

## NUMERICAL MODELING OF ORTHOSILICIC ACID NUCLEATION IN THE HYDROTHERMAL SOLUTIONS AT DIFFERENT TEMPERATURES AND PH

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### ABSTRACT

Nucleation of orthosilicic acid with formation of colloidal silica particles in hydrothermal solutions was studied by the method of numerical simulation. Numerical simulation was done at different parameters: chemical composition, temperatures, pH, ionic strengths of hydrothermal solutions. The rates of nuclei formation and its growth, time dependence of orthosilicic acid concentration, final sizes of colloidal silica particles were calculated. Results of calculations were compared with experimental data. Experiments were carried out with solutions of Mutnovskoye and Pauzhetskoye geothermal fields. The approach based on numerical simulation can be used for developing of technology of silica extraction from hydrothermal solutions.

### INTRODUCTION

There is a problem to study physical and chemical characteristics of colloidal silica in hydrothermal heat carrier in the context of silica extraction technology and increasing of effectiveness of heat carrier using (Potapov V.V., Karpov G.A., Podverbny V.M., 2002; Potapov V.V., 2003).

Colloidal silica forms in the hydrothermal solution during several stages (Potapov V.V., 2003). Silica comes into the solution as molecules of silicic acid as a result of water chemical interaction with silica-alumina rocks of hydrothermal fields at the depth 1.0-3.5 km in thermal anomaly zones under a high temperature (up to 250-350°C) and pressure (4.0-20 MPascal). Hydrothermal solution is multicomponent. Compounds with Na, K, Si, Ca, Mg, Al, Fe, Cl, S, C, B, Li, As, Cu, Zn, Ag, Au and others are present at the solution as ions and molecules.

Under the temperature 250-350°C when solution contacts with rocks minerals a total silica content  $C_t$  (mole/kg) in water can be estimated by  $\alpha$ -quartz solubility (Crerar D.A., 1971):

$$\lg C_t = -1,468 + 252,9/T - 3,217 \cdot 10^5/T^2 \quad (1)$$

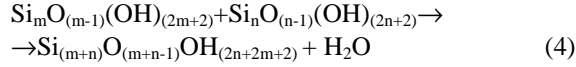
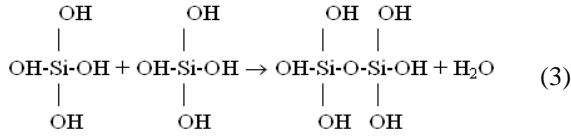
Equation (1) gives the following values of quartz solubility  $\text{SiO}_2$  (mg/kg): 25°C – 3.46, 50°C – 10.29, 100°C – 47.6, 200°C – 256.0, 250°C – 415.6, 300°C – 592.5. Over rising filtration in fractured-and-porous rocks or during solution movement through the producing wells of geothermal electric power plants (GeoPP) pressure and temperature of the solution reduce and solution is divided in steam and liquid phases. Total silica content  $C_t$  in a liquid phase can reach 700-1500 mg/kg. Consequently water solution becomes supersaturated relative to a solubility of amorphous silica  $C_e$  (Marshall W.L., 1980). In accordance with experimental data (Marshall W.L., 1980)  $C_e$  value (mole/kg) for pure water depends on an absolute temperature  $T$  in the following way:

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

Under the temperature 200°C solubility  $C_e$  is 940.8 mg/kg, under the temperature 150°C – 651.8 mg/kg, 100°C – 405.3 mg/kg, 25°C – 130.8 mg/kg.

Such condition of monomeric silicic acid in water solution is unstable. Solution supersaturation  $S_m$  which is equal to the difference ( $C_s - C_e$ ) of orthosilicic acid concentration  $C_s$  and solubility  $C_e$  causes nucleation and polymerization of silicic acid molecules with condensation of silanol groups and formation of siloxane linkes and partial dehydration

in accordance with the following reactions (Iler R., 1982):



### CHEMICAL COMPOSITION OF HYDROTHERMAL SOLUTION

Table 1. Ions and cations concentrations in hydrothermal separate from the pipe-line of reverse pumping of Verkhne-Mutnovskaya GeoPP, ionic strength  $I_s = 14.218$  mmole/kg, conductivity  $\sigma = 1250$  microS/sm, n/d means that concentration was not determined, (-) means that values were not estimated.

