Al₂(SO₄)·18H₂O, aluminium chloride AlCl₃·6H₂O, ferric chloride FeCl₃·6H₂O, copper CuSO₄·5H₂O and cobalt CoSO₄·7H₂O sulphates, plumbous nitrate Pb(NO₃)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 dispersed coagulants were carried out at 20°C and 96°C.

Table 1

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

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 ·5H ₂ O	Cu ²⁺	200.0	50.9	0.801
CoSO ₄ ·5H ₂ O	Co ²⁺	400.0	83.88	1.423
Pb(NO ₃) ₂	Pb ²⁺	150.0	93.6	0.451
Al ₂ (SO ₄)·18H ₂ O	Al ³⁺	250.0	20.2	0.748
AlCl ₃ ·6H ₂ O	Al ³⁺	150.0	16.65	0.617
FeCl ₃ ·6H ₂ O	Fe ³⁺	250.0	55.66	0.996

Concentrations of basic components in the solution before treatment had the following values (mg/kg): Na⁺ - 239.4, K⁺ - 42.0, NH₄⁺ - 1.1, Ca²⁺ - 1.6, Mg²⁺ - 0.72, Li⁺ - 0.71, Fe²⁺ - 0.1, Al³⁺ - 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 mmol/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+} , 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.

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 consumptions 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 - $\sigma_s = 0.66 \text{ nm}^{-2} = 10.62 \text{ } \mu\text{C}/\text{cm}^2$, pH = 9.3 - $\sigma_s = 1.39 \text{ nm}^{-2} = 22.26 \text{ } \mu\text{C}/\text{cm}^2$, pH = 10.0 - $\sigma_s = 1.495 \text{ nm}^{-2} = 23.92 \text{ } \mu\text{C}/\text{cm}^2$.

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°C			96°C		
		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	H.O.	H.O.	H.O.
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 20⁰-96⁰C. Monomeric silica concentration started decreasing at CaO concentration over 400 mg/kg at 20⁰C, and over 700 mg/kg at 96⁰C. Decrease of the total content C_t of silica at 94-96⁰C because of the higher content of monomeric silica occurred slower than at 20⁰C. 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 $\text{Ca}^{2+} = 210 \text{ mg/kg}$ and $\text{Mg}^{2+} = 699 \text{ mg/kg}$. Treatment was carried out at lime concentration lower than the critical one $\text{CaO} = 70\text{-}40 \text{ mg/kg}$, 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 occurred already after addition of 100 cm^3/kg .

Concentration of hydrolyzed salts of calcium, magnesium, copper, cobalt, lead, 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 counter 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 direct current regime. 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 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 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$.

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°C - $\sigma=1.28 \cdot 10^{-3}$ S $\cdot\text{cm}^{-1}$, at 99°C - $\sigma=2.92 \cdot 10^{-3}$ S $\cdot\text{cm}^{-1}$, at 130°C - $\sigma=3.85 \cdot 10^{-3}$ S $\cdot\text{cm}^{-1}$. 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/m² and current strength $I=0.5$ -1.5 A per 1 kg of water solution, distance between electrodes $h_{\text{el}}=8$ -10 mm, treatment duration $t_{\text{el}}=10$ -40 min consumption of electric energy per 1 kg of treated solution accounted for $Q_{\text{EL}}=0.0009$ -0.0033 kW $\cdot\text{h}/\text{kg}$ and per 1 kg of precipitated silica - $Q_{\text{Si}}=1.8$ -6.0 kW $\cdot\text{h}/\text{kg}$.

After treatment by calcium chloride pH of the solution reduced to the value of 8.2 (Table 2). In a result, obviously, negative electric charge of the colloid 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.

During the hydrothermal solution treatment by easily hydrolyzed salts decrease of pH is more considerable. After treatment $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ pH reduced to 3.5-4.0, after treatment $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ to pH = 3.6, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ - to pH = 4.6, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ - to pH = 5.0, $\text{Pb}(\text{NO}_3)_2$ - to pH = 5.12. The largest decrease of pH was observed at solution treatment by ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$: 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, $\text{Cu}(\text{OH})_2$ - at pH = 6.2, $\text{Fe}(\text{OH})_2$ - at pH = 2.3, $\text{Co}(\text{OH})_2$ - at pH = 7.6, $\text{Pb}(\text{NO}_3)_2$ - 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. In 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.

Table 3
Results of the hydrothermal solution probe treatment by hydrolyzed salts at 20°C (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 $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ correspondingly).

CC, mg/kg	CaCl_2			$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$			$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$		
	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

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°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.

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 $C_t = 300\text{-}1500$ mg/kg; 2) average radius of colloidal silica particles $R = 3.0\text{-}16.0$ nm and specific area of particle surface $A_s = 500\text{-}2000$ cm^2/cm^3 (30-300 m^2/g); 3) density of the surface electric charge of silica particles $\sigma_s = 10.62\text{-}23.92$ $\mu\text{C}/\text{cm}^2$; 4) solution pH before treatment - from 9.4 to 7.0; 5) mineralization $M_h = 1000\text{-}2500$ mg/kg; 6) ionic strength of the solution $I_s = 10\text{-}20$ mmol/kg; 7) a ratio between the concentrations of basic cations (Na^+/K^+) and anions ($\text{Cl}^-/\text{SO}_4^{2-}$).

Technological scheme of colloidal and monomeric silica precipitation at a temperature from 20 to 140–160° 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 effectiveness 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°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 $\tau_p = 123.6$ min at 20°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 1.0-30.0 nm, average radius $R = 7.2\text{-}16.0$ nm, diffusion coefficients $D = 2.9 \cdot 10^{-7}$ cm^2/s .

2. 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 .

3. 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.

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