

PRECIPITATION OF COLLOID SILICA FROM HYDROTHERMAL SEPARATE BY COAGULANTS ADDITION (KAMCHATKA, RUSSIA)

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ABSTRACT

We have carried out the experiments on coagulation and precipitation of silica from the separate of Verkhne-Mutnovsky geothermal electric power plant (Mutnovskoe hydrothermal field). Silica precipitation from the water solution was conducted in two ways: by adding slaked lime CaO and by electrocoagulation treatment on aluminium electrodes. Silica precipitation with addition of slaked lime was carried out under laboratory conditions at the temperature of 20 and 96 °C. Colloid and monomeric silica concentrations, solution pH, flakes sizes and physical-chemical properties of material precipitated with different quantities of added lime were determined. We also carried out series of experiments on solution treatment of mixed type: addition lime with freshly precipitated flakes, and addition lime with sea water. In the experiments on electric coagulation, current intensity and distance between electrodes were changed. Dependence of silica concentration on treatment duration was studied. Quantities of electric energy and anode aluminium consumed for reducing of silica concentration to a certain level were obtained. The results of our experiments can be used for developing of technological scheme of silica precipitation and utilization optimal for Verkhne-Mutnovsky geothermal electric power plant.

INTRODUCTION

Geothermal power engineering faces the problem of increasing the high-temperature heat carrier utilization efficiency (Harper R.T., Thain I.A., Johnston J.H., 1992). Hydrothermal heat carrier of a such type initially exists as a liquid at the temperature of 250-300°C. When ascending to the surface along the producing wells, water solution is oversaturated on amorphous silica due to the pressure and temperature decrease and evaporation, and solids are formed in heat equipment and reinjection wells.

Therefore, the liquid phase of the waste heat carrier (separate) has to be injected into the geothermal reservoir at a high temperature (130-150°C) (Britvin O.V., Povarov O.A., et al. 1999). It makes impossible direct use of heat and operation the binary-type station and decreases the efficiency of the heat carrier utilization. Addition of solid deposit inhibitors into the separate is quite an expensive approach that didn't find any application in geothermal power engineering. In Russia, the problem of the control for solid deposits and increasing of utilization efficiency is quite actual in connection with construction and operation of geothermal electric power plants of the Mutnovskoye hydrothermal field (Kamchatka) (Britvin O.V., Povarov O.A., et al. 1999, Potapov V.V., Kashpura V.N., Alekseev V.I., 2001, Potapov V.V., 2001, 2002).

We have conducted the experiments on silica precipitation from hydrothermal separate as well as studies of physical-chemical properties of the precipitated material. Precipitation was carried out by two different ways (by adding slaked lime CaO and electrocoagulation), which allow comparing the types of chemical processing. The final goal of such experiments is working out the technology of silica precipitation and utilization, which would be optimal for the heat carrier of the Mutnovskoye hydrothermal field. The results of our investigations can find wide application when designing geothermal power plants with binary facilities.

CHEMICAL COMPOSITION OF THE HYDROTHERMAL SEPARATE

For the experiments on lime treatment, separate samples were taken from the reinjection line of the Verkhne-Mutnovskaya geothermal electric power station. Producing wells of the station bring out to the surface the heat carrier in the form of steam-and-water mixture (SWM) with steam weight content of 0.2-0.3. In the separators of the first and the second

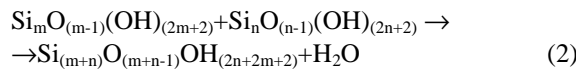
lines, at the temperature of 170.4°C and the pressure of 8.0 bar, vaporous phase of SWM is separated from the liquid phase (the separate). Vaporous phase is supplied onto the turbines. Separate with mass rate of 50-55 kg/s passes into the flash unit where the pressure is decreased to 4.0 bar and the temperature is 143.6°C (Britvin O.V., Povarov O.A., et al. 1999). From the flash unit the separate is injected back to the rocks of the geothermal system through the reinjection wells at the pressure of 4.0 bar. The sampler of the separate was settled on the reinjection pipeline.

