POLYCONDENSATION KINETICS OF ORTHOSILICIC ACID IN HYDROTHERMAL SOLUTIONS

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ABSTRACT

The polycondensation kinetics of orthosilicic acid in hydrothermal solutions were studied experimentally at different temperatures, pH, and ionic strengths. As a result of the mathematical processing of experimental data, equations approximating the time dependence of the polycondensation process and the dependence of the polycondensation rate constant on the solution ionic strength were obtained. Experimental data on the kinetics of the reverse process of dissolving colloidal silica were obtained for different temperatures and pH. Experimental data on polycondensation kinetics were compared with the results of numerical simulation.

INTRODUCTION

Colloidal silica formed in hydrothermal solution in several stages (Chukhrov F.V., 1955, Potapov V.V., 2000б 2001, 2003). Primarily silicium enters the solution as molecules of silicic acids as the result of chemical interaction of water with alumosilicate minerals of hydrothermal field rocks at a depth of 1.0-3.5 km in zones of thermal anomalies at increased temperature (up to 250-350^{0}C) and pressure (4.0-20 MPa). Hydrothermal solution is multicomponent: Na, K, Si, Ca, Mg, Al, Fe, Cl, S, C, B, Li, As, Cu, Zn, Ag, Au and other compounds are present in it in ionic and molecular form.

At the temperature of 250-350^{0}C, when solution has a contact with rock minerals, total content of silicium C_t (mole/kg) in water can be evaluated by α-quartz solubility (Crerar D.A., Anderson G.M. , 1971) :

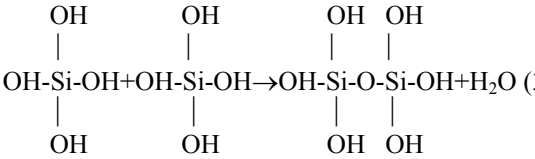
$$\lg C_t = -1.468+252.9/T-3.217\cdot10^5/T^2, \quad (1)$$

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-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 (mole/kg) for pure water depends on absolute temperature T by the following way:

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

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 siilica) 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):



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

As the result of nucleation and polymerization particles of the colloid-sized hydrated silica $mSiO_2 \cdot nH_2O$ are formed in the solution. Part of the silanol groups SiOH on the particle surface dissociate with the detachment of H^+ proton, and the particle surface get negative electric charge. The negative surface charge prevents particle from coagulation due to the forces of electrostatic repulsion and stabilize of colloidal silica in the solution.

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 (mol/kg) (Weres 0., Yee A., Tsao L., 1980, 1981):

$$\lg C_{dimer} = -2.10 - 775/T, \quad (5)$$

$$\lg C_{trimer} = -3.22 - 919/T, \quad (6)$$

Constant dependence of the 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) :

$$\lg K_1 = -2549/T - 15.36\cdot10^{-6}\cdot T^2, \quad (7)$$

$$\lg K_2 = 5.37 - 3320/T - 20\cdot10^{-3}\cdot T, \quad (8)$$

Ions of metasilicic acid H_2SiO_3 are present in water solution except ions of orthosilicic acid. According to the equations (5), (6), 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, 1981) - < 0.1 %. Fraction of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ ions under these conditions is not more than 14.0 %.

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 and 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 (Harper R.T., Thain I.A., Johnston J.H., 1992, 1995; Harper R.T., Johnston J.H., Wiseman N., 1997): for making paper, rubber, glue, glass, ceramics, brick, cement, concrete, sorbents, catalysts, and in chromatography and electronics also.

1. CHEMICAL COMPOSITION OF LIQUID PHASE OF HYDROTHERMAL HEAT CARRIER

Experiments on researching of physical and chemical characteristics were carried out using hydrothermal separate from productive wells of Verkhne-Mutnovsky geothermal electric power plant and, besides, from wells 014, 4E, 5E, A2 of Mutnovskoe field. pH value of samples of solution at 20°C was within 8.0-9.4, total mineralization – 1.0 – 2.5 g/kg, ionic strength of solution – 10 – 20 mmole/kg. Total content of silica in samples was 650 – 820 mg/kg, concentration of monomeric silica (monomeric orthosilicic acid) corresponded to solubility C_e at the temperature of the experiments. The most experiments were carried out with separate samples from the reinjection pipe-line of Verkhne-Mutnovsky geothermal electric power plant.

