PRINCIPLES OF INCREASING THE EFFICIENCY OF THE BINARY POWER UNITS OF GEOTHERMAL POWER STATIONS

V. V. Potapov [1]

[1] *Scientific and Research Geotechnological Centre of the Far East Branch of the Russian Academy of Sciences,*
Severo-Vostochnoe shosse 30, Petropavlovsk-Kamchatskii, Kamchatskaya oblast, 683002 Russia,
E-mail: vadim_p@inbox.ru

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ABSTRACT

In the paper there is an analysis of the problem of increasing the efficiency of usage of high temperature hydrothermal fluid. It was demonstrated that at 250-300 ^{0}C fluid temperature in the reservoir it is possible to obtain a substantial increase of the efficiency at the expense of the control over the velocity of a growth of solid silicon depositions in wells, pipelines, and the GeoPP or GeoHP equipment. Growth of solid depositions is accounted for the mass transfer in the water flow of colloid silicon particles. Colloidal silica is formed in the supersaturated hydrothermal solution while rising to the surface in productive wells due to reducing the pressure, temperature, and partial evaporating. Growth of solid depositions results in the necessity of re-injecting the waste brine at higher temperature of 140-160 ^{0}C that restricts electricity and heat generation. The state-of-the-art control methods of silica deposition growth velocity were analyzed. They fall into two groups: 1. with extraction of silica fron the brine solution; 2. inhibiting the growth of depositions excluding silica. The paper comprises the results of experimental studies of silicic acid polimerization and formation of colloid silica particles, and coagulation and deposition of colloid silica from the Verkhne-Mutnovsky GeoPP brine as well. Silica deposition experiments were carried out by adding different coagulants. The cost of processing with coagulants was estimated as it is necessary to select optimum deposition modes. Based on the experiments done economical principles of increasing the efficiency of usage of hydrothermal fluid at the expense of silica deposition were justified: 1. reduction of running costs associated with drilling the reinjection wells in case of filling them with solid depositions; 2. reduction of brine reinjection temperature and obtaining of additional electric power in binary units using low-boiling organic working body; 3. origination of mineral product in the nature of amorphic silica, utilized in silicate and chemical industry; 4. extraction of valuable chemical compounds (Li, B, As, etc.).

1. INTRODUCTION

The power of the binary power unit of Geothermal Power Stations (GeoPSs) depends on the value to which the temperature of the separate at the heat-exchanger outlet can be reduced (Fig. 1) [1]. However, the growth of solid depositions of amorphous silica in the heat-exchange equipment and reinjection wells of a GeoPS hampers the reduction of the temperature and impedes an increase in the power of the unit [1].

There are two methods to control the rate of the solid deposition growth in heat exchangers and pipes: with extraction of silica and without it. The methods that do not use extraction of silica are based on inhibiting the reaction of polymerization of monomeric silica with the formation of colloidal particles or on inhibiting the process of the deposition growths. To do this, the following methods are used: aging the separate [2], its acidification to pH = 1.0-4.0 [3, 4], dilution of the separate by the steam condensate [1], inhibitor injection [5-9], heating of the waste separate by partial use of the steam energy [9].

The main methods of silica extraction are as follows: introduction of precipitating agents (coagulants, flocculants, primary particles and silica sludge, and surfactants) and silica precipitation [10]; ultrafiltration through ultra membranes and obtaining concentrated silica hydrosol [11]; and precipitation of monomeric silica in a fluidized bed [12]. We should point out the success of the group of specialists from the Brookhaven National Laboratory of the United States. They have developed the technology of extraction of an ultra pure geothermal silica (99.9% SiO_2 by mass), which uses introduction of the coagulant (5--10 mg / kg $MgCl_2$) and subsequent filtration of the coagulated colloidal particles. This technology was included into the list of the one hundred best technologies of the United States [13]. The silica obtained was used in chromatography and in producing chips for electronic devices. These applications considerably increase the silica cost and the profitability of the extraction technology [13].