Component	mg/l	mg·equ/l	
		mg·equ/l	%mg·equ/l
Na <sup>+</sup>	239.4	10.413	88.044
K <sup>+</sup>	42.0	1.074	9.080
Ca <sup>2+</sup>	1.6	0.0798	0.6747
Mg <sup>2+</sup>	0.72	0.0592	0.5005
Fe <sup>2,3+</sup>	<0.1	<0.0053	0.0448
Al <sup>3+</sup>	0.27	0.033	0.2790
NH <sub>4</sub> <sup>+</sup>	1.1	0.0609	0.5149
Li <sup>+</sup>	0.71	0.102	0.8624
Cations sum	285.9	11.827	100.0
Cl <sup>-</sup>	198.5	5.591	47.664
HCO <sub>3</sub> <sup>-</sup>	81.0	1.327	11.312
CO <sub>3</sub> <sup>2-</sup>	19.9	0.663	5.652
SO <sub>4</sub> <sup>2-</sup>	192.1	3.9995	34.096
HS <sup>-</sup>	4.95	0.15	
H <sub>2</sub> S <sup>0</sup>	5.92	-	-
F <sup>-</sup>	n/d	n/d	-
Anions sum	496.5	11.73	100.0
H <sub>3</sub> BO <sub>3</sub>	106.9	-	
(H <sub>4</sub> SiO <sub>4</sub> ) <sub>t</sub>	1190	-	
(H <sub>4</sub> SiO <sub>4</sub> ) <sub>s</sub>	222	-	
Mineralization		1638.9	
M <sub>n</sub> , mg/kg		1638.9	
pH		9.35	

It is necessary to study the process of orthosilicic acid nucleation to work out the technology of extraction of silica-containing materials with given characteristics from the hydrothermal heat carrier. Final concentration and the size of colloidal particles before their extraction from aqueous solution depend on the parameters of the process nucleation of orthosilicic acid. Numerical simulation in different conditions corresponding to the heat carrier

characteristics of Verkhne-Mutnovsky GeoPP was made to study the process of nucleation.

Table 1 presents physical and chemical characteristics of liquid phase of hydrothermal heat carrier (separate) of GeoPP. This phase is separated from two-phase water-steam flow in separators of GeoPP. Aqueous solution of separate refers to natrium-potassium-chloride-sulphate type of thermal waters. Total silica content in solution varies in the range of 500-1000 mg/kg, pH=8.0-9.4, ionic strength  $I_s = 0.01-0.02$  mole/kg.

### MATHEMATICAL MODEL

Mathematical model (Weres O., Yee A., Tsao L., 1981) worked out by Veres, Yee and Tsao in Lawrence Berkeley Laboratory (USA) was used for numerical simulation. Supersaturation  $S_N(T)$  which is equal to  $C_s/C_e$  and pH are main factors defining nucleation rate  $I_N$  of silicic acid in aqueous 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  $\Delta F_{cr}$  is a free energy change connected with nuclei formation of critical radius  $R_{cr}$ ,  $A_{cr}$  is the surface area of critical nuclei,  $A_{cr}=4 \cdot \pi \cdot R_{cr}^2$ ,  $\sigma_{sw}$  is the surface tension on silica-water boundary,  $R_{md}$  is the rate of molecular precipitation of SiO<sub>2</sub> onto a solid surface,  $g \cdot (sm^2 \cdot min)^{-1}$ ,  $k_B$  is Boltzmann constant,  $M_{Si}$  is the molar mass SiO<sub>2</sub>,  $N_A$  is Avogadro constant,  $Q_{LP}$  is Lothe-Paund factor,  $Q_{LP} = 3,34 \cdot 10^{25} \text{ kg}^{-1}$ ,  $Z$  is Zeldovich factor,  $n_{cr}$  is the quantity of molecules of SiO<sub>2</sub> in nuclei of critical size.

Critical radius, quantity of molecules in nuclei of critical radius, free energy and Zeldovich factor were estimated in accordance with the following formulas (Weres O., Yee A., Tsao L., 1981):

$$R_{cr} = 2 \cdot \sigma_{sw} \cdot M_{Si} / (\rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N) \quad (6)$$

$$n_{cr} = (4 \cdot \pi / 3) \cdot (\rho \cdot N_A / M_{Si}) \cdot R_{cr}^3 \quad (7)$$

$$\Delta F_{cr} = \sigma_{sw} \cdot A_{cr} / 3 = (16 \cdot \pi / 3) \cdot \sigma_{sw}^3 \cdot (M_{Si} / \rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N)^2 \quad (8)$$

$$Z = [-(\partial^2 \Delta F_{cr} / \partial n_{cr}^2) / (2 \cdot \pi \cdot k_B \cdot T)]^{0.5} = (2/3) \cdot [3 \cdot M_{Si} / (4 \cdot \pi \cdot \rho \cdot N_A \cdot n_{cr}^2)]^{1/3} \cdot (\sigma_{sw} / k_B \cdot T)^{0.5} \quad (9)$$

$\rho$  is the density of amorphous silica.