Heat carrier composition is formed as a result of chemical interaction of water with the rocks of the hydrothermal system at the temperature of 250-300°C (Karpov G.A., 1976). Water solution includes the compounds of Na, K, Ca, Mg, Cl, S, C, B, O, Si and other elements. Data on anion-cation composition of the separate are presented in Table 1. Besides it, the following compounds are present in the separate (mg/kg): Ca²⁺- 1.6, Mg²⁺- 0.72, Fe²⁺ - 0.1, Al³⁺ - 0.27, Li⁺ - 0.71, NH₄⁺- 1.1, HS⁻- 5.0, H₃BO₃ – 106.9. According to monitoring data from March till September 2001, average content of SiO₂ in the separate of the station is 680 mg/kg, while pH is 9.2-9.4 (20°C).

Table 1. Concentrations of anions and cations in separate from the reinjection line of Verkhne-Mutnovsky Geoelectric power plant (mg/kg)

Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻
239.4	42.0	198.5	192.1	81.0	19.9

Oversaturation of the heat carrier liquid phase relatively to solubility of amorphous silica leads to the reaction of polymerization (compounding) of the silica acid molecules (Iler R., 1982):



As the result of the polymerization reaction, colloid particles of hydrated silica (mSiO₂·nH₂O) are formed in the solution. Kinetics of reaction of polymerization and the final size of the particles depend upon the temperature and solution pH. Mass transfer of the particles from the separate flow to the inner surface of heat equipment and wells results in formation of amorphous silica solid deposits.

METHODS OF STUDING OF SOLID DEPOSITS

Solid deposits and corrosion products were sampled from different elements of heat equipment of Verkhne-Mutnovskaya Geoelectrical power plant:

separators, flash unit, silencer, turbogenerator TG1 (exhaust, blades, bandage rings and a vacuum tank), as well as from the heat-exchanger pipes of ejector's cooler, the drain tank of the station and from the snow surface where separate was frozen to produce dispersed silica.

The samples were studied by using methods of X-ray-powder analysis, thermochemical and spectral analyses, as well as by silicate analysis (Kashpura, V.N., Potapov, V.V., 2000). Table 2 shows the chemical composition of typical samples of solid deposits and corrosion: the VM1 sample from the upper part of the silencer, the VM4 sample from the walls of the separator of the second line's first stage.

Table 2. Chemical composition of samples VM1 and VM4

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	Na ₂ O	K ₂ O
VM1	84.5	1.74	0.10	1.50	1.40	1.14
VM4	5.30	0.36	63.50	15.50	0.48	0.10

All the solid deposits samples such as VM1 sample, had high percentage of SiO₂ and were of amorphous structure. Spectrums of the X-ray-powder analysis of the corrosion samples and deposits samples appeared quite different. Within the spectrums of the corrosion samples there were lines of magnetite Fe₃O₄, hematite and maghemite Fe₂O₃, goethite FeO(OH) and pyrite FeS₂. Magnetite, hematite (or maghemite) and pyrite dominated in the samples from separators and the flash unit. In the samples from the turbine, which formed during interruption of turbine operation, the ferric iron was mainly in the form of goethite, less in the form of magnetite and hematite. Samples from the turbine contained practically no pyrite at all. Deposits from the vacuum tank of the turbine contained rozenite FeSO₄·4H₂O.

Sizes of colloid particles in hydrothermal separate probes were measured by the method of photon correlation spectroscopy. This method allows to record fluctuations of concentration of colloid-sized particles participating in the Brownian motion, by the intensity of the dispersed monochromatic laser light, as well as to determine the coefficient of the particles diffusion in the solution, and on basis of it, to calculate the radiuses of particles. The scheme of the PhotoCor-Complex plant included a laser with wavelength of 6330Å⁰, goniometer with sample cells for the solution, detector of dispersed radiation, photoelectric multiplier, photo-correlator and personal computer for mathematical treatment of the recorded data on fluctuations of light intensity.

Using the method of nitrogen absorption at the temperature of 77.2 K, we determined the

characteristics of the pores of fine silica, precipitated during the experiments on freezing out the separate solution drops on the snow surface: specific area (BET-area) – 274 m²/g, porosity – 1.08 cm³/g, average pore diameter (BET-method) – 126.9 Å.

