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SILICA COAGULATION AND PRECIPITATION IN HYDROTHERMAL SOLUTION (KAMCHATKA, RUSSIA)

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ABSTRACT

Studied were the processes of coagulation and precipitation of silica in the hydrothermal solution. Experiments were carried out on colloid silica coagulation and precipitation by various types of metal cations. Residual concentrations of silica and cations in the treated solution were determined, as well as pH and amount of Ca, Mg, Al and Fe in the settled material depending upon the coagulants consumption at 20°C and 96°C. Stability of colloid silica in hydrothermal solution was studied, as well as the mechanism of coagulation and precipitation of silica by metal cations.

INTRODUCTION

In December 1999 at the Mutnovskoye geothermal field Verkhne-Muntovskaya geothermal electric power station with capacity of 12 MW was set in operation (Britvin O.V., Povarov O.A., et al., 1999). In October 2002 Mutnovskaya geothermal electric power station with capacity of 50 MW started functioning. Because of the danger of solid deposits' formation in reinjection wells reinjection of the separate at the stations is carried out at high temperature (140–160°C), which reduces the efficiency of geothermal power usage (Kashpura, V.N., Potapov, V.V., 2000, Potapov V.V. et al., 2001, 2002).

To increase the efficiency of high-temperature hydrothermal heat carrier utilization it is necessary to work out technology of silica extraction from the separate flow (Harper, R.T., 1992, 1995, 1997, Rothbaum, H.P., Anderton, B.H., 1975). Parameters of the extraction technology depend upon physical-chemical characteristics of the colloid silica system in hydrothermal solution, that is kinetics of monomeric silica polymerization, size and mobility of colloid silica particles, electric charge of the particle surface and sorption capacity of particle surface with respect to cations-coagulants.

The paper reveals the results of the experiments on silica coagulation and precipitation in hydrothermal solution by metal cations of Ca^{2+}, Mg^{2+} and Al^{3+}, Fe^{3+}. The data obtained can be used to develop the technology of precipitation of silica with variable physical-chemical properties.

FORMATION OF COLLOID SILICA IN HYDROTHERMAL SOLUTION

Synthesis of colloid silica system in hydrothermal solution passes several stages (Chan, S.H., 1989). Primarily silica enters the solution together with other compounds as the result of chemical interaction of water with silica-alumina minerals of hydrothermal field rocks deep in the zones of thermal anomalies at increased temperatures (250–300°C and more) and pressures (40–10.0 bar and more). At temperature of 250–300°C silicium is present in solution mainly in monomeric form as molecules of silica acid H_4SiO_4 (Fleming B.A., Crerar D.A., 1982). Total content C_t of silica SiO_2 in water under such conditions can be estimated by the solubility of quartz at 250-300°C: C_t=500-700 mg/kg (Karpov G.A., 1976).

When accending to the surface along the productive wells of hydrothermal electric power stations, pressure and temperature of the solution decrease and the solution partially evaporates. Total silica content C_t in water reaches 700-1000 mg/kg and more. Water solution becomes oversaturated with respect to the solubility of amorphous silica C_e. Such a state of monomeric silica in water solution is unstable. Oversaturation of the solution S_m equal to the difference (C_s-C_e) of monomeric silica concentration 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.K., 1982):

$Si(OH)_4 + Si(OH)_4 \rightarrow Si_2O(OH)_6 + H_2O$ (1)

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

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 colloid silica in the solution.

Unsteadiness of the colloid system near the surface of the conducting channel leads to the formation of amorphous silica deposits from hydrothermal heat-carrier flow on the inner surface of thermal equipment and wells of the Geothermal electric power stations.

STUDIES OF THE KINETICS OF MONOMERIC SILICA POLYMERIZATION

Kinetics of colloid silica polymerization reaction was studied at 20°C and pH from 8.0-9.4 to 5.0. At the natural value of pH=8.4, dependence of oversaturation S_m (mg/kg) upon the duration of polymerization t_p was as follows: 0 h- 230.6, 1.0 h- 140.0, 2.0 h- 74.4, 3.0 h- 41.9, 4.0 h- 30.6, 5.0 h- 23.1, 6.0 h- 21.25, 7.0 h- 21.25, 8.0 h- 19.37, 9.0 h- 18.75, 10.0 h- 18.12. All the curves $S_m(t_p)$ obtained from the series of measurements at 20°C and natural pH = 9.4-8.0 were of the same shape with convexity faced downward to the abscissa axis and characterized by close values of the derivative dS_m/dt_p.