The dependence of the function  $R_{md}$  of the rate of SiO<sub>2</sub> molecules deposition on the temperature and pH solution in a given model is shown in the following equations (Weres O., Yee A., Tsao L., 1981):

$$R_{md} = F(\text{pH}, \text{pH}_{nom}) \cdot k_{OH}(T) \cdot \text{ff}(S_a) \cdot (1 - S_N^{-1}) \quad (10)$$

$$\lg k_{OH}(T) = 3.1171 - 4296.6/T \quad (11)$$

$$f_f = S_a^5, S_a < S_t \quad (12-1)$$

$$f_f = S_t^5 + 5 \cdot S_t^4 \cdot (S_a - S_t), S_a > S_t \quad (12-2)$$

$$\lg S_t = 0.0977 + 75.84/T \quad (12-3)$$

$$F(pH, pH_{nom}) = h_f \cdot f'(pH) + (1-h_f) \cdot f'(pH_{nom}) \quad (13-1)$$

$$f'(pH_{nom}) = f(pH_{nom})/f(7.0) \quad (13-2)$$

$$\lg f = pH - pK_i + \lg[Na^+] \quad (13-3)$$

The dependence of surface tension on the temperature and pH coefficient  $\sigma_{sw}$  is given by the function  $I(pH, pH_{nom})$ :

$$\sigma_{sw} = H_\sigma \cdot T \cdot S_\sigma \cdot 2.302 \cdot 10^{-3} \cdot n_o \cdot k_B \cdot T \cdot I(pH, pH_{nom}) \quad (14-1)$$

$$I(pH, pH_{nom}) = 0.119 \int_{-\infty}^{pH} F(pH', pH_{nom}(pH')) dpH' \quad (14-2)$$

where  $S_a = (1-\alpha_i) \cdot S_N$ ,  $\alpha_i$  is a fraction of silicic acid in ionic form,  $pH_{nom} = pH + \lg([Na^+]/0.069)$ ,  $[Na^+]$  is an ion activity  $[Na^+]$ , mole/kg,  $pK_i=6.4$ ,  $f(7.0) = 0.119$ ,  $h_f=0.45$ ,  $H_\sigma$ ,  $S_\sigma$  are specific enthalpy and entropy of silica surface in water,  $H_\sigma = 63.68 \cdot 10^{-3}$  Joule/m<sup>2</sup>,  $S_\sigma = 0.049 \cdot 10^{-3}$  Joule/m<sup>2</sup>·K,  $n_o = 6.84$  nm<sup>-2</sup>.

Equation (5) shows maximum rate  $I_N$  of nucleation for the particles with the radius that is higher then critical. Its molecules quantity of SiO<sub>2</sub> is equal to  $n = n_{cr} + 0.5/Z$ .  $I_N(t)$  value reaches to maximum in induction time  $\tau_{in}$  that is necessary to grow and form stable population of the particles which sizes are close to critical. Time dependence  $I_N(t)$  has got the form (Weres 0., Yee A., Tsao L., 1981):

$$I_N(t) = I_N \cdot (1 - e^{-t/\tau_{in}}) \quad (15)$$

To calculate time  $\tau_{in}$  the following formula is used:

$$\tau_{in} = 1.08 \cdot 10^{-6} \cdot (6R_{md})^{-1} \cdot (Q_{LP} \cdot Z \cdot R_{cr}^2 \cdot \exp(-\Delta F_{cr}/k_B \cdot T))^{-0.25} \quad (16)$$

### **PROGRAM FOR NUMERICAL SIMULATION**

The system of equations (1), (2), (5)-(16) was used to develop MSANUC.FOR program. The solution algorithm in accordance with MSANUC.FOR was the following:

1) Initial values entry: temperature T, pH, concentration of ions and ionic strength of solution, the assignment of total silica  $C_t$  content of initial time "TIME" and time step DT, the assignment of initial

radii R(I) and particles quantity MP(I) of every class "I" which are present in the solution before nucleation.

2) The calculation of colloidal silica content in solution by summation of particles of all classes:

$$M_{col} = \sum_{I=1}^{I=N} \frac{4 \cdot \pi \cdot \rho \cdot R^3(I) \cdot MP(I)}{3} \quad (17)$$

3) The calculation of concentration of monomeric orthosilicic acid as difference between total content and colloidal silica content:

$$C_s = C_t - M_{col} \quad (18)$$

4) The calculation of current value of supersaturation solution  $S_N$ :

$$S_N = C_s / C_c(T) \quad (19)$$

5) The calculation of values of  $\sigma_{sw}$ ,  $R_{md}$ ,  $R_{cr}$ ,  $Z$ ,  $\tau_{in}$ ,  $I_N(t)$  corresponding to current values  $S_N$ , pH and T by equations (5)-(16).