EXPERIMENTS ON SILICA PRECIPITATION WITH LIME ADDITION AT THE TEMPERATURE OF 20 °C

Before the treatment by slaked lime, separate probes in the volume of 1.0 litre were preliminarily poured into transparent polyethylene cylindrical containers. Immediately before the addition, lime was pounded and slaked in a vessel by 20-50 cm³ of a hot water with the temperature of 95-100°C during 1-2 minutes. After that the slaked lime was added into the separate, the probe was intensively stirred for 30-40 seconds.

After the stirring we observed increased turbidity of the solution, and in 1-2 minutes mealy-white flakes were formed in the water volume. The flakes precipitated on the bottom of the container, and the solution volume was clarified. Effective size of the flakes and the time of solution clarification were determined by the velocity of flakes precipitation:

$$d = (18 \cdot \mu \cdot u / \Delta \rho \cdot g)^{0.5}, \quad (3)$$

where u is the velocity of flakes settling, μ is dynamic viscosity of water, $\Delta \rho$ is the difference of silica and water density, kg/m³, g is gravity acceleration.

Fraction of the solution volume with precipitated flakes on the bottom of the container was not more than 0.2. The precipitated material was separated from the clarified solution by decantation, and afterwards it was dewaterized in the centrifuge by 20 minutes run at the frequency 5000-6000 rev/min. This provided solid phase content in dewaterized material of 5 weight percents. Then dewaterized material was dried out at temperature of 105°C.

In 40-60 minutes after the treatment, residual concentration of colloid and monomer silica was determined in aliquots of clarified solution, as well as concentration of Ca²⁺ and Mg²⁺ cations and solution pH. Concentration of silica was determined by colorimetric method with ammonium molybdate (Martynova O.I. et al. 1980), whereas concentration of calcium cations was determined by complex compound titration with EDTA (ethylen diamine tetraacetate natrium) in the alkaline medium with murexide. The presence of dissolved hydrogen sulphide in the water made it difficult to determine the content of silica due to its influence on silica-molybdate complex. To avoid this influence during

the analysis, before adding ammonium molybdate, potassium persulphate K₂S₂O₈ or ammonium persulphate (NH₄)₂S₂O₈ in quantity of up to 5 mg per 50 cm³ of the analysed aliquot was injected into the solution.

The quantity of lime CaO added to the solution in the experiments on silica precipitation ranged from 40 to 1500 mg/kg. It allowed to study physical and chemical characteristics of the processes of coagulation, flakes formation and solution clarification. The results of the separate treatment at the temperature of 20°C in relative to the quantity of lime CaO added to the solution are presented in Table 3.

Table 3. Results of separate treatment by lime at the temperature of 20 °C. C_t – residual total content of SiO₂, C_s – monomeric silica concentration, Ca²⁺ – residual concentration of calcium cations

CaO mg/kg	pH	Ca ²⁺ mg/kg	C _t mg/kg	C _s mg/kg
0	9.29	1.6	697.0	150.3
100	10.10	43.0	158.1	158.1
150	10.48	58.5	158.0	158.0
200	10.82	77.1	158.0	158.0
300	11.42	89.2	153.0	153.0
400	11.68	87.2	137.5	131.9
500	11.6	73.1	75.6	73.8
600	12.07	76.2	75.0	71.3
800	12.16	58.1	41.3	36.3
1000	12.25	60.0	24.0	24.0

The silica concentration in the solution was decreasing, and pH was increasing as the quantity of added lime CaO increased (Table 3). At the same time, precipitation of both colloid and monomeric silica took place. However, stability of monomeric silica was much higher and for its precipitation great quantity of added lime was necessary. Residual concentration of Ca²⁺ cations was about 40-90 mg/kg (Table 3).

The following peculiarity was observed for the process of silica coagulation and precipitation with lime addition at the temperature of 20°C: practically all colloid silica precipitated already with addition of 80-100 mg/kg CaO. With addition of 60-70 mg/kg CaO precipitation was quite unstable, and with addition of 40-50 mg/kg CaO only the increasing of solution turbidity took place without any silica precipitation.