The function S_m follows the differential equation (Iler, R.K., 1982, Rothbaum H.P., Rohde A.G. 1979):

$$dS_m/dt_p = -k_p \cdot S_m^n, \quad (3)$$

where k_p- is a constant of polymerization reaction depending upon temperature, pH, ionic strength of the solution, n- 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=1:

$$\ln S_m(t_p) = \ln S_0 - t_p/\tau_p, \quad (4)$$

$$S_m(t_p) = S_0 \cdot \exp(-t_p/\tau_p), \quad (5)$$

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

Experimental dependence $\ln S_m(t_p)$ was approximated by equation (4) based on which constants τ_p and k_p were found. At 20^0C and pH=8.0-9.4 average value of τ_p was 1.98-2.06 h, k_p=0.485 h^{-1}. According to Fleming's model polymerization reaction is the first order reaction regarding both the difference (C_s-C_e), and surface concentration C_{SIO} of ionized hydroxyl groups SiO^-, that is the surface charge σ_s of colloid particles (Fleming B.A., 1986):

$$dC_s/dt_p = -k_f \cdot A_s \cdot (C_s - C_e) \cdot C_{SIO}, \quad (6)$$

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

$$k_f = k_{f0} \cdot \exp((A_{DH} \cdot I_s^{0.5})/(1 + I_s^{0.5})), \quad (7)$$

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

$$\ln k_{f0} = 22.1 - E_p/R_gT \pm 2.0, \quad (8)$$

where E_p- activation energy of polymerization reaction, E_p=54836.6 J/mole (Fleming B.A., 1986), R_g- gas constant, R_g=8.31 J/mole·K. At A_{DH}=1.238, I_s=0.0106 mole/l, pH=7.20, A_s=4200 cm^2/cm^3 and T=25 C, value k_p, obtained by Fleming (Fleming B.A., 1986), equaled $1.36 \cdot 10^{-4}$ c^{-1}=0.489 h^{-1}, which was close to the value we obtained at 20°C, I_s=0.0142 mole/kg, pH=8.0-9.4, A_s=753.4-1076.3 cm^2/cm^3.

Calculated by equations (6)–(8) constants k_p and τ_p showed the following values at high temperatures: 50^0C- τ_p=36.01 min; 75^0C- τ_p=20.91min; 100^0C- k_p=7.221 h^{-1}, τ_p=0.138 h=8.3min. Optimal duration of the separate ageing stage at 100°C is 30-40 min.

At pH=7.0 dependence $S_m(t_p)$ changed significantly, at t_p from 0 to 6 h the curve $S_m(t_p)$ was directed convexity up, derivative dS_m/dt_p was notable lower than in the solution with pH=8.9-9.4. At pH=5.0 inhibition of polymerization reaction was observed and significant changes of concentration C_s occurred only a few days after initiation of the reaction.

Primary silica particles in unpolymerized solution are sized within the limits of 0.5-1.5 nm (Potapov V.V., Kashpura V.N., Alekseev V.I., 2001). Photon correlation spectroscopy measurements showed that average radius of polymerized silica particles ranged from 7.0 to 16.0 nm.

COAGULATION AND PRECIPITATION OF SILICA WITH SLAKED LIME ADDITION

Experiments on colloid silica particles precipitation were carried out with the probes of hydrothermal solution from the productive wells of Verkhne-Mutnovskaya geothermal electric power station and from wells 014, 4E, 5E, A2 of Mutnovskoye hydrothermal field. Solution probes had identical physical-chemical characteristics, while concentration of basic compounds was as follows (mg/kg): Na^+- 239.4, K^+- 42.0, NH_4^+- 1.1, Ca^{2+}- 1.6,

Mg^{2+}- 0.72, Li^{+}- 0.71, Fe^{2+}- 0.1, Al^{3+}- 0.27, Cl^{-}- 198.5, SO_4^{2-}- 192.1, HS^{-}- 5.0, HCO_3^{-} -81.0, CO_3^{2-}- 19.9, H_3BO_3- 106.9, SiO_2- 680.0, pH=9.2. Prior to the treatment pH level of the solution probes at 20°C ranged 7.0-9.4, total mineralization - 1.0-2.5 g/kg, ionic strength of the solution – 10-20 mmole/kg.