The technologies above were tested with the heat-transfer agents of different geothermal fields, which have different physical and chemical properties. We conducted experiments to study polymerization and precipitation of silica from the solution of the separate from the wells of the Mutnovsk geothermal field (Kamchatka, Russia), with the $Ca^{2+,}$ $Mg^{2+,}$ $Al^{3+,}$ and Fe^{3+} cations being introduced in the solution. The results obtained are urgent in the context of construction of the fourth power unit of the Verkhne-Mutnovsk GeoPS with the combined (the direct plus binary) cycle of the heat-transfer agent. This unit is being constructed by the OAO Geoterm Company.

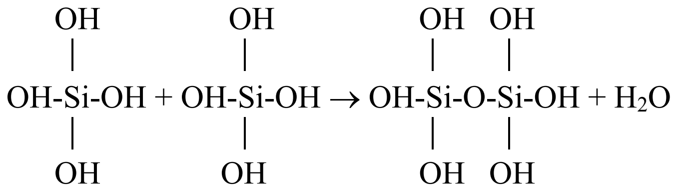
2. SYNTHESIS OF THE COLLOIDAL SILICA SYSTEM IN THE HYDROTHERMAL SOLUTION

Synthesis of the colloidal silica system in the hydrothermal solution proceeds in several stages. At first, the silica enters the solution together with the other compounds, which are formed due to the chemical interaction of water with the aluminosilicate minerals of the geothermal deposit rocks. These reactions take place deep in the zones of thermal anomalies at elevated temperatures of 250-300°C and higher and a pressure of 4.0-10.0 MPa or more. At a temperature of 250-300°C, in the solution, the silica mainly exists as individual molecules of the silica acid H_4SiO_4. Under these conditions, the total content C_t of silica SiO_2 can be assessed from the solubility of quartz in pure water.

In the course of the solution flow in the productive wells of geothermal power stations, its pressure and temperature decrease and partial evaporation of the solution takes place. The total silica content C_t in the water reaches 700-1000 mg/kg and more. Because of this, the water solution becomes supersaturated as to solubility of the amorphous silica C_e. According to the experimental data, the dependence of C_e in pure water on the absolute temperature T(K) can be written as follows [14]:

$$\log (C_e/60) = -0{,}1185 - 1{,}126\cdot 10^3/T + 2{,}3305\cdot 10^5/T^2 - 3{,}6784\cdot 10^7/T^3, \quad (1)$$

In the supersaturated water solution, the monomeric state of silica is unstable. The super saturation S_m of the solution is equal to the difference $(C_s\text{-}C_e)$ of the concentration of the monomeric silica C_s and its solubility C_e. This supersaturation is the driving force of the processes of nucleation and polymerization of the silica acid molecules, which are accompanied by condensation of silanolic groups, formation of siloxane bonds, and partial dehydratation in accordance with the following reactions:



$$\text{OH-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}\text{-OH} + \text{OH-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}\text{-OH} \rightarrow \text{OH-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}\text{-O-}\underset{\text{OH}}{\overset{\text{OH}}{\text{Si}}}\text{-OH} + H_2O \qquad (2)$$

$$Si_mO_{(m-1)}(OH)_{(2m+2)} + Si_nO_{(n-1)}(OH)_{(2n+2)} \rightarrow Si_{(m+n)}O_{(m+n-1)}OH_{(2n+2m+2)} + H_2O \qquad (3)$$

As a result of nucleation and polymerization, particles of hydrated silica $mSiO_2 \cdot nH_2O$ of colloidal size are formed in the solution. A part of silanolic groups SiOH located at the particle surface dissociates, with the proton H+ being separated, and the particle surface gains negative electric charge. The latter impedes coagulation of the particles due to electrostatic repulsion, thus providing colloidal silica stability in the solution. The instability of the colloidal system near the inner surface of the flow channel provides the formation of amorphous-silica depositions from the hydrothermal solution flow in the heat-exchange equipment, in the wells of the GeoPS, and in the cracked porous rocks after reinjection of the heat-transfer agent [15].

3. EXPERIMENTAL STUDIES ON THE KINETICS OF THE REACTION OF THE MONOMERIC SILICA POLYMERIZATION

The kinetics of the reaction of the monomeric silica polymerization with formation of the colloidal particles was studied at a temperature of 20^0C and pH index from 8.0-9.4 to 5.0. Super saturation curves $S_m(t_p)$, obtained during measurements at 20^0C and natural value of pH from 8.0 to 9.4, were of the same form, with the convexity down to the axis of X, and characterized with values close to dS_m/dt_p.