Concentration of monomeric silica started to decrease only with CaO addition of more than 400 mg/kg, when the total residual content of SiO₂ decreased to solubility of amorphous silica 120-150 mg/kg at the

treatment temperature of 20°C – (Table 3). With CaO addition of less than 400 mg/kg, monomeric silica practically did not precipitate at all.

DETERMINATION OF THE FLAKES SIZE OF PRECIPITATED SILICA

In our experiments the velocity of flakes movement and the time of solution clarification were measured. Effective sizes of the flakes were calculated by the equation (3). The velocity of flakes precipitation and their sizes depended upon the quantity of added coagulant. Table 4 shows the measured values of the depth h of settling of the upper margin of the layer with flakes in the solution depending upon the time t_{at} which has passed after the treatment, for various quantities of lime addition: CaO– 100, 200, 300, 400, 500, 600 and 800 mg/kg.

The curves $h(t_{at})$ have two sections. The first section, in which velocity of the layer margin movement is quite substantial, at $t_{at} = 10$ min is characterised by average flakes movement velocities of 6.5-10.2 mm/min (Table 4). Such velocities in Stokes regime of flakes movement correspond to the following effective sizes of the flakes: 100 mg/kg CaO – 6.5 mm/min, $d = 14.1 \mu\text{m}$; 200-300 mg/kg CaO – 10.2 mm/min, $d = 17.7 \mu\text{m}$; 400-500-600 mg/kg CaO – 8.3-8.5 mm/min, $d = 15.9-16.1 \mu\text{m}$; 800 mg/kg CaO – $d = 15.6 \mu\text{m}$.

Table 4. Dependence of depth h (sm) of settling of the layer with flakes upon the time after treatment t_{at} (min) at the temperature of 20 °C

t_{at} , CaO,	1	4	10	14	18	22	26	30
100	0.1	1.3	6.5	9.3	10.6	11.5	12.0	12.2
200	0.8	4.6	10.2	11.4	12.3	12.6	13.0	13.1
300	0.8	4.8	10.2	11.8	12.4	12.8	13.1	13.3
400	0.5	3.4	8.3	10.1	10.9	11.5	11.7	12.0
500	0.5	3.1	8.5	10.1	10.8	11.3	11.6	12.1
600	0.6	3.0	8.4	10.1	11.3	11.6	12.1	12.5
800	0.7	3.3	8.0	9.6	10.3	10.8	11.1	11.6

After the beginning of precipitation, the velocity of flakes movement and their effective sizes start to increase due to their aggregation. The second section is flatter, the curves being placed convexity up. In this section the velocity of flakes movement is slowing down as a result of reducing of the volume with flakes and increasing of effective viscosity during the flakes movement. At the temperature of 20 °C the solution clarified in 20-30 minutes after the treatment.

According to the Table 4, the velocity of flakes precipitation after the treatment first increases as the

quantity of added lime CaO increases from 100 to 200-300 mg/kg, and then slows down with the further increasing of lime quantity to 400-800 mg/kg. It is connected with the fact that when coagulant concentration increases, the flakes sizes and the velocity of their movement increase as well; however, alongside with that, the volume ratio of the flakes in the solution goes up and water viscosity increases. With addition of 400 mg/kg CaO and more, the effect of viscosity increasing becomes predominating.

EXPERIMENTS WITH ADDITION OF FLAKES AND SEA WATER

In our experiments with lime addition, flocculation capacity of silica sludge had been studied. For this purpose, separate probe treatment with addition of freshly precipitated flakes and small quantities of lime CaO (60 mg/kg) was carried out. At such quantity of lime the effect of additional flocculation was more evident. Immediately after slaked lime addition and stirring, 200 cm³ of water with fresh flakes from another probe (previously treated with addition of 100 mg/kg CaO in 50-60 minutes before) was added to the solution. Without flakes addition with addition of 60 mg/kg CaO only, silica precipitation did not occur at all.

The process of precipitation with flakes addition passed in two stages. After the flakes addition the solution turbidity increased, and in 5-10 minutes after the treatment precipitation of primary added flakes could be observed. In 30-40 minutes after the treatment, precipitation of smaller secondary flakes became visible. Secondary flakes contained a considerable portion of additionally precipitated silica. Double-layered precipitate was formed at the bottom of the vessel.