Before its addition to the separate coagulant was dissolved in 20-50 cm^3 of hot water at temperature of 95-100°C and kept in water solution for 1-2 minutes. After addition of the coagulant the separate probe was intensively stirred during 30-40 seconds. Treatment by coagulants resulted in the color change and increasing of the solution turbidity, formation of flakes in water volume, their precipitation onto the vessel bottom and accumulation of the sediment. By the rate of flakes' settling in the Stokes movement regime effective flake size d_f was determined (Babenkov E.D., 1977):

$$d_f = (18 \cdot \mu \cdot u / \Delta\rho \cdot g)^{0.5}, \quad (10)$$

where u- rate of flakes' settling, μ- dynamic viscosity of solution, Δρ- difference between the density of silica and water, g- gravity acceleration.

Volume fraction of precipitated flakes was not more than 0.1-0.2. Precipitated material was separated from the clarified solution by pouring and dewaterized in a centrifuge with frequency up to 5500-6000 rev/min (2500-6000 g) by a 20 minutes' run, which provided the solid phase content level of about 4-6 weight %, and dried afterwards at 110-120°C. 20-60 minutes after the treatment residual concentration of silica acid (total content and concentration of monomeric silica), coagulant cations concentration and pH were determined in aliquots of the clarified solution.

Table 1

Results of lime treatment of the separate at 20°C (Ca-quantity of calcium cations injected into the solution with lime, Ca^{2+} - residual concentration of calcium cations).

CaO mg/kg	Ca, mg/kg	pH	Ca^{2+} mg/kg	C_t mg/kg	C_s mg/kg
0	0	9.29	1.6	697.0	150.3
100	71.4	10.10	43.0	158.1	158.1
150	107.1	10.48	58.5	158.0	158.0
200	142.8	10.82	77.1	158.0	158.0
300	214.2	11.42	89.2	153.0	153.0
400	285.6	11.68	87.2	137.5	131.9
500	357.0	11.6	73.1	75.6	73.8
600	428.4	12.07	76.2	75.0	71.3
800	571.2	12.16	58.1	41.3	36.3
1000	714.0	12.25	60.0	24.0	24.0
1500	1071.4	12.25	124.0	1.6	1.6

In the experiments with slaked lime at 20°C CaO consumption varied widely, ranging from 40 to 1500 mg/kg (Table 1, 2). Silica acid content in the solution decreased, while pH level grew up as the lime consumption increased (Table 1). Both colloid and monomeric silica precipitated, however monomeric silica was much more stable than colloid one. Residual concentration of Ca^{2+} cations was about 40-200 mg/kg (Table 1).

Table 2

Results of lime treatment of hydrothermal solution probes at high temperatures of 94-98^{0}C (n.d. – concentration could not be determined).

CaO mg/kg	Ca, mg/kg	pH 20^0C	C_t, mg/kg	C_s, mg/kg
0	0	9.26	718.8	135
100	71.4	9.73	344.9	244.4
200	142.8	9.76	329.8	273.0
300	214.2	9.88	315	275
400	285.6	10.32	345	322.5
500	357.0	10.1	339	334.4
600	428.4	10.16	307.8	307.8
700	499.8	10.48	260.9	260.9
800	571.2	10.92	229.7	217.2
900	642.6	11.16	190.6	190.6
1000	714.0	11.16	203.1	203.1
1100	785.4	11.57	157.0	n.d.
1200	856.8	11.68	64.9	n.d.
1300	928.2	12.09	25.6	n.d.
1500	1071	12.24	6.3	n.d.