Productive wells 048, 049, 055 of Verkhne-Mutnovsky geothermal electric power plant(GeoPP) bring heat carrier to the surface as vapour-water mixture (VWM) with mass vapour content of 0.2-0.3. Mouth binding of productive wells is united in one common collector in which three flows of heat carrier mix. In separators of first and second line at pressure of 0.8 MPa and temperature 170.4°C vapour-water mixture is divided into vapour phase which is fed to the turbines and liquid phase (separate) with consumption of 50-55 kg/s. Separate comes to expander where pressure is about 0.4 MPa, and temperature – near 143.6°C. From expander separate with pressure of 0.4 bar is pumped through two reinjected wells back to the rocks of hydrothermal field. Heat-exchanger was settled on the reinjection pipe-line of geothermal electric power plant.

Table 1

Concentrations of anions and cations in hydrothermal separate from reinjection line of Verkhne-Mutnovsky geothermal electric power plant, I_s = 14.218 mmole/kg. n.d.- concentration was not determined, (-)- values were not calculated.

Component	mg/l	mg·equiv/l	
		mg·equiv/l	%mg·equiv/l
Na^+	239.4	10.413	88.044
K^+	42.0	1.074	9.080
Ca^{2+}	1.6	0.0798	0.6747
Mg^{2+}	0.72	0.0592	0.5005
$Fe^{2,3+}$	<0.1	<0.0053	0.0448
Al^{3+}	0.27	0.033	0.2790
NH_4^+	1.1	0.0609	0.5149
Li^+	0.71	0.102	0.8624
Sum of cations	285.9	11.827	100.0
Cl^-	198.5	5.591	47.664
HCO_3^-	81.0	1.327	11.312
CO_3^{2-}	19.9	0.663	5.652
SO_4^{2-}	192.1	3.9995	34.096
HS^-	4.95	0.15	
H_2S^0	5.92	-	-
F^-	n.d.	n.d.	-
Sum of anions	496.5	11.73	100.0
H_3BO_3	106.9	-	-
$(H_4SiO_4)_t$	1190	-	-
$(H_4SiO_4)_s$	222	-	-
Mineralization M_h,	1638.9	-	-
pH	9.35	-	-

Table 2c

Results of chemical analysis of condensate and separate samples from well 4E, mg/kg. T Na/K – *resrvoir temperature calculated from Na-K geotermometer, T SiO_2 - resrvoir temperature calculated from SiO_2 geotermometer.*

	separate			
date	5.11.98	7.11.98	9.11.98	12.11.98
pH	9.06	9.09	9.14	9.15
NH_4^+	0.3	0.3	0.3	0.55
Na^+	273	275	271	272
K^+	54	54.5	53.5	54.5
Li^+	1.42	1.43	1.43	1.42
Ca^+	3	3	3	3
Mg^{2+}	<0.24	<0.24	<0.24	<0.24
$Fe^{2+\ 3+}$	<0.3	<0.3	<0.3	<0.3
Al^{3+}	<0.27	<0.27	<0.27	<0.27
Cl^-	244.9	244.9	244.9	244.9
SO_4^{2-}	249.7	249.7	249.7	249.7
HCO_3^-	81.1	80.5	79.3	79.3
CO_3^{2-}	6.3	6.6	7.2	7.2
F^-	4.24	4.24	4.24	4.24
H_3BO_3	110.8	109.5	110.8	109.5
H_4SiO_4 (p)	187.3	200.3	186.6	197.7
H_4SiO_4 (к)	1048	1087	1160	1116
As	3.3	4.07	4.9	4.2
T Na/K, ^{0}C	275.1	275.4	274.8	277.1
T SiO_2, ^{0}C	254.1	259.7	265.8	258.7
T SiO_2(2), ^{0}C	278.8	282.5	289.3	285.3

Conentrations of basic components of hydrothermal separate solution selected from the reinjection pipeline of GeoPP are given in Table 1. Data on gas concentration in vapour phase of hydrothermal heat carrier of well 4E obtained in the tests with wells of Mutnovskoye field (Potapov V.V., Kashpura V.N., Alekseev V.I., 2001) shows that CO_2, H_2S, N_2 prevail in gas composition of heat carrier. Table 2 contains data on chemical composition of separate from well 4E of Mutnovskoye geothermal field.