Residual concentration of silica C_i in the probes treated in such way with flakes addition was within the limits of 168-198 mg/kg. Average value of C_i 186 mg/kg practically coincided with the residual concentration in the probes treated with addition of 100 mg/kg CaO confirmed the flocculation capacity of freshly precipitated flakes. The flakes addition facilitated precipitation of colloid silica only, while concentration of monomeric silica did not reduce.

In order to study the possibility of reducing lime consumption, a series of experiments on separate treatment by slaked lime with sea-water injection had been conducted. Probes of sea water showed pH level of 8.3 and concentrations of calcium Ca^{2+} cations 210 mg/kg and magnesium Mg^{2+} 699 mg/kg. Treatment was carried out with addition of small quantities of lime CaO 70-40 mg/kg. With addition of such

quantities of lime only without of sea water flakes precipitation did not occur at all. This was made in order to reveal the coagulating effect of sea water (Table 5).

Table 5. Results of separate probes treatment with addition of sea water at the temperature of 20 °C (SW – volume of sea water added to the solution)

CaO, mg/kg	SW, cm ³ /kg	pH	C _t , mg/kg	C _s , mg/kg
0	0	9.10	740.6	212.5
70	15	9.73	194.4	168.8
70	20	9.62	156.3	155.0
70	100	9.21	149.4	125.6
60	20	9.51	188.8	156.9
60	30	9.53	178.1	146.3
50	50	9.26	175.0	145.6
50	100	9.24	140.6	133.1

Sea water was injected into the separate probes immediately prior to the slaked lime addition, after which the solution was intensively stirred. After the treatment with sea water addition, opalescence of the solution could be observed. pH of the probes treated with addition of sea water was not increased so significantly as in the probes treated by lime only (Table 5).

At stable precipitation of silica, flake formation and solution clarification started in 1-2 minutes after the treatment. For stable precipitation it was necessary to inject the following volumes of sea water: 15-20 cm³/kg of sea water – with addition of 70 mg/kg lime CaO, 25-30 cm³ of sea water – with addition of 60 mg/kg CaO, and about 40 cm³/kg of sea water – with addition of 40-50 mg/kg CaO. At the same time, total content of SiO₂ C_t reduced to 160-190 mg/kg, and with injection of 100 cm³/kg of sea water – to 140-149 mg/kg (Table 5), which corresponded to almost complete precipitation of colloid silica.

We also conducted the experiments on silica precipitation with only sea water injection, adding no lime at all. The results show that sea water can act as a coagulant, and with addition already of 100 cm³/kg it provides stable precipitation of colloid silica and reduction of C_t concentration to the values of 160-190 mg/kg.

EXPERIMENTS ON SILICA PRECIPITATION WITH LIME ADDITION AT HIGH TEMPERATURE

Treatment of hot separate probes at the temperature of 94-97 °C was carried out to study the process of silica precipitation at high temperatures. The quantity of added lime CaO ranged within the limits from 100

to 1500 mg/kg. Slaked lime was put into the probes treated with addition of 100 and 200 mg/kg CaO. Into the other probes lime was added without preliminary slaking.

Before the treatment, transparent hermetic tanks with the separate probes were placed into a thermostatically controlled chamber, where they were kept for 5 hours to complete the reaction of depolymerization. During depolymerization colloid silica transferred into monomeric one in accordance with solubility of amorphous silica at high temperatures. After the addition of lime all the probes were quickly stirred and then the vessel with the solution was put back into the thermostat, so after treatment the precipitation occurred at high temperature.

After the stirring, increasing of solution turbidity, flakes formation and precipitation could be observed. This process appeared much rapider in hot solution than in cold at the temperature of 20°C. With addition of great quantities of lime (400-500 mg/kg and more) flakes formation started immediately during the injection of CaO and stirring. 20-25 minutes after the treatment and keeping in the thermostat, water aliquots were taken from the vessels with solution and were tested afterwards on residual content of silica. The results of probes treatment at high temperatures are presented in Table 6 (pH was measured after the solution cooling at the temperature of 16-20°C).