During lime treatment practically all colloid silica precipitated already at CaO consumption of 80-100 mg/kg, which was critical at 20°C. Monomeric silica concentration started decreasing at lime consumption over 400 mg/kg at 20°C, and over 700 mg/kg at 96°C (Table 1, 2). Flake settling rate and their effective sizes depended upon the coagulant consumption and ranged within the limits of 6.5-10.2 mm/min and 14.1-17.7 μm.

Coagulation, flake formation and settling occurred much faster in hot solution than in cold one at 20°C (Table 2). Reduction of residual total silica content C_t at 94-98^{0}C occurred more slowly than at 20°C: when CaO consumption increased from 300 up to 1000 mg/kg, C_t concentration fell only from 315 down to 203.1 mg/kg (Table 2).

Freshly precipitated silica flakes appeared capable of flocculation. Flakes that were separated from the solution 50-60 minutes after addition of 100 mg/kg of CaO, were then added to the solution simultaneously with lime. Residual concentration C_t of the probes treated with addition of 60 mg/kg CaO and simultaneous addition of 500-550 mg/kg SiO_2 in the composition of fresh flakes averaged about 186 mg/kg, which indicated practically total precipitation of colloid silica.

Calcium amount and ratio of CaO/SiO_2 in the composition of the precipitated material depended upon lime. CaO consumption varied from 1500 to 80 mg/kg and CaO/SiO_2 ratio reduced from 1.50 to 0.0296. The sample precipitated at a critical value of CaO consumption – 80 mg/kg, showed the smallest amount of calcium. Amount of aluminium and iron in the samples was not great: Al_2O_3/SiO_2- 0.00916-0.00490, Fe_2O_3/SiO_2 -0.0003-0.0028. Precipitated material was of amorphous structure. Samples with low CaO/SiO_2 ratio, precipitated at modest lime consumption, turned into cristobalite after ignition at 900°C. Samples with high CaO/SiO_2 ratio showed lines of calcite $CaCO_3$ against the background of amorphous halo in the spectrums of X-ray analysis, and after ignition they turned into wollastonite $CaSiO_3$ or into a mixture of wollastonite and cristobalite.

CaO/SiO_2 ratio in the material precipitated at CaO consumption of 80 mg/kg showed that for coagulation and precipitation of all the colloid silica (500-550 мг/кг SiO_2) in hydrothermal solution it is necessary to add a critical amount of divalent cations Ca^{2+}, that is about 57-60 mg/kg=1.425-1.50 mmole/kg. At that only a small portion of them, not more than 7-8 mg/kg Ca^{2+} was absorbed by the colloid particles surface due to hydrogen H^+ substitution by calcium in SiOH groups. The cations sorbed newtralized the negative surface charge of colloid particles and participated in the formation of bridge bonds between the particles and in coagulation of the particles. Mechanism of colloid particles coagulation and precipitation was similar to that established in the experiments of Iler R.K. and James R.O., Healy Th.W., (Iler, R.K., 1975, James R.O., Healy Th.W., 1972).

In reactions of neutralization and bridge bond formation up to 47-48 molecules of precipitated SiO_2 corresponded to 1 Ca^{2+} cation. If CaO consumption increase over 80 mg/kg unlimited saturation of colloid particles surface by calcium cations occurred, as well as increase of CaO/SiO_2 ratio in the precipitated material.

COAGULATION AND PRECIPITATION OF SILICA WITH SEA WATER ADDITION

A series of experiments on separate treatment by slaked lime with seawater injection were conducted. Seawater showed pH level of 8.3 and increased natural concentrations of cations of calcium (Ca^{2+} = 210 mg/kg) and magnesium (Mg^{2+} = 699 mg/kg. Treatment was carried out at lime consumption lower than the critical one (CaO = 70-40 mg/kg), seawater consumption amounted 15-100 cm^3/kg.

For stable precipitation of silica and flake-formation it was necessary to inject the following volumes of seawater: 15-20 cm^3/kg of seawater – at lime consumption of 70 mg/kg, 25-30 cm^3 of seawater – at CaO consumption of 60 mg/kg, and about 40 cm^3/kg of seawater – at lime consumption of 40-50 mg/kg. Total content of SiO_2 reduced to 140-190 mg/kg, which corresponded to almost complete precipitation of colloid silica. Seawater addition compensated the increasing pH of the solution after its treatment with lime.