Solution of separate from Mutnovskoye field is of chloride-sulphate-sodium-potassium type of hydrothermal solutions. Kurlov's formula of chemical composition of water which reflects percentage of anions and cations in milligram-equivalents is the following: $Cl47.66 \cdot SO_4 34.09/Na88.04 \cdot K9.08$. Dependence of ionic strength I_s (mole/kg) of hydrothermal solution from wells of Mutnovskoe field on mineralization M_h (mg/kg) is expressed by the equation:

$$I_s = A_I \cdot 10^{-6} \cdot M_h, \qquad (9)$$

where A_I – is coefficient which is (7.35 – 8.68) mole/mg for separate, and 17.34 mole/mg for vapour condensate.

Chemical composition of separate from well 103 of Pauzhgetskoe field is presented in the Table 3.

Table 3

Concentrations of anions and cations in hydrothermal separate of well 103 of Pauzhgetskoe field. I_s=52.401 mmol/kg, σ=5.03·10^{-3} (Om·cm)$^{-1}$ (18.4 ^{0}C), n.d.- concentration was not determined, (-)- values were not calculated.

Component	mg/l	mg·equiv/l	
		mg·equiv/l	mg·equiv/l, %
Na^+	877.5	38.15	86.1
K^+	98.9	2.54	5.7
Ca^{2+}	54.08	2.7	6.1
Mg^{2+}	<1.2	-	-
$Fe^{2,+}$	<0.1	-	-
Fe^{3+}	<0.3	-	-
Al^{3+}	n.d.	-	-
NH_4^+	1.0	0.06	0.1
Li^+	6.1	0.88	2.0
Sum of cations	1037.58	44.33	100.0
Cl^-	1418.4	40.0	91.1
HCO_3^-	44.82	0.73	1.7
CO_3^{2-}	0.45	0.02	0.0
SO_4^{2-}	134.48	2.8	6.4
$H_3SiO_4^-$	3.98	0.04	0.1
$H_2BO_3^-$	14.51	0.24	0.6
F^-	1.56	0.082	0.19
Sum of anions	1618.2	43.91	100.0
H_3BO_3	207.02	-	-
$(H_4SiO_4)_t$	512.0	-	-
Minera-lization	3458	-	-
pH	8.03	-	-

2. MEASUREMENT OF RADII OF COLLOIDAL SILICA PARTICLES IN SEPARATE SAMPLES

When heat carrier comes up through the productive wells of geothermal electric power plant, then because of decrease in temperature and transformation of a part of heat carrier in vapour phase solution oversaturated relatively to solubility of amorphous silica comes to the surface. This leads to the development of nucleation and polymerization of orthosilicic acid molecules, in form of which silicium is mainly present in solution before coming to the surface. Formation of colloidal silica particles is the consequence of nucleation and polymerization. Flowing of separate through pipelines, heat equipment and reinjection wells is accompanied by the formation of complexes of silica particles on the walls of canals and growth of solid deposits layers.

The sizes and diffusion coefficients of colloidal silica particles which formed in hydrothermal solution during nucleation and polymerization were measured by the method of photon correlation spectroscopy (PCS). Table 4 presents results of measurement in one of the samples of hydrothermal solution as dependence of amplitude of monochromatic laser light scattering with wave length 633.0 nm S_{am} on radius of particles R. Amplitude of scattering is proportional to quantity of particles with radii in corresponding value range. Mathematical processing of data on light scattering was done for particles having radii from 1.0 to 10000 nm. Average radius for particles of mentioned solution sample was 11.09 ± 0.18 nm, diffusion coefficient – 1.923 ± 0.03 cm^2/s (Table 4).

Investigations carried out by the method of photon correlation spectroscopy in hydrothermal solution samples showed, that the main fraction of particles had dimensions from 1.0 to 50.0 nm. Average radius of particles has values from 7.0 to 25.0 nm. Quantity of particles with dimensions more than 100.0 – 200.0 nm is relatively small.