Table 6. Results of hydrothermal separate treatment by lime at a high temperature (n.a. – not analysed)

Temperature of treatment, °C	CaO mg/kg	pH	C _t , mg/kg	C _s , mg/kg
20	0	9.26	718.8	135
96	100	9.73	344.9	244.4
95-96	200	9.76	329.8	273.0
95-97	300	9.88	315	275
95-97	400	10.32	345	322.5
96	500	10.1	339	334.4
96	600	10.16	307.8	307.8
95	700	10.48	260.9	260.9
96	800	10.92	229.7	217.2
96	900	11.16	190.6	190.6
96	1000	11.16	203.1	203.1
94	1100	11.57	157.0	n.a.
94	1200	11.68	64.9	n.a.
94	1300	12.09	25.6	n.a.
94	1500	12.24	6.3	n.a.

With addition of more than 100-200 mg/kg CaO (Table 6) the residual concentration C_t of silica reduced to the value less than 345 mg/kg, which was

lower than solubility of amorphous silica at the temperatures of 90-100 °C. Difference between the concentrations C_t and C_s was practically zero for these probes. With addition of more than 200 mg/kg CaO at temperature of 94-97 °C all colloid silica precipitated.

With addition of more than 700 mg/kg CaO (Table 6) residual concentration C_t reduced to the value of less than 261 mg/kg, which was essentially lower than amorphous silica solubility at the temperature of 90-100°C, and it corresponded to the beginning of monomeric silica precipitation. Stability of monomeric silica at the temperature of 94-97 °C was much higher than in cool solution at 20 °C: when quantity of added lime increased from 300 to 1000 mg/kg, residual concentration C_t reduced from 315 only to 203.1 mg/kg (Table 6).

Concentration of monomeric silica C_s in all the probes was much higher than solubility of amorphous silica at temperature of 16-20°C (Table 6). Monomeric silica, which concentration in hot solution reached 300-400 mg/kg, did not polymerise again when the solution was cooled and did not transform into colloid silica. After treatment by lime pH of the solution increased and solubility of amorphous silica C_E respectively increased as well. Owing to that, motive force of the polymerisation reaction ($C_s - C_E$) reduced, and the rate of the reaction became so low that monomeric silica practically did not transform into colloid one at all.

The process of silica precipitation was significantly enhanced by injection of sea water into the solution before addition of slaked lime. In probe treated with addition of 100 mg/kg CaO and 50 cm³/kg of sea water, residual concentration of silica C_t 171.0 mg/kg was lower than in probe treated only by 100 mg/kg CaO.

CHEMICAL COMPOSITION OF THE MATERIAL PRECIPITATED WITH LIME ADDITION

The portion of calcium in the composition of precipitated material depended upon the quantity of added lime. Data on chemical composition of the precipitated material and value of the ratio CaO/SiO₂ at various quantities of added lime are presented in Table 7.

The quantity of added lime CaO varied from 1500 to 80 mg/kg. Respectively, the ratio CaO/SiO₂ in the precipitated samples reduced from 1.00 to 0.0196. The smallest portion of calcium was found in the sample L99 precipitated with addition of 80 mg/kg

CaO. For samples precipitated with addition of 60 mg/kg CaO and fresh flakes, CaO/SiO₂ ratio was 0.0331.

The portion of aluminium and ferrum in the samples precipitated with lime addition was also quite small: the ratio Al₂O₃/SiO₂ ranged within the limits of 0.00916 – 0.00490, and the ratio Fe₂O₃/SiO₂ – 0.003 – 0.028 (Table 7). The value of this ratio was much higher than in the separate. Aluminium and ferrum penetrated into the precipitated material from the original quicklime in which concentrations of aluminium and ferrum were much higher than in the separate.