In the general case, the function S_m follows the differential equation in [16]:

$$dS_m/dt_p = -k_p \cdot S_m^n, \qquad (4)$$

where k_p- is the constant of the polymerization reaction rate, which depends on the temperature, pH index, and ionic strength of the solution, n_p - is the order of the reaction of polymerization. It was found that the dependence of $lnS_m(t_p)$ within the range of t_p from 0 to 6 h was close to linear, and thus, the rate of n_p of the reaction in hydrothermal solution equalled 1.0.

The experimental dependence $lnS_m(t_p)$ was approximated by the equation $lnS_m(t_p)=lnS_0 – t_p/\tau_p$, from which the constants $\tau_p = 1/k_p$ and k_p were found. At 20^0C and pH = 8.0-9.4 the average value of τ_p was 1.98-2.06 h, k_p = 0.485 ч$^{-1}$. According to the Fleming's model, the constant k_p of the polimerization reaction speed is proportional to the surface concentration C_I of the ionized hydroxyl groups of SiO^-, that is, to the surface charge σ_s of the colloidal silica particles and the specific area of the particles surface A_s [16]:

$$k_p = k_f \cdot A_s \cdot C_I, \qquad (5)$$

The factor k_f depends on the ionic strength of the solution I_s [16]:

$$k_f = k_{f0} \cdot exp((A_{DH} \cdot I_s^{0.5})/(B_F + I_s^{0.5})), \qquad (6)$$

The factor k_{f0} is the function of temperature T in accordance with the Arrehenius equation:

$$lnk_{f0} = 22,1 - E_p/R_gT \pm 2.0, \qquad (7)$$

where E_p is the energy of activation of the polymerization reaction, E_p= 54836.6 J/mol [16], R_g is the gas constant, R_g = 8.31 J/mole·K, A_{DH} is the Debye-Hukkel constant; A_{DH} = 1.238, B_F = 1.0 $(mole/kg)^{0,5}$.

According to the thermodynamic model, the concentration C_I of the ionized groupson the surface of the silica particles conforms to the following equation [16]:

$$\frac{a_H}{K_0} = \frac{(n_{SH} - C_I)}{C_I \cdot (C_B \cdot C_I + (1 + „_B{}^2 \cdot C_I{}^2)^{0.5})^2}, \tag{8}$$

where a_H is the activity of the hydrogen ions H+ in the bulk of the solution at a large distance from the surface of the colloidal silica particles; $K_0=(5,13 \pm 1,59) \cdot 10^{-8}$ is the constant of the reaction of ionization of the surface silanolic groups SiOH, n_{SH} is the concentration of SiOH groups at the surface of the particles, which are capable of being ionized with separation of the proton H^+, $n_{SH} = (1,34 \pm 0,24)\ nm^{-2}$; C_B is the constant in the approximate solution to the Poisson -Boltzmann equation for the electric potential φ in the solution having an interface between it and a solid phase (the Debye--Hukkel approximation for spherical particles).

The calculations using (4)-(8) (with $k_r = 7.221\ h^{-1}$) gave the following values of the constant τ_p: 36.01, 20.91, and 8.3 min for 50, 75, and 100°C, respectively. The optimal time of aging of the separate of the Mutnovsk deposit is 30-40 min at 100°C.

After acidification to pH=7.0, the dependence $S_m(t_p)$ changed considerably; namely, with t_p from 0 to 6 h the curve $S_m(t_p)$ had a convex shape and the derivative dS_m/dt_p was substantially smaller than that in the solution with pH=8.9-9.4. With pH=5.0, we observed inhibition of the polymerization process and remarkable changes in the concentration C_s took place only several days after the beginning of the reaction.

4. THE EXPERIMENTS ON COAGULATION AND PRECIPITATION OF COLLOIDAL SILICA PARTICLES

In nonpolymerized solution, the size of original silica particles is 0.5-1.5 nm [15]. The measurements conducted by means of photon correlative spectroscopy showed that the mean radius of the particles of the polymerized silica was 7.0-16.0 nm [15].