3. RESULTS OF EXPERIMENTS ON ORTHOSILICIC ACID POLYMERIZATION AT DIFFERENT PARAMETERS OF HYDROTHERMAL SOLUTION

Experiments on orthosilicic acid polymerization were carried out at 50 ^{0}C (Table 5). For the accomplishment of the experiment the sample of hydrothermal solution was heated from 20 to 100 ^{0}C and the tempreture was of 100 ^{0}C during the time enough to dissolve of colloidal silica. So initial concentration orthosilicic acid C_s was equal to of amorphous silica solubility at 100 ^{0}C. After heating at 100 ^{0}C solution sample was quickly cooled to 50^{0}C and then decreasing of concentration C_s in time was determined. The time of orthosolicic acid polymerization τ_p was about 4,0 hours and the constant k_p= 0,25 h^{-1}.

Table 4

Results of measurements by the method of photon correlation spectroscopy in sample of hydrothermal separate of Verkhne-Mutnovsky geothermal electric power plant.

R, nm	S_{am}	R, nm	S_{am}
1.0 - 1.44	0.0222322	83.17 - 120.22	0.0270527
1.44 -2.089	0.0335038	120.226 - 173.78	0.0169228
2.0893 - 3.01995	0.0479776	173.78 - 251.189	0.00925547
3.019 - 4.365	0.0649203	251.189 - 363.078	0.00361224
4.365 - 6.309	0.0820874	363.078 - 524.807	0.0
6.309 - 9.12	0.0956918	524.807 – 758.578	0.0
9.12 -13.18	0.101794	758.578 – 1096.48	0.0
13.18 - 19.05	0.0986029	1096.48 – 1584.89	0.0
19.05 - 27.54	0.0875023	1584.89 - 2290.87	0.0
27.54 - 39.81	0.0718849	2290.87 – 3311.3	0.0
39.81 - 57.54	0.0552209	3311.3 – 4786.3	0.0
57.544 - 83.176	0.0398972	4786.3 – 10000.0	0.0

Table 5.

Experimental data on orthosilicic acid polymerization at the temperature of 50 ^{0}C, pH=8,75. C_e (50^{0}C)=206,95 mg/kg.

t_p	0	2 min	10 min	20 min	30 min	40 min
C_s, mg/kg	412.5	403.1	387.5	375.0	365.6	356.25
t_p	40 min	50 min	1 hour	1 h 10 min	1h 20 min	1 h 30 min
C_s, mg/kg	356.25	350.0	331.25	321.9	321.9	321.9
t_p	1 h 40 min	1 h 50 min	2 h	2 h 20 min	2 h 40 min	3 h
C_s, mg/kg	321.9	321.9	312.5	312.5	312.5	306.25
t_p	3 h	3 h 20 min	3 h 40 min	4 h	4 h 30 min	5 h
C_s, mg/kg	306.25	296.9	296.9	281.25	281.25	281.25

Table 6.

Results of experiments on kinetics of orthosilicic acid polymerization at different pH of hydrothermal solution, 20^{0}C

t_p	C_s, mg/kg pH=8	t_p	C_s, mg/kg pH=7	C_s, mg/kg pH=6	C_s, mg/kg pH=5	C_s, mg/kg pH= 4
0 min	415.6	0 min	406.25	403.1	406.3	403.1
5 min	412.5	5 min	403.1	403.1	396.9	403.1
10 min	406.3	1 h	387.5	393.8	393.8	403.1
20 min	406.2	2 h	387.5	387.5	393.8	403.1
30 min	393.8	3 h	375.0	387.5	393.8	396.9
40 min	384.4	4 h	371.9	387.5	393.8	396.9
50 min	375.0	5 h	371.9	387.5	387.5	393.75
1 hour	371.9	1 day	212.5	384.4	387.5	393.75
1 h 10 min	371.9	2 day	171.9	365.6	371.9	378.1
1 h 20 min	365.6	3 day	150.0	362.5	365.6	375.0
1 h 30 min	356.25	4 day	150.0	362.5	365.6	375.0
1 h 40 min	351.9	7 day	146.9	306.25	353.1	375.0
1 h 50 min	350.0	8 day	146.9	287.5	343.75	375.0
2 hour	340.6	9 day	146.9	259.4	340.6	375.0
2 h 20 min	331.25	10 day	143.75	234.4	331.25	365.6
2 h 40 min	321.9	11 day	140.6	212.5	321.9	356.25
3 hour	312.5	14 day	140.6	193.75	296.9	356.25
3 h 20 min	296.9	17 day	137.5	171.9	215.6	356.25
3 h 40 min	290.6	21 day	137.5	156.25	171.9	325.0
4 hour	287.5	24 day	137.5	156.25	165.6	325.0
4 h 30 min	287.5	28 day	137.5	156.25	165.6	325.0
5 hour	287.5	31 day	137.5	156.25	165.6	325.0

Results of the experiments on orthosilicic acid polymerization at different pH of hydrothermal solution are shown in the Table 6. It was found that solution acidification lead to decreasing of reaction rate constant k_p. At pH=5.0-4.0 inhibition of polymerization reaction was observed. 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.