Table 3

Results of the hydrothermal separate probe treatment with addition of lime and sea water at 20° (SW – seawater consumption, (Ca+Mg) – overall quantity of calcium and magnesium cations added with sea water).

CaO, mg/kg	SW, cm^3/kg	(Ca+Mg), mg/kg	pH	C_t, mg/kg	C_s, mg/kg
0	0	0.0	9.10	740.6	212.5
70	10	61.0	9.66	178.8	170.6
70	15	66.5	9.73	194.4	168.8
70	20	72.0	9.62	156.3	155.0
70	50	105.0	9.38	172.5	132.5
70	100	160.0	9.21	149.4	125.6
60	20	64.8	9.51	188.8	156.9
60	25	70.34	9.70	164.3	156.3
60	30	75.8	9.53	178.1	146.3
50	50	90.7	9.26	175.0	145.6
50	60	101.7	9.28	166.8	148.4
50	75	118.2	9.22	162.2	152.4
50	100	145.7	9.24	140.6	133.1
40	40	72.5	9.02	181.2	150.0
40	50	83.5	9.05	164.3	137.5
40	100	138.5	9.20	121.9	115.6

Table 4

Results of hydothermal solution treatment with addition of sea water at 20°C; (Ca+Mg) – overall quantity of Ca^{2+} и Mg^{2+} cations injected with sea water, SW – seawater consumption, cm^3/kg

SW	(Ca+Mg), mg/kg	pH	C_t, mg/kg	C_s, mg/kg	Ca^{2+}, mg/kg	Mg^{2+}, mg/kg
0	0	9.15	678.12	143.75	1.6	0.72
100	147.8	9.08	181.25	137.5	32.06	114.20
150	221.8	8.95	175.0	137.5	42.53	156.86
200	295.7	8.86	175.0	125.0	53.87	198.21
300	443.6	8.78	175.0	125.0	76.56	282.12
400	591.48	8.78	175.0	125.0	86.76	319.81
500	739.5	8.65	131.25	100.0	115.23	386.08
750	1109.0	8.45	95.0	78.12	160.32	480.32
1000	1478.7	8.48	96.87	78.1	164.33	565.44

The smallest value of CaO/SiO_2 ratio (0.006) was obtained in the sample precipitated at lime

consumption of 40 mg/kg and seawater discharge of 40 cm^3/kg, Mg/Ca ration being 2.513. At such a treatment regime about 65 mg/kg of cations Ca^{2+} and Mg^{2+} was injected into the solution. Judging by (CaO+MgO)/SiO_2 ratio, total cations Ca^{2+} and Mg^{2+} having participated in the reactions of colloid particles charge neutralization and formation of bonds between particle surfaces amounted about 7.5 – 8.3 mg/kg. On the average 30-31 molecule of SiO_2 corresponded to one cation-coagulant in the reaction of neutralization and bridge-bond formation. 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 are presented in Table 4. The results have shown that seawater acted as a coagulant and secured stable colloid silica precipitation and reducing of C_t concentration to the values of 160-190 mg/kg already after addition of 100 cm^3/kg (Table 4).

Calcium portion in samples precipitated with seawater addition appeared quite small, CaO/SiO_2 ratio being below the value of 0.0004. Magnesium portion in the precipitate was much larger than that of calcium. MgO/SiO_2 ratio ranged 0.02 – 0.029 and showed a poor tendency for increasing as seawater consumption increased from 100 to 1000 cm^3/kg. Hence, when treated by seawater, colloid silica particles' surface was not saturated Mg^{2+} and Ca^{2+} cations over some critical quantity of 10-11 mg/kg necessary for particle coagulation. In reactions of neutralization and formation of bonds between particles 20-21 SiO_2 molecules corresponded to one ion-coagulant most of which were Mg^{2+} cations.

COAGULATION AND PRECIPITATION OF SILICA WITH $CaCl_2$ ADDITION

In the course of the experiments consumption of $CaCl_2$ varied from 500 to 10000 mg/kg (Table 5). Critical $CaCl_2$ consumption at 20°C made up 500 mg/kg, critical Ca^{2+} cation concentration being 180 mg/kg, that is, much more than at lime treatment.