The experiments on coagulation and precipitation of colloidal silica particles were conducted with the samples of the hydrothermal solution from the productive wells of the Verkhne-Mutnovsk GeoPS and also from wells 014, 4E, 5E, A2, M01 of the Mutnovsk field. The cations of metals were introduced in the solution in the course of treatment by slaked lime, sea water, calcium chloride $CaCl_2$, aluminium sulfate $Al_2(SO_4) \cdot 18H_2O$, $FeCl_3 \cdot 6H_2O$, and electro coagulation as well.

The samples of the solution had similar physical and chemical characteristics. With pH=9.2, I_s=14.218 mmole/kg and the mineralization M_h=1638.9 mg/kg, the concentrations of the main compounds were 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.

The efficient diameter d_f of the flakes was determined from their velocity of precipitation in the Stokes motion:

$$d_f=(18 \cdot \mu \cdot u/\Delta\rho \cdot g)^{0.5}, \tag{9}$$

where *u* is the velocity of precipitation of flakes, μ is the dynamic viscosity of water, Δρ is the difference of the densities of the silica and water, g is the acceleration due to gravity. The residual concentration of the silica (C_t, C_s), the concentration of the coagulating cations, and the pH index in aliquots of the clarified solution, as well as the content of Ca, Mg, Al, and Fe in the deposited material, were determined 20-60 min after the treatment of the solution.

Table 1. The results of separate treatment with slaked lime (Ca is the amount of calcium cations introduced in the solution with lime)

CaO mg/kg	Ca, mg/kg	20^0C			96^0C		
		pH	C_t, mg/kg	C_s, mg/kg	pH	C_t, mg/kg	C_s, mg/kg
0	0	9.29	697.0	150.3	9.26	718.8	135
100	71.4	10.10	158.1	158.1	9.73	344.9	244.4
150	107.1	10.48	158.0	158.0	-	-	-
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	275
400	285.6	11.68	137.5	131.9	10.32	345	322.5
500	357.0	11.6	75.6	73.8	10.1	339	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 the experiments with slaked lime, the flow rate of CaO was changed in a wide rage from 40 to 1500 mg/kg. After the treatment with lime, both colloidal and monomeric silica precipitated; however, the stability of the monomeric silica was considerably higher than that of the colloidal one. With a CaO flow rate of 80-100 mg/kg, essentially all of the colloidal silica was precipitated. This flow rate is the critical one at temperatures of 20 and 96°C. At 20°C, the concentration of the monomeric silica began to decrease with a lime flow rate of more than 400 mg/kg; at 96°C, this process started with a lime flow rate of more than 700 mg/kg (Table 1). At a temperature of 94-96°C, due to higher content of the monomeric silica, the decrease in the residual total content of silica C_t was slower than that at 20°C (Table 1). The velocity of the flake precipitation and the flake dimensions depended on the coagulant flow rate; they were 6.5-10.2 mm/min and 14.1-17.7, respectively.

The fraction of calcium in the precipitated material and the ratio CaO/SiO_2 depended on the lime flow rate. The latter was changed from 1500 to 80 mg/kg; correspondingly, the above ratio in the samples of the deposition decreased from 1.50 to 0.0196. The lowest fraction of calcium was recognized in the sample which was precipitated with the critical value of the CaO flow rate of 80 mg/kg.

The ratio CaO/SiO_2 in the material precipitated with a CaO flow rate of 80 mg/kg showed that, to coagulate and precipitate all the colloidal silica (500-550 mg/kg SiO_2) from the hydrothermal solution, it is necessary to introduce the critical amount of two-charge cations Ca^{2+}. The latter is approximately 57--60 mg/kg = 1.425-1.50 mmole/kg. At the same time, only a small part of them (no more than 7-8 mg/kg Ca^{2+}) was sorbed by the surface of the colloidal silica particles due to Ca^{2+}cation substitution for the hydrogen H+ in the SiOH groups. The cations sorbed neutralized the negative surface charge of the colloidal particles, then participated in forming bridge bonds between the particles and promoted coagulation of the particles.

In the reactions of neutralization and formation of the bridge bonds, up to 47-48 molecules of the deposited silica SiO_2 were accounted for one calcium cation Ca^{2+}.With an increase in the CaO flow rate, the pH index increased, the charge of the colloidal particles also increased, and unbounded saturation of their surface by the calcium cations and an increase in the CaO/SiO_2 ratio in the precipitated material took place.