6) The calculation of the quantity of new particles appearing during the time DT in accordance with current value of nucleation rate  $I_N$  on a given program step and educing a new class of particles N+1:

$$MP(N+1) = I_N \cdot DT \quad (20)$$

7) The calculation of summary concentration of particles:

$$CONP = \sum_{I=1}^{I=N+1} MP(I) \quad (21)$$

8) The calculation of particle mass difference DPM of every class during the time DT in accordance with the equation:

$$DPM(I) = 4 \cdot \pi \cdot R^2(I) \cdot R_{md} \cdot DT$$

9) The calculation of particle radius R(I) corresponding to a new value of particle mass in every class:

$$R(I) = (R^3(I) + 3 \cdot DPM(I) / 4 \cdot \pi \cdot \rho)^{1/3} \quad (22)$$

And the calculation of mean values of  $R_{cp}$ ,  $R_{cp}^2$ ,  $R_{cp}^3$  in all classes of particles:

$$R_{cp} = \frac{\sum_{I=1}^{I=N+1} R(I) \cdot MP(I)}{CONP} \quad (23)$$

$$R_{cp}^2 = \sum_{I=1}^{I=N+1} \frac{R^2(I) \cdot MP(I)}{CONP} \quad (24)$$

$$R_{cp}^3 = \sum_{I=1}^{I=N+1} \frac{R^3(I) \cdot MP(I)}{CONP} \quad (25)$$

10) The calculation of new temperature values, pH, ionic strength of solution if these values change with time. After the tenth step we must return to the second step of the program to make the next cycle. Registration of calculations results in a separate file is provided for: mean radius, summary concentration of particles and concentration of monosilicic acid for given time station.

## RESULTS

Table 2 a,b presents the results of numerical simulation of nucleation with MSANUC.FOR program under different temperatures and pH solution. During the initial time colloidal silica content supposed to be zero and all silica was in a monomeric orthosilicic acid form:

$$C_s(t=0) = C_t$$

Simultaneous results show that critical radius  $R_{cr}$  increases due to supersaturation reduce when temperature becomes higher. Consequently the tendency for decrease of nucleation rate  $I_N$  and increase of induction time  $\tau_{in}$  takes place; it leads to reduce of particles concentration  $N_p$  and increase of final mean radius of the particles  $R_f$ . Under the temperature 120-150°C and higher nucleation hasn't time to develop during a real residence time of hydrothermal solution in wells and thermal equipment of GeoPP.

After nucleation and polymerization completion a part of silica continues to be as molecules of orthosilicic acid  $H_4SiO_4$  which concentration is close to solubility of  $C_e$ . It is in equilibrium with colloidal silica. Small amount of silicic acids ions ( $H_3SiO_4^-$ ,  $H_2SiO_4^{2-}$ ,  $HSiO_3^-$ , etc.) and macromolecules of polysilicic acids are in the solution parallel with colloidal particles and molecules of silicic acids. Data processing obtained by Rozbaum and Rode (Rothbaum H.P., Rohde A.G., 1979) has showed the concentrations of dimmers  $C_{dimer}$  and trimers  $C_{trimer}$  of silicic acid are approximated by the equations (mole/kg):

$$\lg C_{dimer} = -2.10 - 775/T \quad (26-1)$$

$$\lg C_{trimer} = -3.22 - 919/T \quad (26-2)$$

The dependence of constants of orthosilicic acid ionization of the first  $K_1 = [H^+] \cdot [H_3SiO_4^-] / [H_4SiO_4]$  and second  $K_2 = [H^+] \cdot [H_2SiO_4^{2-}] / [H_3SiO_4^-]$  stages on the temperature has the following form:

$$\lg K_1 = -2549/T - 15.36 \cdot 10^{-6} \cdot T^2 \quad (27-1)$$

$$\lg K_2 = 5.37 - 3320/T - 20 \cdot 10^{-3} \cdot T \quad (27-2)$$

In accordance with equations (26-1, 26-2) under the temperature 20-180°C and pH=7.0-9.2 a fraction (portion) of dimmers with respect to orthosilicic acid which concentration is close to a solubility of  $C_e(T)$  doesn't exceed 1.0%, a fraction(portion) of trimers is 0.1%, a fraction(portion) of tetramers and low-molecular circular polymers (up to 6 units  $SiO_2$ ) (Rothbaum H.P., Rohde A.G., 1979) is < 0.1%. A fraction (portion) of ions  $H_3SiO_4^-$  and  $H_2SiO_4^{2-}$  under such conditions is not more than 14.0%.

