

STUDY OF THE AMORPHOUS SILICA SCALES FORMATION AT THE MUTNOVSKOE HYDROTHERMAL FIELD (RUSSIA)

Kashpura V.N.¹, Potapov V.V.²

¹Open joint-stock company «Kamchatskenergo»,
(Russian joint-stock company United Energy System),
engineer of the Laboratory of geothermal power engineering,
Russia, 683000, Petropavlovsk-Kamchatsky,
Naberezhnaya street, 10.

²Geotechnological Research Center,
Far East Branch of the Russian Academy of Sciences,
research worker of the Laboratory of geotechnology and geochemistry.
Russia, 683002, Petropavlovsk-Kamchatsky,
Severo-Vostochnoe shosse, 30,
P.O. box 56, (41522) 51323.

Key words: geothermal system, reinjection, solids, geothermal silica,
rate of scales growth, isobar-isothermic potential, chemical equilibrium,
alkalization, acidification, electrochemical treatment.

ABSTRACT

Formation of the amorphous silica solid scales in wells, separators, pipes and heat exchangers is the essential problem that makes difficult wide usage of geothermal resources. Various types of amorphous silica were selected at the Mutnovskoe field and their silicate, X-ray diffraction and thermochemical analyses were done. The possibility of disposal brine treatment by alkali and acid before reinjection was studied under conditions of Verkhne-Mutnovskaya geothermal electric power station by the numerical modeling study of the chemical equilibrium in the multicomponent solution. Data of the test on determining the rate of the silica scales growth in heat exchanger and results of the electrochemical treatment of hydrothermal solution are given. Results of this study can be used in technology of geothermal silica precipitation which is considered as a by-product.

INTRODUCTION

Geothermal systems are one of the alternative sources of energy and mineral compounds, which has economic and ecological advantages. However, in spite of these advantages, there are some problems that make it difficult to use widely geothermal resources.

Such problems include: exploration of geothermal reservoirs, evaluation of reserves, drilling in zones of high-temperature anomalies, conducting the logging activities in geothermal wells, prevention of corrosion of the technical equipment. Large difficulties concern also the multicomponent chemical composition of the geothermal heat carrier that contains dilute gases (hydrogen, carbon dioxide, hydrogen sulphide, methane) and solid mineral com-

pounds. When temperature and pressure are decreasing in the course of the extraction and heat-carrier exploitation then deposition of dilute substances occurs that requires taking measures on prevention of this process.

Liquid phase of the fluid and geothermal gases (CO₂, H₂S) must be pumped backwards into the rocks through the reinjection wells in order to maintain pressure in reservoir and decrease influence on the environment. Motion of brine in the heat equipment and reinjection wells is often complicated by silica scaling from solution that decreases amount of obtained energy and leads to the additional expenses for solid material removal. In view of this the process of solids formation is of special importance for geothermal systems and needs to be studied and controlled.

MECHANISMS OF GEOTHERMAL SILICA FORMATION

Solids formation is one of the most important factors that restrict in many cases rate and scales of using the geothermal system resources (Thomas D.M., Gudmundsson J.S., 1989). Basic part of solids consists of the following components: oxides, sulphides of iron, calcium carbonate and dioxide of silicium SiO₂ (silica).

Silica scaling is the largest problem that displays practically at all geothermal fields, especially at the high-temperature, because fluid forms in contact with rocks where silicium is the basic rock-forming element. The solubility of silica is decreasing when temperature decreases. As opposed to carbonate, silica deposition is controlled by kinetics and can begin on the surface in several minutes or hours after reaching supersaturation. Silica scales are hard to mechanical removal.

Formation of silica scales is a physical-chemical process. It is controlled by the following factors: amorphous silica solubility, temperature, composition, pH of solution, rate of growth, dimension, concentration of colloidal particles, hydrodynamic conditions in brine flow.

Depending on the degree of supersaturation processes of nucleation and colloidal particles growth develop as a result of interaction of silaneous groups (polymerization reaction, Iler R.K., 1979) and aggregation of particles. Colloidal particles are moved to the surface by mass transfer in a flow and silica precipitates finely as a solid amorphous matter. Increase in alkalinity to $\text{pH} > 8.0$ speeds up aggregation of particles.

In view of this study of silica solubility and kinetics of deposition has evident practical importance for solving technical problems of geothermal power engineering and for technology of silica extraction. Silica can find application in chemical production: as an addition to the paper, plastic, rubber, special types of concrete, glues, paints, washing powders, for ceramics and liquid glass production. Cost of silica at the New Zealand market is of US\$ 1,300/t.

In geothermal plants Vairakey and Kaverau in New Zealand commercial experience of silica extraction for production of high-quality paper has been obtained (Harper R.T., Thain I.A., Johnston J.H., 1995). Extraction of silica at these objects will allow to obtain additional amount of electric (up to 20 MW, 10%) and thermal (up to 180 MW) energy as the temperature of reinjection decreases.