The separate was also treated by slaked lime with an addition of sea water (Table 2), which had pH = 8.3 and increased natural concentrations of calcium Ca^{2+} (210 mg/kg) and magnesium Mg^{2+} (699 mg/kg) cations. The treatment was conducted with a lime flow rate of 70-40 mg/kg, which was lower than the critical one. The sea water flow rate was 15--100 cm^3/kg.

With a CaO flow rate of 70, 60, and 40-50 mg/kg, for intense formation of flakes and precipitation of silica, it was necessary to add 15-20, 25-30, and about 40 cm^3/kg of sea water, respectively. In this case, the total content of SiO^2 decreased to 140-190 mg/kg. This shows that essentially full precipitation of the colloidal silica occurred. The addition of sea water compensated for an increase in the pH index of the solution after the treatment with lime. The lowest value of the ratio CaO/SiO^2 of 0.006 was obtained in the sample which was precipitaed with a lime flow rate of 40 mg/kg, sea water flow rate of 40 cm^3/kg, and the ratio Mg/Ca = 2.513.

The results of experiments on silica precipitation with the addition of only a considerable amount of sea water showed that it actually acted as a coagulant and, beginning at a flow rate of 100 cm^3/kg, provided stable precipitation of the colloidal silica and a decrease in C_t concentration to 160-190 mg/kg.

After sea water treatment, the pH index of the separate somewhat decreased (to 9.0--8.48). In this connection, with an increase in the sea water flow rate from 100 to 1000 cm^3/kg, a slight trend of an increasing $(CaO+MgO)/SiO^2$ ratio was seen. The latter was within 0.02-0.029. Hence, when being treated with the sea water, the surface of the colloidal silica particles was not saturated with Mg^{2+} and Ca^{2+} cations above a certain critical value of 10-11 mg/kg that is necessary to coagulate silica particles.

In the experiments, the flow rate of the hydrolizing salts $CaCl_2$, $Al_2(SO_4)_3 \cdot 18H_2O$, and $FeCl_3 \cdot 6H_2O$ was changed from 200 to 10 000 mg/kg (Table 3). The treatment of the separate by the hydrolizing salts with a flow rate higher than the critical one provided full precipitation of the colloidal silica. Nevertheless, the monomeric silica remained stable even with the highest flow rates of the coagulants (up to 10 000 mg/kg) (Table 3).

Table 2. Results of treatment of the hydrothermal separate samples at a temperature of 20^{0}C with the addition of slaked lime and sea water (SW is the sea water flow rate; (Ca+Mg) is the total amount of the calcium and magnesium cautions introduced with the lime and sea water)

CaO, mg/kg	MB, sm3/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 3. Results of treatment of the hydrothermal solution samples by hydrolizing salts at a temperature of 20^0C (CFW is the coagulant flow rate, Ca, Al, Fe and Fe are the amount of the calcium Ca^{2+}, aluminum Al^{3+}, and iron Fe^{3+} cations introduced into the solution as a component of the calcium chloride $CaCl_2$, aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$, and ferric chloride $FeCl_3 \cdot 6H_2O$)

PK, mg/kg	$CaCl_2$			$Al_2(SO_4)_3 \cdot 18H_2O$			$FeCl_3 \cdot 6H_2O$		
	Ca, mg/kg	pH	C_t, mg/kg	Al, mg/kg	pH C_t,	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	-	-	-	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	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

With an increase in the $CaCl_2$ flow rate, the pH index of the solution decreased to 8.3-8.7 (Table 3) and the CaO/SiO_2 ratio slightly increased from 0.0163 with a flow rate of 1500 mg/kg of $CaCl_2$ to 0.0755 with a flow rate of 10 000 mg/kg. When treating the solution with calcium chloride, simultaneous introduction of 50 cm^3/kg of sea water made possible the coagulation and precipitation of the silica at a temperature of 20^oC and a $CaCl_2$ flow rate that is five times less than the critical 100 mg/kg. At a temperature of 96-98^oC, the critical flow rate of $CaCl_2$ decreased to less than 300 mg/kg, the flow rate of the Ca^{2+} cations decreased to 108 mg/kg, and the CaO/SiO_2 ratio in the precipitated material decreased to 0.00865.