Table 7.

Orthosilicic acid concentration C_s (mg/kg) versus time of polymerization t_p at different concentration m_{NaCl} of added salt NaCl, 20 ^{0}C. n.d. - not determined.

t_p	m_{NaCl}, mole/kg										
	0.0	0.05	0.1	0.125	0.25	0.375	0.5	0.563	0.625	0.75	1.0
0 min	440.6	428.1	465.6	425.0	443.7	443.7	434.4	431.2	418.7	428.1	437.5
10 min	409.4	400.0	443.7	368.7	325.0	312.5	353.1	343.7	321.9	306.2	303.1
20 min	359.4	331.2	356.2	306.2	275.0	243.7	234.4	250.0	250.0	221.9	218.75
30 min	325.0	303.1	300.0	271.9	240.6	221.9	218.7	234.4	212.5	200.0	203.1
40 min	296.9	293.7	271.9	256.2	234.4	212.5	218.7	212.5	200	196.9	196.9
50 min	278.1	262.5	250.0	234.4	225.0	206.2	209.4	200.0	193.7	187.5	187.5
1 h	271.9	240.6	240.6	225.0	218.7	200.0	196.9	200.0	190.6	178.1	184.4
2 h	234.4	221.9	234.4	206.2	200.0	187.5	181.2	181.2	171.9	178.1	184.4
2. 33 h	234.4	212.5	209.4	206.2	196.6	187.5	181.2	181.2	171.9	178.1	n.d.
2. 66 h	231.3	209.4	209.4	200.0	196.6	187.5	181.2	181.2	171.9	171.9	n.d.
3 h	228.1	206.2	206.2	190.6	196.6	178.1	178.1	171.9	165.6	171.9	n.d.
3. 33 h	228.1	203.1	206.2	187.5	196.6	171.9	178.1	171.9	165.6	168.7	n.d.
3.66 h	225.0	203.1	203.1	184.4	196.6	168.7	178.1	171.9	162.5	168.7	n.d.
4 h	212.5	200.0	203.1	184.4	184.4	165.6	178.1	171.9	156.2	168.7	n.d.
4.5 h	212.5	193.7	203.1	181.2	181.2	165.6	178.1	171.9	156.2	162.5	n.d.
5 h	209.4	193.7	200.0	181.2	181.2	168.7	171.9	171.9	156.2	162.5	n.d.
24 h	175.0	181.2	200.0	165.6	n.d.	n.d.	150.0	n.d.	n.d.	n.d.	n.d.

Values of the time τ_p and constant of reaction rate k_p for pH from 8 to 4 were the follows: pH=8 -k_p=0.108 h^{-1}, τ_p=9.2 h; pH=7 - k_p=0.07 h^{-1}, τ_p=14.2 h; pH=6 - k_p=0.0044 h^{-1}, τ_p=225 h; pH=5 - k_p=0.00264 h^{-1}, τ_p=377.5 h; pH= 4 k_p=0.00031 h^{-1}, τ_p=3240 h.

Table 8.

Constants k_p and τ_p of reaction of orthosilicic acid polymerization versus ionic strength I_s and parameter x_I.

m_{NaCl}. mole/kg	I_s, mole/kg	x_I	τ_p,		k_p, h^{-1}	ln k_p
			min	hour		
0	0.0142	0.10648	100	1.66	0.602	-0.506
0.05	0.0642	0.2022	60	1.0	1.0	0.0
0.1	0.1142	0.2526	40	0.66	1.515	0.415
0.125	0.1392	0.27172	40	0.66	1.515	0.415
0.25	0.2642	0.3395	25	0.416	2.403	0.877
0.375	0.3592	0.37474	19	0.316	3.146	1.152
0.5	0.5142	0.417615	18	0.30	3.33	1.204
0.563	0.5772	0.43173	18	0.30	3.33	1.204
0.625	0.6392	0.44429	18	0.30	3.33	1.204
0.75	0.7642	0.4664	15	0.25	4.0	1.386
1.0	1.0142	0.5018	15	0.25	4.0	1.386

Kinetics of orthosilicic acid polymerisation at different values of solution ionic strength was investigated at 20 ^{0}C. Ionic strength was changed by NaCl addition, the quantity of added salt was from 0 to 1.0 mole/kg. Results of the experiments at different concentrations of added salts are given in the Table 7. Results show how the constant k_p increase with rising of solution ionic strength.