The purpose of this paper was to study the possibility of solids formation and methods of control for amorphous silica scaling from geothermal solution under conditions of Verkhne-Mutnovskaya geothermal electric power station. Modeling study of the chemical equilibrium in the system of multicomponent geothermal fluid was one of the investigation methods. Effectiveness of modeling study can be explained by the fact that the chemical composition of fluid is different at every geothermal field, at various wells of the same field and at the same well in different moments of time.

BASIC EQUATIONS FOR MODELING STUDY OF THE GEOTHERMAL FLUID CHEMICAL COMPOSITION

Pressure and temperature in a flow of fluid are continuously changed during the extraction and exploitation. During the modeling study a supposition was taken into account that in every moment of its motion fluid substance had time to reach the thermodynamic equilibrium. It means that concentrations of components C_i^e , activities of water components a_i , fugacities of the gases f , Eh, pH and ionic force I of solution are determined by condition of the minimum of Gibbs' potential G of system. Values of equilibrium concentrations and other parameters are, thus, functions of pressure and temperature.

Such approach allows to reveal the possibility of solid phase deposition, if amount of silica in solution exceeds solubility value. Also it is possible to evaluate the prospect of increasing silica solubility (for example, by alkalization), to consider various variants of the water fluid treatment.

In this connection a criterion of the possibility of silica deposition that was discussed in paper of Fleming B.A. and Crerar D.A. (1982) was used: if the amount of silica in the system is not more than two times higher than the amorphous form solubility, then the existence time of the supersaturated metastable state is indefinitely long and there will not be any solids. If the supersaturation degree is more than 2, then kinetics of polymerization is high and there is a probability of solids presence. Decrease in pH up to 5-5,5 by adding acid is the other method to inhibit the reaction of polymerization.

A program complex of the type introduced in paper of Karpov I.K., Chudnenko K.V. and Kulik D.A. (1997) was used. Given isobar-isothermic potential of the system is presented as the following:

$$G(x, P, T) = \sum C_j x_j + \sum x_j \ln \frac{x_j}{x_a} - \sum x_j \ln \frac{x_{jw}}{x_a}, \quad (1)$$

where x_j is a number of moles of the dependent component (combination) j , x_a is a total amount of moles of dependent components in a phase a , $x_a = \sum x_j$, $j \in a$; x_{jw} is a number of water moles and C_j are functions of isobar-isothermic potentials of the system components j .

Potential was minimized by numerical method with the additional condition of mass balance, its application is described in paper of Karpov I.K., et al (1997).

PARAMETERS OF VERKHNE-MUTNOVSKAYA GEOTHERMAL ELECTRIC POWER STATION

Complex of the Verkhne-Mutnovskaya geothermal electric power station with producing wells is located within eroded caldera of volcano Zhirovisky that refers to the Mutnovsky volcanic region which is 70 km southward of Petropavlovsk-Kamchatsky city. Mutnovskaya hydrothermal system includes two parts: the upper one with cold water and the lower consisting of the steam-and-water zone (in two-phase state) and zone with prevalence of hot water with the temperature of 250-300°C.

Geothermal wells (048, 049, 055) of Verkhne-Mutnovskaya station produce to the surface a heat-carrier as a steam-water mixture. Average steam content x of producing wells is 0.3. Wells 024, 043 and 054 are provided for reinjection. Chemical composition of liquid phase from 048 well is the following (mg/kg): SiO_2 -830, Cl^- -325, SO_4^{2-} -167, HCO_3^- -55, Na^+ -290, K^+ -35.5, Ca^{2+} -1.6, Mg^{2+} 0.2, TDS=1704, pH=9.2. Chemical composition of the fluid in wells 049 and 055 is close to that in well 048.

Complex of geothermal electric station includes three power modules with capacity of 12 MW (3×4). Turbine of

the electric module works on saturated steam (8.9 kg/s) with inlet pressure 8 bar and outlet pressure 0.011 bar. It is necessary to pump 48-50 kg/s of separate liquid into the reinjection wells.

In this paper we studied only the possibility of solid silica scales appearing in a liquid phase flow of the reinjection well that had the temperature of 143.62° (4.0 bar).

CHEMICAL AND MINERAL COMPOSITION OF THE SILICA SCALES SAMPLES

In conditions of the Mutnovskaya geothermal system several types of amorphous silica scales were distinguished: 1. white fine-dispersed silicate powder (specific volume of pores is about 3.0 cm³/g)(AS1) ; 2. solid hard thin coating on the rock surface (is formed when pouring steam-and-water mixture into the surface) (AS2); 3. glass-like solid hard scales (AS3); 4. pinkish fragile uneven scales (two last on the inner surface of the pipes of the heat-exchangers and separators) (AS4).

In most of samples dioxide of silicium is up to 85 weight percents. Composition of the first type scales is the following (wt. %): SiO₂ – 85.02, TiO₂ – 0.08, Al₂O₃ – 1.37, Fe₂O₃ – 0.53, FeO – 0.06, MnO – 0.04, MgO – 0.09, CaO – 0.40, Na₂O – 0.27, K₂O – 0.75, H₂O⁻ (physically bound water) – 5.63, ignition losses – 5.15.