In the experiments on the solution treatment with aluminium sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ and ferric chloride $FeCl_3 \cdot 6H_2O$, coagulation of the colloidal silica occurred due to the action of three-charge cations of aluminium and iron. The critical flow rate of the aluminium and iron cations was considerably smaller than that of the two-charge cations of calcium and magnesium. The increased coagulation capacity of the Al^{3+} and Fe^{3+} cations can be explained by the formation of polycation hydrated colloidal complexes. When treating with the aluminium sulphate, the solution was acidified to pH=4.35-3.66, while, with ferric chloride treatment, it was acidified to pH=1.98-2.10 (see Table 3).

Alkalization of the solution after its treatment with readily hydrolizing salts considerably improved the kinetics of coagulation and precipitation of silica. After alkalization of the samples which were treated with a high flow rate of ferric chloride (3000-10 000 mg/kg) up to pH=8.5 by the NaOH solution, essentially full precipitation of the colloidal and monomeric silica occurred, namely, the total content of silica C_t decreased to 12.5-3.0 mg/kg and the residual concentration of Fe^{3+} cations was no more than 4.0-1.2 mg/kg.

The treatment with calcium chloride with alkalization up to pH=9.3 made possible the formation of flakes and precipitation of a considerable part of the colloidal silica at a temperature of 20^oC and $CaCl^2$ flow rates that are lower than the critical one (250, 300, and 400 mg/kg). The treatment with the aluminium sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ with a flow rate less than the critical one (200 mg/kg) ensured coagulation and precipitation of a considerable part of the colloidal silica after alkalization to pH=9.0.

The following types of flocculants were used as precipitators: polydiallyldimethylammonium chloride; Multifloc-231 with a molecular mass m_f of $6.7*10^6$; and Zetag 7689, Zetag 7623, and

Praestol 854BC high-molecular cationic polyacrylamides, $m_f = 20*10^6$. The treatment was conducted with low (5-50 mg/kg) and high (100-1000 mg/kg) flocculant's flow rates. With high flow rates, it appeared to be inefficient because of stabilization of high-molecular structures at a raised concentration. With a flocculant flow rate of 20-50 mg/kg, an increase in the solution turbidity and a decrease in the silica concentration took place a considerable amount of time after the treatment, while there was no intense precipitation immediately after introducing the above flocculants. The flocculation ability of the cationic flocculants increased with an increase in the charge.

It seems promising to simultaneously introduce the coagulant and 10-20 mg/kg of the flocculant's to improve flake formation and increase the velocity of the flake deposition.

5. THE EXPERIMENTS ON PRECIPITATION OF SILICA BY ELECTROCOAGULATION

The experiments on precipitation of silica from the separate by means of electro coagulation technology were conducted using direct current [15]. Electrodes made of aluminium, copper, and zinc-plated and stainless steels were used. Application of the aluminium electrodes appeared to be most efficient. In this case, the coagulant was admitted in the solution due to dissolution of the aluminium anode and subsequent hydrolysis of the Al^{3+} cations.

With different values of the electric current I and its density j, the dependences of the residual concentration of silica and pH index of the solution, as well as of the specific consumption of electricity and on percentage (by mass) of the silica deposited were obtained [15]. At the first stage of treatment, the specific consumption of electricity per 1 kg of silica precipitated was rather high; at the second stage, it decreased; and at the third (final) stage, whose contribution into silica precipitation was rather high, they sharply increased (Figs. 3, 4). The values of Q_{Si} and Q_{EL} decreased with a decrease in the current density j [15].

Silica precipitation by electro coagulation had the following characteristics: colloidal and monomeric silica were precipitated simultaneously and gradually in three stages [15]. With I = 1.5 A and j = 112.7 A/m^2, a decrease in the total silica content C_t to 100-120 mg/kg took place with the introduction of approximately 90 mg/kg of aluminium in the solution, which is considerably greater than the critical flow rate of cations Al^{3+}, when treating with aluminium sulphate. The colloidal system of silica in the hydrothermal solution appeared to be more stable against gradual introduction of coagulant, as compared to the case of treatment using $Al_2(SO_4)_3 \cdot 18H_2O$.