The calculations by the method of photon correlation spectroscopy show that particles mean radius of polymerized silica in hydrothermal solution has values from 7.0 up to 30.0 nm, values of particles radii vary from 1.0 up to 50.0 nm (Potapov V.V., 2003).

With the help of MSANUC.FOR final mean size of silica particles under different constant temperatures 20°C, 40°C, 50°C, 60°C, 80°C, 100°C and different constants pH=4-8.5 were estimated. Table 2 presents estimated final mean sizes of the particles (nm).

Table 2. Final mean sizes of silica particles under a constant temperature and different pH;  $C_s=700$  mg/kg; (-) means that it was not estimated.

pH	t, °C					
	20	40	50	60	80	100
4	5.289	19.247	48.067	156.551	6342.132	-
5	5.290	19.054	47.305	153.158	5858.727	-
6	2.983	16.823	40.691	128.018	4684.754	-
7	2.978	7.667	15.282	38.175	701.463	-
8	0.988	1.219	1.508	1.775	3.488	18.77
8,5	0.645	0.731	0.784	0.841	1.013	1.268

When pH=5-6 and the temperature is 50°C the calculations were made with step by pH 0.1. It made the possibility to study the influence of pH solution on the size of silica particles more detailed. The estimated results are shown in table 3 and on figure 1.

Table 3. Final mean sizes of silica particles under the temperature 50°C and different pH;  $C_S=700$  mg/kg.

pH	$R_A$ , nm	pH	$R_A$ , nm
5	47.305	5.5	45.423
5.1	46.995	5.6	44.854
5.2	46.771	5.7	44.007
5.3	46.42	5.8	43.077
5.4	45.954	5.9	42.028

On figure 2 the dependence of concentration of dissolved silicic acid  $C_S$  (mg/kg) on time  $T_p$  (min) is shown for  $t=50^\circ\text{C}$ , initial concentration  $C_S=700$  mg/kg and different values pH; figure 3 presents the dependence of supersaturation  $S_N$  on time  $T_p$  (min); figure 4 (a-f) presents the dependence of distribution of final sizes of silica particles.

The influence of initial solution concentration  $C_S$  (mg/kg) on a final mean size of silica particles (nm) is shown in table 4 and figure 5. Calculations were made under different solution temperatures: 20°C, 40°C, 60°C, 80°C, 90°C; different initial solution concentrations  $C_S$  (mg/kg): 500, 600, 700, 800, 1000.

Table 4. Values of final mean size of silica particles (nm) under different temperatures  $t$  and initial concentrations of solution  $C_S$ , pH=8; (-) - means that it was not estimated.

$C_S$ , mg/kg	$t$ , °C			
	20	40	50	60
300	93.57	-	-	-
350	12.46	1019.9	-	-
400	4.35	49.11	586.3	-
500	1.79	4.088	8.968	32.71
600	1.246	1.846	-	3.808
700	0.988	1.219	-	1.775
800	0.876	1.054	-	1.311
1000	0.739	0.836	-	0.952
$C_S$ , mg/kg	$t$ , °C			
	70	80	85	90
300	-	-	-	-
350	-	-	-	-
400	-	-	-	-
500	-	-	-	-
600	7.56	24.14	56.14	169.8
700	-	3.488	-	6.496
800	-	1.815	-	2.308
1000	-	1.108	-	1.212

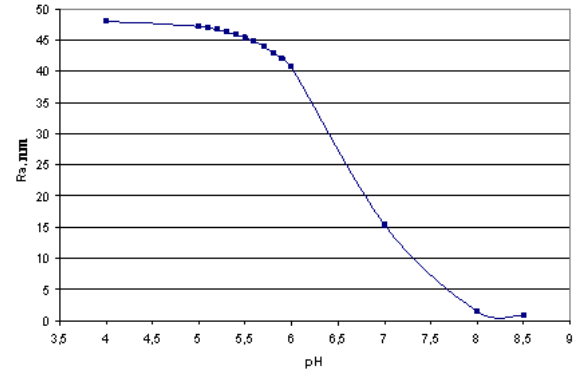


Fig. 1. The dependence of final mean size of silica particles on pH.  $t=50^\circ\text{C}$ ,  $C_S = 700$  mg/kg.