Calcium chloride treatment at a consumption above critical resulted in a complete settling of colloid silica but monomeric silica proved stable even at the highest $CaCl_2$ consumption up to 10000 mg/kg (Table 5). As $CaCl_2$ consumption increased pH of the treated solution came down (Table 5), while CaO/SiO_2 ratio was slightly rising from 0.0163 at $CaCl_2$ concentration 1500 mg/kg up to 0.0755 at $CaCl_2$ concentration 10000 mg/kg.

Insignificant increase of CaO/SiO_2 ratio at an increasing $CaCl_2$ consumption indicated that colloid particles' surface was slightly saturated with Ca^{2+} cations after reaching some critical amount. Not more than 8-9 mg/kg of Ca^{2+} cations participated in the reactions of neutralization and bridge-bond formation between colloid particles, 40-41 SiO_2 molecules corresponded to one Ca^{2+} cation.

Simultaneous injection of 50 cm^3/kg of seawater during calcium chloride treatment allowed to carry out coagulation and precipitation of silica at $CaCl_2$ consumption 5 times lower than the critical one at 20^0C – 100 mg/kg. 112.5 mg/kg of Ca^{2+} and Mg^{2+}cations was injected into the solution at such a regime of treatment.

Table 5

Results of the hydrothermal solution probe treatment by calcium chloride $CaCl_2$, (Ca – equivalent quantity of calcium added together with the coagulant $CaCl_2$; Ca^{2+}, Cl^-residual concentrations of calcium, magnesium and chlorine ions)

pH	Ca, mg/kg	pH	C_t, mg/kg	C_s, mg/kg	Ca^{2+}, mg/kg	Cl^-, mg/kg
0	0	8.90	687.5	146.9	n.d.	159.75
500	180.0	8.70	468.8	134.4	158.31	408.25
750	270.0	8.51	151.25	120.6	242.48	543.15
1000	360.0	8.54	131.25	125.6	326.65	710
1500	540.0	8.41	129.4	121.25	478.95	1057.9
2000	720.0	8.41	129.4	125.0	633.26	1256.7
2500	900.0	8.52	126.25	120.0	815.63	1615.2
3000	1080.0	8.46	131.25	125.0	965.93	1934.7
4000	1440.0	8.34	129.4	121.25	1298.6	2396.2
5000	1800.0	8.37	135.6	123.75	1633.2	3195
6000	2162.1	8.36	135.6	125.0	1943.9	3728
8000	2880.0	8.20	131.25	123.75	2735.4	5360.5
10000	3600.0	8.29	130.6	123.75	3286.5	6390.0

Critical $CaCl_2$ consumption rate at 96-98^{0}C reduced to a value below 300 mg/kg, Ca^{2+} consumption - to 108 mg/kg, and CaO/SiO_2 ratio in the precipitated material fell down to 0.00865. At such a ratio of CaO/SiO_2 not more than 3.07-4.37 mg/kg of Ca^{2+} cations took part in the neutralization of surface charge and bridge-bond formation between the particles. At least 108-109 molecules of precipitated silica SiO_2 corresponded to one Ca^{2+} cation sorbed by the particle surface.

COAGULATION AND PRECIPITATION OF SILICA WITH ADDITION OF ALUMINIUM SULPHATE $Al_2(SO_4)_3 \cdot 18H_2O$ AND FERRIC CHLORIDE $FeCl_3 \cdot 6H_2O$

In the course of the experiments on the solution treatment by aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ coagulation of colloid silica was carried out under the effect of trivalent Al^{3+} cations. Critical consumption

of $Al_2(SO_4)_3 \cdot 18H_2O$ at 20°C made up 250 mg/kg, that of Al^{3+} cations – 20.2 mg/kg=0.522-0.748 mmole/kg. It is much smaller than critical consumption of divalent Ca^{2+} and Mg^{2+} cations. Treatment by aluminium sulphate led to the precipitation of colloid silica only. After addition of aluminium sulphate the solution acidified up to the pH level of 4.35-3.66 (Table 6).