The studies of the electro coagulation process in the hydrothermal solution made it possible to reveal the optimal parameters of this technology for silica precipitation: j = 30-200 A/m^2 and I = 0.5-1.5 A per 1 kg of the water solution; the space between the electrodes h_{el} = 8-10 mm; the time of treatment is from 10 to 40 min; the specific consumption of electricity per 1 kg of the solution to be treated Q_{EL} = 0.0009-0.0033 (kW h)/kg; and per 1 kg of the silica deposited Q_{Si} = 1.8-6.0 (kW h)/kg [15].

When treating the solution with coagulants, silica precipitation was performed due to the individual or combined action of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} cations. The results of the experiments showed that the mechanisms of silica coagulation and precipitation due to the action of different cations, which are introduced into the solution as a part of one coagulant or another or their mixture, or a certain combination of these cations are similar (Table 4).

The key to the following Table is: CC is the coagulating cation, which is introduced in the solution with the coagulant; CFRC is the critical flow rate of the coagulant; CFRI is the critical flow rate of the corresponding ion-coagulant; ACC is the amount of the cation-coagulants, which are sorbed by the surface of the colloidal silica; SiO2/(1 ion) is the mean number of molecules of the precipitated silica per one ion-coagulant in the reactions of neutralization and development of bridge bonds between the surfaces of the silica particles with the participating cation-coagulants; SW is sea water; EC is electro coagulation.

Table 4. Data on mechanisms of coagulation and precipitation of the colloidal silica in the hydrothermal solution with different coagulants being added (the temperature is 20^0C)

Coagulant	**CC**	**CFRC, mg/kg**	**CFRI mg/kg**	**ACC, mg/kg**	**SiO_2/1ion**	**Cost, rbl./kg**
Caustic lime	Ca^{2+}	80.0	57.1	6.99-7.69	47-48	0.0015
Lime +MB	Ca^{2+}, Mg^{2+}	40 mg/kg + 40 sm^3/kg	72.5	6.68-7.35	34-35	0.0006
MB	Ca^{2+}, Mg^{2+}	<100 sm^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
$CaCl_2$ + MB	Ca^{2+}, Mg^{2+}	100 mg/kg+ 50 sm^3/kg	112.5	6.96-7.65	35-36	0.0166
$Al_2(SO_4)\cdot 18H_2O$	Al^{3+}	250.0	20.2	18.0-19.8	12-13	0.03363
$FeCl_3\cdot 6H_2O$	Fe^{3+}	250.0	55.66	48.7	10	0.03061
flocculants	-	20.0	-	-	-	0.002
Al EC	Al^{3+}	90.0	90.0	32.5	12	0.01285

6. COST OF CHEMICAL TREATMENT AND ECONOMICAL FACTORS OF INCREASING THE EFFICIENCY OF THE FLUID USAGE

The mechanism of coagulation and precipitation of the colloidal silica consists of the following stages: introduction of the critical amount (50-120 mg/kg) of Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} cations into the solution (individually or in combination); sorption of a fraction of these cations (5-20 mg/kg) or their hydrated polycationic complexes by the surface of the colloidal silica particles up to neutralization of the negative surface charge of the particles; development of bridge bonds between the surfaces of the silica particles with the participating cation-coagulants; and coagulation and precipitation of the particles.

The amount of Ca in the material, which was precipitated with the addition of calcium chloride and lime at the critical flow rate of the coagulants, was used to assess the density of the surface charge σ_s at the colloidal silica particles. It was assumed that the mean particle radius is 10.0 nm (the specific surface is approximately 150 m^2/g). Then, the particle charge σ_s constituted 0.66 nm^{-2} = 10.62 microCoulombs/sm^2, 1.39 nm^{-2} = 22.26 microCoulombs/sm^2, and 1.495 nm^{-2}= 23.92 microCoulombs/sm^2 with the pH index equal to 8.5, 9.3, and 10.0, respectively.

The cost of treatment is given in Table 4 for a coagulant flow rate that is close to the critical one at a temperature of 20°C. For the case of electro coagulation, the cost was assessed with an account of electricity consumption, which, with $j = 112.7$ A/m^2, the specific electricity consumption $Q_{EL} = 3.99$ (kW h)/kg, and the amount of the silica precipitated equal to 86.1% (by mass), constituted 77.62% of the total cost of treatment. According to Table 4, the cheapest treatment is that with slaked lime; the costs of the other technologies can be listed in the following sequence (from least to most expensive): electro coagulation with aluminium electrodes; treatment with ferric chloride; treatment with aluminium sulphate; and treatment with calcium chloride.