In the Table 8 results of mathematical analyses of experimental data are presented: values of the constants k_p and τ_p at different values of ionic strength I_s calculated from experimental data. We checked the possibility to approximate logarithm ln k_p by the function with argument $x_I = I_s^{0,5}/(1+I_s^{0,5})$ (Table 8).

Table 9.

Concentration of orthosilicic acid in hydrothermal solution of Pauzhgetskoye field, well GK-3, 20 ^{0}C.

t_p, hour	C_s, mg/kg
0	315.6
1	315.6
2	306.25
3	306.25
4	296.9
5	278.1
21	171.9
25	168.75
26	159.4

Mathematical analyses lead us to the conclusion that in the region of x_I values from 0 to 0.4, that is values of I_s from 0 до 0.36-0.51 mole/kg the dependence of k_p versus x_I is near linear:

$\ln k_p = A + B \cdot x_I$
where A=-1.0, B=5.0.
When x_I greater than 0,4 dependence ln k_p become slower than linear.

Table 9 shows results of experiments with separate from well GK-3 of Pauzhgetskoye field are presented. Constant k_p for solution of Pauzhgetskoye field is lower than for Mutnovskoye field though ionic strength of the water from Pauzhgetskoye field higher than for Mutnovskoye.

4. MODELING STUDY OF NUCLEATION OF SILICIC ACID MOLECULES

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

$I_N = Q_{LP} \cdot Z \cdot (R_{md} \cdot A_{cr} \cdot N_A \cdot M_{Si}^{-1}) \cdot \exp(-\Delta F_{cr}/k_B \cdot T)$ (10)

where ΔF_{cr} – is a change in free energy, connected with the formation of critical radius nucleus R_{cr}, $R_{cr} = 2 \cdot \sigma_{sw} \cdot M_{Si}/(\rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N)$, A_{cr} – surface area of critical nucleus, $A_{cr} = 4 \cdot \pi \cdot R_{cr}^2$, $\Delta F_{cr} = \sigma_{sw} \cdot A_{cr}/3 = (16 \cdot \pi/3) \cdot \sigma_{sw}^3 (M_{SI}/\rho \cdot N_A \cdot k_B \cdot T \cdot \ln S_N)^2$, σ_{sw} – coefficient of surface tension at the boundary silica-water, R_{md} – rate of molecular deposition of SiO_2 on the solid surface, г·(cm^2·min)$^{-1}$, k_B – Boltzmann's constant, M_{Si} – molecular mass SiO_2, N_A – Avogadro number, Q_{LP} – Loze-Paunde's factor, $Q_{LP} = 3.34 \cdot 10^{25}$ 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:

$R_{md} = F(pH, pH_{nom}) \cdot k_{OH}(T) \cdot f_f(S_a) \cdot (1 - S_N^{-1})$ (11)

$\lg k_{OH}(T) = 3.1171 - 4296.6/T$ (12)

$f_f = S_a^5$, $S_a < S_t$ (13-1)

$f_f = S_t^5 + 5 \cdot S_t^4 \cdot (S_a - S_t)$, $S_a > S_t$, (13-2)

$\lg S_t = 0.0977 + 75.84/T$, (13-3)

$F(pH, pH_{nom}) = h_f \cdot f(pH) + (1 - h_f) \cdot f(pH_{nom})$ (14-1)

$f'(pH_{nom}) = f(pH_{nom})/f(7.0),$ (14-2)

$\lg f = pH - pK_i + \lg [Na^+]$ (14-3)

$\sigma_{sw} = H_\sigma - T \cdot S_\sigma - 2.302 \cdot 10^{-3} \cdot n_o \cdot k \cdot T \cdot I(pH, pH_{nom})$ (15-1)

$$I = 0{,}119 \int_{-\infty}^{pH} F(pH', pH_{nom}(pH'))dpH' \quad , \qquad (15\text{-}2)$$

where $S_a = (1-\alpha_i) \cdot S_N$, α_i – fraction of silicic acid in ionized form, $pH_{nom} = pH + \lg ([Na^+]/0.069)$, $[Na^+]$ – 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·K, $n_o = 6.84$ nm^{-2}.