Table 7. Content of basic compounds in the material precipitated with addition of lime at 20 °C (n.f. – not found), 0 mg/kg CaO corresponds to composition of the lime used as a precipitant, 60 mg/kg CaO corresponds to the material precipitated with addition of lime and fresh flakes

CaO, $\frac{mg}{kg}$	$\frac{CaO}{SiO_2}$	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O
0	31.24	2.96	0.36	0.31	92.49	1.13	0.42
1500	1.00	29.4	0.27	n.f.	29.48	1.80	0.29
1000	0.89	32.0	0.18	n.f.	28.68	1.64	0.29
800	0.74	35.8	0.24	n.f.	26.60	1.18	0.29
700	0.60	38.5	0.25	n.f.	23.36	1.16	0.48
600	0.37	51.6	0.32	n.f.	19.60	1.10	0.29
500	0.29	59.8	0.54	0.09	17.55	1.11	0.32
100	0.125	82.4	0.62	0.19	10.30	1.16	0.48
80	0.019	71.3	0.35	n.f.	1.40	4.50	1.10
60	0.033	80.3	0.46	n.f.	2.66	1.60	0.48

The material precipitated with addition of lime had an amorphous structure. Samples with low value of CaO/SiO₂ ratio, precipitated at small quantity of added lime, turned into cristobalite SiO₂ after ignition at 900°C. Samples with high CaO/SiO₂ ratio, precipitated at great quantity of added lime, contained amorphous halo and lines of calcite (CaCO₃) in the spectrums of X-ray-powder analysis. After ignition these samples turned into wollastonite CaSiO₃ or into a mixture of wollastonite and cristobalite.

EXPERIMENTS ON SILICA PRECIPITATION BY ELECTROCOAGULATION ON ALUMINIUM ELECTRODES

Experiments on silica precipitation from separate by the method of electrochemical coagulation were conducted at direct current mode (Potapov V.V, 2001, 2002). Electrodes made of aluminium, copper, stainless steel and galvanized steel were used for electrical treatment. Most part of the experiments was

conducted using aluminium electrodes. Coagulant was supplied to the solution as a result of aluminium anode dissolution and consequent hydrolysis of cations Al^{3+} (Babenkov E.D., 1977).

In these experiments current strength ranged within the limits of 0.5-3.0 A, current density – 37-112 A/m^2 , electrodes voltage– 4-11 V, electric field strength – 400-110 V/m, distance between the electrodes – 5-15 mm, temperature of the solution – 20-60°C. We determined the dependence of silica residual concentration and solution pH upon the treatment duration t_m and electric charge Q_K which had passed through the solution, at various values of current strength I.

The process of silica precipitation by electrocoagulation differed from the precipitation with addition of lime in two essential ways. Firstly, during the electrical treatment, colloid and monomeric silica precipitated simultaneously. Concentrations ratio C_t/C_s remained practically constant with the value of 6-8 during the treatment till the total silica content C_t was more than 118-120 mg/kg, after which C_t/C_s ratio abruptly increased up to the value of 40. When treated with addition of lime, monomeric silica started to precipitate only with addition of 400-700 mg/kg CaO.

Secondly, silica concentration during electrocoagulation reduced gradually: the process took three stages [4]. Dependence of silica residual concentration C_t (mg/kg) upon the amount of electric charge Q_K (Coulombs) which had passed through the solution at the second stage of the treatment, can be expressed by the equation [4]:

$$C_t = 713 \cdot \exp(-C_Q \cdot (Q_K - 300)), \quad (4)$$

where $Q_K=(300-1200)$ coulombs, C_Q is a coefficient, which values depend upon current strength. After treatment with lime addition, silica content did not reduce gradually, but very rapidly: with addition of 80-100 mg/kg CaO and more, practically all colloid silica precipitated. Thus, electrical treatment allows to reduce silica concentration in a more controlled way.

The amount of electrical energy Q_E (Joule) necessary for the treatment of 1 kg of the separate to reduce silica concentration from 800 mg/kg down to the value of C_t (mg/kg), can be determined by the formula [4]:

$$Q_E = R \cdot I \cdot ((1/C_Q) \cdot \ln(713/C_t) + 300)), \quad (5)$$

where R is ohmic resistance of the coagulator, Ohm. Consumption of electrical power per 1 kilogram of precipitated silica SiO_2 was 1.85-6.0 kWh/kg, anodic

aluminium consumption rated as much as 124-155 g/kg. Material, precipitated by electrocoagulation, had amorphous structure, with Al/SiO_2 ratio within the limits of 0.1-0.2.