Based on the experiments, the principle technological scheme for precipitation of the colloidal and monomeric silica from the hydrothermal separate flow was developed. It is intended for operation at temperatures from 140-160 to 20°C. This scheme is the optimal one for the heat-transfer agent with the following particular physical and chemical characteristics: the total content of silica SiO_2 in the separate is 300-1500 mg/kg; the mean radius of the silica colloidal

particles is 5.0-16.0 nm; the specific area of the particle surface is 500-2000 cm^2/cm^3 (50-300 m^2/g); the mineralization is 1000-2500 mg/kg; the ionic strength is 10-20 mmole/kg; and the natural pH index is from 9.5 to 7.0.
This scheme realizes the following main stages:

1. Solution aging and polymerization of the monomeric silica with the formation of colloidal particles;
2. Addition of a precipitator (coagulants, flocculants, primary colloidal particles) at the aging stage at a certain instant of the polymerization process to form a microstructure from the silica-particle complexes without precipitation of silica from the solution;
3. Introduction of a precipitator or a mixture of precipitators (coagulants, flocculants, electro coagulation, recirculation of silica slime) into the solution with the polymerized silica to provide coagulation, flake formation, and precipitation of silica;
4. Regulation of the pH index of the solution (acidification, alkalization) at the stage of silica coagulation and precipitation by adding reagents to control the coagulation and flake-formation kinetics and the content of Ca, Mg, Al, and Fe in the precipitated material;
5. Separation of flakes of the precipitated material and clarification of the solution; dehydrotation and drying of the material precipitated.

The dispersity of the material precipitated is controlled by the solution temperature at which silica polymerization takes place, the composition and amount of precipitators, and the duration of addition of the latter in the course of polymerization and precipitation. The value of the minimal temperature to which the separate can be cooled in heat exchangers without forming depositions and, hence, the electric capacity of the binary power unit depends on the amount of silica precipitated.
The increasing of the efficiency of usage is obtained by implementing an economically viable extraction technology at the expense of the total contribution of the following several factors: 1. elimination of GeoHP shutdowns, required to remove solid depositions of amorphic silicon from wells and heat equipment, and reduction of running costs associated with drilling and construction of new reinjection wells in case of filling the well with depositions and loss of full-capacity discharge; 2. obtaining of additional volume of electric (up to 10 % to the designed plant capacity) and thermal energy at the expense of reducing the brine reinjection temperature and further use of brine in binary or combined (direct plus binary) cycle with low-boiling working body; 3. origination of supplementary mineral product in the nature of amorphic silicon with given physical and chemical characterics (chemical purity, density, dispersibility, porosity, oil-consuming capacity, optical and sorption surface features), which may be utilized in different domains of silicate and chemical industry, when producing the paper for printing, photographic paper, rubber, plastic, paints, glue, glass, ceramics, bricks, cement, boring materials, adhesive means, sorbents, soil fertilizations, catalysts, in chromatography, to produce the electronic device chips; 4. extraction of other chemical compounds (Li, B, As, etc.) from the brine, which is unlikely without removing any silicon due to the surface pollution of ionic selective materials.

7. CONCLUSIONS

1. There were studied the physical and chemical parameters of silicon in the geothermal solution: the rate and constants of polymerization reaction velocity was identified; radiuses and the rate of diffusion of colloid silicon particles were measured, and the surface charge of articles was assessed.
2. Experiments on treatment of a geothermal fluid with coagulants a sorption capacity of the colloid silicon surface towards the cations of those of different metal types; a mechanism of coagulating and depositing the colloid particles was identified. Based on the obtained results the methodology of silicon deposition from geothermal fluid with the certain physical and chemical

characteristics, which can be used to increase the efficiency of the binary power units of GeoPPs, was designed.

3. Based on the carried out experiments there were found the economical factors of increasing the efficiency of the fluid usage, allowing justifying an expedience of different silicon precipitation regimes.

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