Equation (10) 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:

$I_N(t) = I_N \cdot (1 - e^{-t/\tau in})$, (16)

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:

$\tau_{in} = 1.08 \cdot 10^{-6} \cdot (6 \cdot R_{md})^{-1} \cdot (Q_{LP} \cdot Z \cdot R_{cr}^2 \cdot \exp(-\Delta F_{cr}/k_B \cdot T))^{-0,25}$ (17)

Calculations by equations (1), (10)-(17) 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 $S_N = 5.952$, $\sigma_{sw} = 24.46 \cdot 10^{-3}$ J/m^2, $R_{cr} = 0.30$ nm, $\tau_{in} = 2.66$ min, $I_N = 2.00 \cdot 10^{21}$ nuclei/kg·s,; at 100^{0}C - $S_N = 1.726$, $\sigma_{sw} = 13.84 \cdot 10^{-3}$ J/m^2, $R_{cr} = 0.44$ nm, $\tau_{in} = 0.69$ min, $I_N = 6.40 \cdot 10^{21}$ nuclei/kg·s; at 153^{0}C - $S_N = 1.046$, $\sigma_{sw} = 6.91 \cdot 10^{-3}$ J/m^2, $R_{cr} = 2.34$ nm, $\tau_{in} = 3966.8$ min, $I_N = 6.72 \cdot 10^9$ nuclei/kg·s,. 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 - $\sigma_{sw} = 46.79 \cdot 10^{-3}$ J/m^2, $R_{cr} = 0.58$ nm, $\tau_{in} = 368.3$ min; at pH = 6.0 - $\sigma_{sw} = 48.96 \cdot 10^{-3}$ J/m^2, $R_{cr} = 0.61$ nm, $\tau_{in} = 3967.2$ min; at pH = 5.0 - $\sigma_{sw} = 49.27 \cdot 10^{-3}$ J/m^2, $R_{cr} = 0.61$ nm, $\tau_{in} = 39162.0$ min. 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.

Ions of metasilicic acid H_2SiO_3 are present in water solution except ions of orthosilicic acid. According to the equations (5), (6), 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) - < 0.1 %. Fraction of $H_3SiO_4^-$ and $H_2SiO_4^{2-}$ ions under these conditions is not more than 14.0 %.

CONCLUSIONS

1. According to concentrations of silica, sodium and potassium in separate solution from wells of Mutnovskoye field temperature of heat carrier in drained zone of hydrothermal reservoir is within a range from 250 to 300^{0}C. In solution of separate ions of sodium and potassium have the largest concentration among cations, chlorine-ion and sulphate-ion - among anions. Separate is referred to chloride-sulphate-sodium-potassium type of hydrothermal solutions. Separate of Pauzghetskoye field is formed at the lower temperatures than at Mutnovskoye field so silica content in separate of Pauzghetskoye field lower. In separate of Pauzghetskoye field cations sodium, potassium and calcium have the largest concentration among cations, chlorine-ion and sulphate-ion - among anions.

2. Experiments with samples of separate from Mutnovskoye field and from Pauzhgetskoye field shows that orthosilicic acid polymerized much more rapidly in solution of Mutnovskoye field. Constant k_p for solution of Pauzhgetskoye field is lower than for Mutnovskoye field though ionic strength of the water from Pauzhgetskoye field higher than for Mutnovskoye.

3. It was found in the experiments on orthosilicic acid polymerization at different pH that solution acidification lead to decreasing of reaction rate constant k_p. At pH=5.0-4.0 inhibition of polymerization reaction was observed. Values of the time τ_p and constant of reaction rate k_p strongly depend on solution pH.

4. Experiments on kinetics of orthosilicic acid polymerisation at different values of solution ionic strength at 20 ^{0}C show that the constant k_p increase with increasing of solution ionic strength. We calculated that in the region of x_I values from 0 to 0.4, that is values of I_s from 0 до 0.36-0.51 mole/kg the dependence of k_p versus x_I is near linear. When x_I greater than 0,4 dependence ln k_p become slower than linear.

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