Addition of sea water during electrochemical treatment increased electrical conductivity of the solution, reduced the treatment duration t_m as well as consumption of aluminium and energy. Thus, the most promising is a mixed type of treatment with addition of slaked lime followed by electrical treatment, or vice versa.

TECHNOLOGICAL SCHEME OF SILICA PRECIPITATION

The results of the conducted experiments allowed to work out a principal scheme for silica precipitation indicating the main stages and elements of the equipment. Before the treatment, separate passes through a flash unit and feeds into the tank for ageing. The pressure within the flash unit determines the water temperature at the ageing stage. Separate ageing is necessary to complete the reaction of monomeric silica polymerization and colloid particles formation. The ageing tank volume for a given separate mass rate must be large enough to let the growth of colloid silica complete. The tank is heat-insulated outside. Inside it there are baffles to force the separate to travel along S-shaped path to avoid stagnant zones.

After ageing the separate is transferred into the mixer tank, where dispersed precipitating agent (coagulant or flocculant) is added. In case of electrical treatment, the separate passes through the electrical coagulator, where coagulant is supplied due to anodic dissolution. If lime is used, it is previously slaked in the tank for lime slaking. Rate of dispersed precipitant addition is regulated by a dosimeter of granular material. The mixer tank is equipped with a variable speed stirrer.

Further on, the treated solution passes into the tank for precipitation (clarifier), where flakes are separated from the solution. Tank for precipitation consists of two concentric cylindrical parts. The tank has a cylinder-shaped inner unit with conical lower part. Clarified solution feeds into a ring space between coaxial cylinders which is called the clarification zone and then overflowed out of the tank. From the bottom part of the tank, precipitated sludge is taken to a vacuum filter for dewaterization and further drying. Part of the sludge is taken back to the precipitating tank by recirculation, it allows to reduce coagulant consumption and get much cleaner material.

Chemical composition of the precipitated material (ration of CaO/SiO₂, Al/SiO₂, etc.) is regulated by the rate of coagulant addition and sludge addition in the recirculation line. Dispersity of precipitated material, characterised by specific surface (BET-area), depends upon the size of colloid particles after ageing and upon the type of precipitant and it's dispersity. The size of colloid particles before precipitation can be regulated by the solution temperature at the stage of ageing (Harper R.T., Johnston J.H., Wiseman N., 1997, Rothbaum, H.P., Anderton, B.H., 1975).

Thus, the technological scheme allows to obtain amorphous material with variable physical-chemical properties: density, chemical purity, porosity, specific surface, whiteness, light reflection coefficient, oil absorption, etc. Depending upon these properties, precipitated silica may find application in industry including paper, rubber, glue, glass, ceramics, brick, cement, drilling materials, sorbents and in other areas (Harper R.T., Johnston J.H., Wiseman N., 1997).

Silica extraction will allow to decrease the temperature of separate reinjection. Owing to this, it will be possible to obtain in binary facilities up to 10% electrical power in addition to the projected power of Geoelectrical power plant operating of high temperature hydrothermal heat-carrier. When combined, amorphous silica extraction, additional electrical energy generation and direct use of heat will give a 10-20% increase of hydrothermal heat-carrier utilization efficiency.

CONCLUSIONS

1. Working out the technology of colloid and monomeric silica extraction is necessary to increase of hydrothermal heat-carrier utilization efficiency.
2. Experiments on silica precipitation from hydrothermal separate with addition of slaked lime and by electrocoagulation have been conducted. Basic peculiarities of each type of treatment have been investigated, as well as dependence of silica residual concentration and pH upon the quantity of added coagulant at different temperatures, flakes sizes of the precipitated material and its physical-chemical properties. Experiments on treatment with addition of fresh flakes and sea water have been carried out.
3. Principal technological scheme for silica extraction from separate flow has been worked out based upon experimental data. Realisation of the proposed scheme will allow to get additional electrical power, heat and minerals in the form of amorphous silica, as well as to increase of hydrothermal heat-carrier utilization efficiency (up to 10-20%).

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