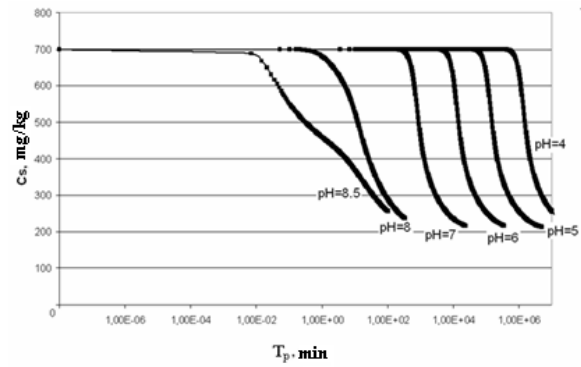


Fig. 2. The dependence of concentration of dissolved silicic acid on time.  $t=50^\circ\text{C}$ , initial concentration  $C_S=700$  mg/kg.

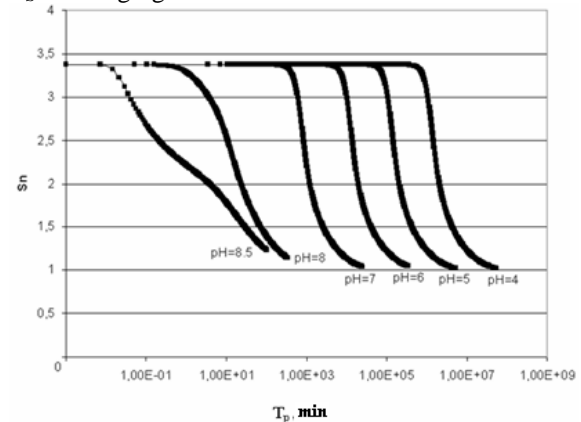


Fig. 3. The dependence of supersaturation  $S_N$  on time.  $t=50^\circ\text{C}$ , initial concentration  $C_S=700$  mg/kg.

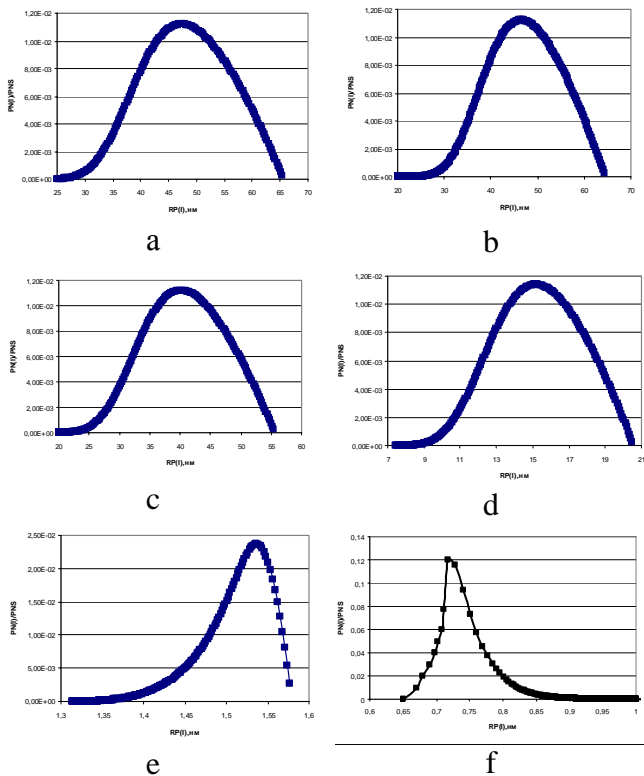


Fig. 4. The distribution of particles sizes under the temperature  $t=50^{\circ}\text{C}$ , initial concentration  $C_S=700$  mg/kg. a – pH=4; b – pH=5; c – pH=6; d – pH=7; e – pH=8; f – pH=8.5.

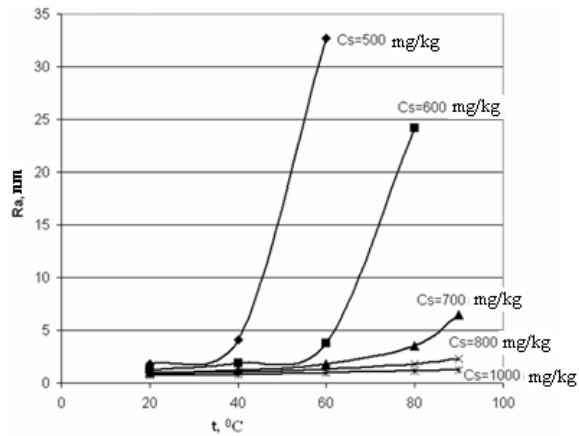


Fig. 5. The dependence of a final mean size of silica particles on different temperatures  $t$  and different initial concentrations of the solution  $C_S$ ; pH=8.