High coagulation capacity of trivalent Al^{3+} could evidently be accounted for by the formation of hydrated multi-charge poly-cation colloid aluminium complexes in the solution. In the reactions of neutralization of a negative charge of colloid particles by such complexes and formation of bonds between particles at least 11 SiO_2 molecules corresponded to one Al^{3+} ion.

Table 6

Results of hydrothermal solution treatment with aluminium sulphate ($Al_2(SO_4)_3 \cdot 18H_2O$) addition at 20°C (Al- quantity of aluminium injected with the coagulant; Al^{3+}- residual concentration of aluminium cations).

$Al_2(SO_4)_3$ $18H_2O$, mg/kg	Al, mg/kg	pH	C_t, mg/kg	C_s, mg/kg	Al^{3+}, mg/kg
0	0	9.22	725.0	162.5	н.о.
500	40.4	4.36	161.25	140.6	37.8
1000	80.8	4.02	153.1	145.0	108.0
2000	161.6	3.78	158.1	156.2	162.0
3000	242.4	3.73	158.1	155.0	278.0
4000	323.2	3.72	153.1	148.75	318.0
6000	484.8	3.66	151.8	140.6	465.75
10000	808.0	3.56	128.1	151.2	864.0

Critical consumption of ferric chloride $FeCl_3 \cdot 6H_2O$ at 20^0C was about 250 mg/kg, iron cations' Fe^{3+} amounted 51.5 mg/kg = 0.922 mmole/kg. Fe^{3+} cations amounted more than those of Al^{3+}, but still notably less than divalent cations of Ca^{2+} and Mg^{2+}. High coagulation capacity of trivalent Fe^{3+} cations can be explained by the formation of their hydrated poly-cation colloid complexes. Coagulation and precipitation of colloid silica occurred within the consumption range of 250 – 2000 mg/kg. Treatment by ferric chloride led to a significant decrease of pH level to the values of 1.98-2.10.

Active co-precipitation of iron hydroxide $Fe(OH)_3$ that had appeared in the result of iron cations' injection into the solution occurred starting from the coagulant consumption value of 400 mg/kg. As the coagulant consumption increased silica precipitation was reducing, while that of iron hydroxide was increasing. At $FeCl_3 \cdot 6H_2O$ consumption rate of 2000 mg/kg only iron hydroxide was settling without any silica precipitation. At $FeCl_3 \cdot 6H_2O$ consumption of 5000-10000 mg/kg both iron hydroxide and silica stopped settling because of the intense acidification of the solution.

In hot solution at 96°C and $FeCl_3 \cdot 6H_2O$ consumption of 1000-5000 mg/kg almost all the iron added to the solution with the coagulant precipitated and co-precipitation of a considerable portion of colloid silica occurred. Acceleration of silica coagulation and precipitation in hot solution can be explained by the diffusion coefficient increasing, rising of colloid particles' mobility, as well as by the variation of iron hydroxide solubility with the increasing temperature.

Alkalization of the solution after its treatment by easily hydrolyzing salines significantly enhanced the kinetics of silica coagulation and precipitation. After alkalization of the probes treated at great $FeCl_3 \cdot 6H_2O$ consumption of 3000-10000 mg/kg by NaOH solution up to pH level of 8.5 practically total precipitation of both colloid and monomeric silica took place, as well as that of iron hydroxide: total silica content C_t dropped down to 12.5-3.0 mg/kg, while residual concentration of Fe cations did not exceed 4.0-1.2 mg/kg.

Treatment by calcium chloride followed by alkalization up to the pH level of 9.3 allowed carrying out flake formation and precipitation of a considerable portion of colloid silica at $CaCl_2$ consumption below the critical values of 250, 300 и 400 mg/kg. For that purpose, it was necessary to add 14-23 mg/kg of NaOH. Treatment by aluminium sulphate at $Al_2(SO_4)_3 \cdot 18H_2O$ consumption below the critical of 200 mg/kg resulted in coagulation and precipitation of a considerable portion of colloid silica after alkalization to the pH level of 9.0 by 79.2 mg/kg NaOH.