Figure 2 shows that curves reflecting the dependence of concentration of dissolved silicic acid on time have two areas: convex curve reflects homogeneous nucleation, i.e. the stage of formation of new particles centres, concave part reflects heterogeneous nucleation, i.e. the growth of centres formed earlier.

Figure 6 (a–c) presents the dependence of quantity of the formed particles PNS (nucl) on time  $T_P$  (min) and dependence of nucleation rate  $R_{\text{nuc}}$  (nucl/kg\*s) on time  $T_P$  (min) under the temperature  $t=50^{\circ}\text{C}$ , initial concentration  $C_S=700$  mg/kg and different pH.

On figure 4 left curve part of particles sizes distribution is concave and right curve part is convex.

Figure 7 presents the dependence of concentration of dissolved silicic acid  $C_S$  (mg/kg) on time  $T_P$  (min) for  $t=60^{\circ}\text{C}$ , pH=8 and different initial; figure 8 shows the dependence of supersaturation  $S_N$  on time  $T_P$  (min); figure 9 (a-e) presents the dependence of distribution of final sizes of silica particles.

It was obtained the following final mean sizes of silica particles (nm) for initial concentration  $C_S=300$ , 350 mg/kg, pH=8 and ionic strength corresponding to the solution characteristics of Pauzhetsky deposit (table 5).

Table 5. Values of final mean size of silica particles (nm) under different temperatures  $t$  and different initial solution concentration  $C_S$ . (-) - means that it was not estimated.

$C_S$ , mg/kg	$t, ^{\circ}\text{C}$			
	20	30	40	50
300	13.99	129.9	9095.69	-
350	3.59	10.26	63.95	2103.6

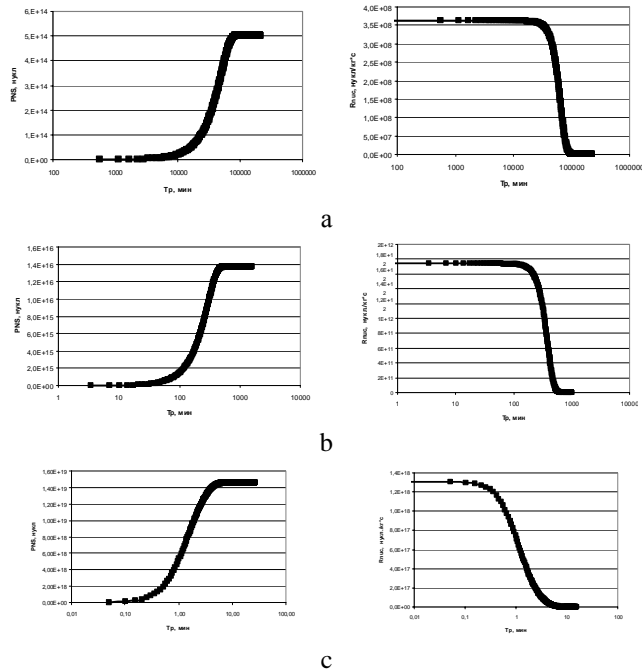


Fig. 6. Dependences of formed particles quantity PNS on time  $T_P$  and dependences nucleation rate  $R_{\text{nuc}}$  on time  $T_P$ ;  $t=50^{\circ}\text{C}$ , initial concentration  $C_S=700$  mg/kg. a – pH=5; b – pH=7; c – pH=8.

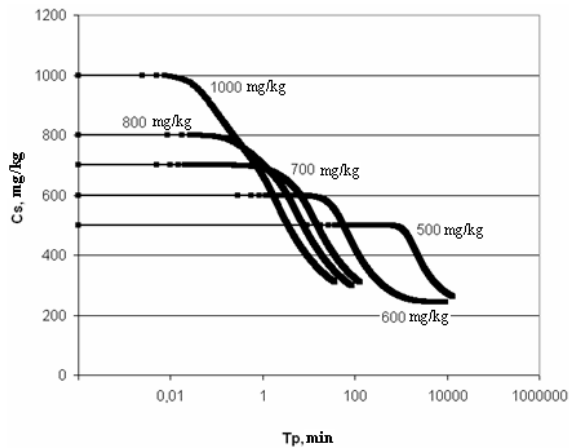


Fig. 7. The dependence of dissolved silicic acid concentration on time.  $t=60^{\circ}\text{C}$ ,  $\text{pH}=8$ .

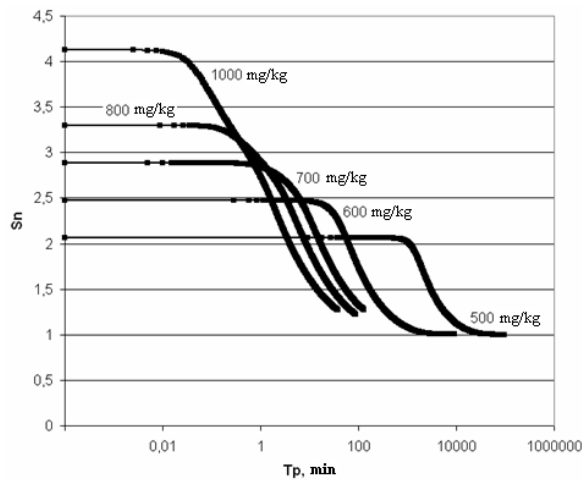


Fig. 8. The dependence of supersaturation  $S_N$  on time.  $t=60^{\circ}\text{C}$ ,  $\text{pH}=8$ .

The results of simulation show that critical radius (nm)  $R_{cr}$  and induction time  $\tau_{in}$  (min) increase when pH is stated and temperature becomes higher due to supersaturation reduce  $S_N$ . Consequently nucleation rate  $I_N$  reduces; it causes to increasing of final mean particles size  $R_A$  (nm).

Under the same temperature when pH reduces the surface tension  $\sigma_{sw}$  increases and rate of molecular deposition of silicic acid reduces. Owing to it critical radius of particles and induction time increase, nucleation rate reduces and final mean size of particles increases.

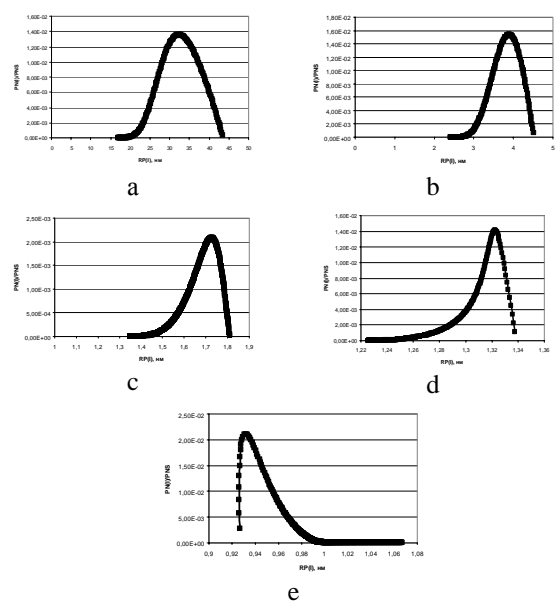


Fig. 9. The distribution of particles sizes under the temperature  $t=60^{\circ}\text{C}$ ,  $\text{pH}=8$ . a –  $C_S=500$  mg/kg; b –  $C_S=600$  mg/kg; c –  $C_S=700$  mg/kg; d –  $C_S=800$  mg/kg; e –  $C_S=1000$  mg/kg.

## CONCLUSIONS

1. The results of numerical simulation show that in hydrothermal solutions the transformation of orthosilicic acid into colloidal silica happens as a result of two sequential processes: 1) homogeneous nucleation during which the transformation of orthosilicic acid into colloidal silica happens mainly as a result of increasing of new centers quantity; 2) heterogeneous nucleation which happens due to increasing of sizes of centers formed earlier if their quantity is practically constant. Durations of these stages depend on process parameters: temperature, pH, ionic strength, total silica content and supersaturation rate.

2. The results of numerical simulation show that the nucleation of orthosilicic acid molecules and formation of colloidal particles in hydrothermal solution actively develop under the temperature below  $120\text{--}150^{\circ}\text{C}$ . Under the temperature  $120\text{--}150^{\circ}\text{C}$  and higher the induction time becomes comparable or exceeds time of heat carriers stay in wells, pipelines and processing units.

3. pH solution is an another factor considerably influencing on nucleation kinetics. When pH is low critical radius of particles increases considerably, the nucleation rate reduces and induction time increases. When pH is 7.0 and lower the induction time considerably exceeds the time of heat carrier movement in wells and thermal equipment.

4. The method on basis of numerical simulation carried out in the paper can be applied to project equipment for flow sheet of silica extraction from the hydrothermal solution during the stage of ageing. Such method gives a possibility to take into account how temperature profile, pH, ionic strength, concentration of solution components, duration of ageing during solution movement through the wells, pipe lines and equipment influence on final concentration and size of colloidal particles.

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