MECHANISM OF COAGULATION AND PRECIPITATION OF COLLOID SILICA IN HYDROTHERMAL SOLUTION

Silica precipitation during the treatment by coagulants was achieved due to individual or combined activity of Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+} cations. Results of the experiments revealed mechanism for coagulation and precipitation of silica under the effect of various cations or their combinations injected into the solution as parts of the composition of either some coagulant or a mixture of coagulants. For comparison Table 8 presents the data on the mechanism of silica coagulation and precipitation in hydrothermal solution by Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} cations. The data were obtained in the course of the experiments using various coagulants. Table 8 also contains the data on the costs of reagents necessary for the separate treatment.

The following markings are given in Table 8: (CC) – coagulant-cation added to the solution; CCC– critical coagulant consumption, at which complete precepitation of colloid silica occurred; CCI – corresponding critical consumption of ions-coagulants; QCC – quantity of coagulant-cations participating in the reactions of neutralization and bridge-bond formation between colloid silica particles; SiO_2/1 ion – average molecule quantity of precipitated silica dioxide corresponded to 1 coagulant-ion in the reactions of neutralization and bridge-bond formation; SW – sea water; AS-aluminium sulphate; FC- ferric chloride.

Ca amount in the composition of the material precipitated with calcium chloride addition at a critical coagulant consumption was used for estimation of the surface charge σ_s of colloid silica particles. Assuming a particle radius equaling 10.0 nm we estimated the particle charge as follows: at pH=8.5, σ_s=0.664 nm^{-2}=$10.62 \cdot 10^{-6}$ Coulomb/cm^2; at pH=9.3-σ_s=1.392nm^{-2}=$22.263 \cdot 10^{-6}$ Coulomb/cm^2; at pH=10.0 - σ_s=1.495 nm^{-2}= $23.92 \cdot 10^{-6}$ Coulomb/cm^2.

Table 8

Data on the mechanism of colloid silica coagulation and precipittion in hydrothermal solution with addition of coagulants and temperature of 20^0C.

Coagulant	CC	CCC, mg/kg	CCI, mg/kg	QCC, mg/kg	SiO_2/ 1ion	Cost, rubles/ kg
slaked lime	Ca^{2+}	80.0	57.1	6.99-7.69	47-48	0.0015
lime + sea water	Ca^{2+}, Mg^2	40 mg/kg + 40 cm^3/kg	72.5	6.68-7.35	34-35	0.0006
SW	Ca^{2+}, Mg^2	<100 cm^3/kg	147.8	6.24-6.86	32-33	-
$CaCl_2$	Ca^{2+}	500	180.18	5.82-6.4	57-58	0.083
$CaCl_2$ + SW	Ca^{2+}, Mg^2	100 mg/kg + 50 cm^3/kg	112.5	6.96-7.65	35-36	0.0166
AS	Al^{3+}	250.0	20.2	18.0-19.8	12-13	0.0336
FC	Fe^{3+}	250.0	55.66	48.7	10	0.0306

Estimation of the treatment cost in Table 8 is made for a coagulant consumption close to a critical on at which total precipitation of colloid silica occurs at 20°C. The cost of the treatment with seawater addition was considered zero which corresponds to the mark (-) in Table 8.

Accordingly, slaked lime treatment is the cheapest one, the cost of the other types of treatment increases as follows (Table 8): 1. treatment by ferric chloride; 2. treatment by calcium chloride.

Results of the experiments can be used for developing of the technology of silica precipitation from hydrothermal separate having the same physical-chemical characteristics as the heat-carrier of the Mutnovskoye hydrothermal field, that is total silica content from 300 to 1500mg/kg, colloid silica particles' radius of 3.0-16 nm, specific area of the particle surface 500-2000 cm^2/cm^3, solution mineralization of 1500-2500 mg/kg, ionic strength of 10-20 mmole/kg, pH from 9.5 to 7.0, treatment temperature from 140-160^{0}C to 20^{0}C.

CONCLUSIONS

In the course of the experiments on hydrothermal solution treatment by various coagulants the mechanism of colloid silica coagulation and precipitation have been determined as follows: 1. injection into the solution of a critical amount (50-120 mg/kg) of Ca^{2+}, Mg^{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 negative surface charge; 3. formation of bridge-bonds between the particle surfaces involving coagulant-cations, coagulation and precipitation of colloid silica.

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