Solid depositions on the blades and inner surface of the Mutnovskaya turbine K-0.4 body represents separate group. Average weight content of silica in them is lower – 70-80 wt. %, iron content is higher– 3-7 wt. %.

The fact that silica deposit in equipment in amorphous form is proved by the X-ray diffraction analysis of the samples formed on the pipes of the heat exchanger and after pouring hot water on the surface. Condition of maximum intensity in the spectrum of reflected radiation is the following (Wulf-Bregg equation):

$$2d \sin (\Theta/2) = n\lambda \quad (2)$$

where λ is length of radiation wave $\lambda=1.542 \text{ \AA}$, $\Theta/2$ - angle between direction of radiation and the plane of the sample, d is a distance between the planes of the crystal lattice, n is an integer number.

In spectrum of the X-ray diffraction analysis of samples besides amorphous halo quartz maximums (3.34 \AA , 4.25 \AA) were revealed. Maximum of amorphous haloes in all spectrums coincides with one of the opal maximum (4.0797 \AA). Some kinds of the thermochemical analysis were done for AS1 sample: differential thermochemical (DTC), thermogravimetric (TG) and differential thermogravimetric (DTG) analyses. DTC-analysis revealed the endothermic minimum with the temperature of 125°C that correspond to opal.

Spectrum of a sample taken from the inner surface of the separator has lines of crystals of quartz, hematite (Fe₂O₃) and probably maghemite. Presence of quartz and compounds of ferric iron with low solubility in this sample is,

probably, explained by the period of exploitation with the high temperatures: more than 180-200°C.

Spectrums of the X-ray diffraction analysis of the samples of scales from the blades of the turbine K-0.4 besides amorphous haloes have maximums corresponding to quartz and pyrite FeS₂.

Contribution of amorphous component in spectra of the samples from the inlet branch pipe of turbine is more less than in scales from the blades but a portion of quartz is higher. In spectrums of other samples from wells 014 and 034 maximums of halite (NaCl), thenardite (Na₂SO₄) and gypsum (Ca₂SO₄·2H₂O) were revealed.

A weight portion of quartz in samples was evaluated by the intensity on quartz maximum (3.34 \AA). A portion of quartz in AS1 sample is 1.2 wt. %, in a sample AS2- 1.3 %. In a sample taken from the inner surface of the separator a portion of quartz is higher – 4.9 wt. %, in a sample of scales from the branch pipe of the turbine 4.5 wt. %.

TEST ON THE SILICA SCALES RATE GROWTH

The heat exchanger was constructed in the laboratory of geothermal power engineering («Kamchatskenergo») and it was tested in field conditions to determine the rate of scales growth at the Mutnovskoe hydrothermal field. Heat exchanger consists of a sequence of sections of the «pipe in a pipe» type located parallelly, 10 sections of 1.95 m length each united by insets. Brine with the initial temperature of 120-140°C was fed through the inner pipes (14 mm in diameter) from separator that have been fixed at the well 014. Brine with the temperature of 90-95°C fed into interpipe space between the outer pipe (37 mm) and the inner pipe (14 mm). Silica content SiO₂ reached 810 mg/kg, supersaturation was 240-430 mg/kg. The flow of hot solution in pipes was maintained within 15-60 l/hour, flow of cold solution in the interpipe space was 100-400 l/hour.

Hot solution in the inner pipes did not precipitate silica. Scales of the pinkish layer of silica were observed in the interpipe space with cold solution. Rate of silica scales growth turned out to be significant – (0.75-2)·10⁻⁵ g/cm²·min. Similar values of the rate were observed during the test with geothermal solution at Vairakey – 2·10⁻⁶ gr/cm²·min (Jamieson R.E., (1984)). Series of experiments at the geothermal field Ohaaki (well BR22) showed the value (2-3)·10⁻⁷ g/cm²·min. Test at Hveragerdi in Iceland showed the rate 6.6·10⁻⁷ g/cm²·min (Jamieson R.E., (1984)).

Modeling study of hydrodynamic conditions the effect on the process of amorphous silica deposition was done according to the results of this test. A model from paper of Jamieson R.K. (1994) was used in analysis.

It is supposed by the model, that the rate of scaling R (g/cm²·min) includes two items: one is the rate of the monomeric form (R_m) deposition, another is the rate of the

deposition of particles formed as a result of polymerization R_p :

$$R = R_m + R_p \quad (3)$$

Rate of monomeric deposition is $R_m = (1.8-3.0) \cdot 10^{-7}$ gr/cm²·min, that is much lower than R_p .

Rate of particle deposition depends on the motive power N (difference of particle concentrations between the core of the flow, m⁻³) and a coefficient of mass transfer of particles k (m/sec) (Jamieson R.K., (1994)):

$$R_p = 4\pi r^3 \rho_s N k / 3, \quad (4)$$

where ρ_s is a density of particles (kg/m³), $\rho_s \approx 2000$ kg/m³, r is a radius of particles (m).

According to this given model rates of deposition R_p in the flow of the interpipe space under the temperature of 100°C are determined. Rate of deposition R_p observed in the test, that is $(0.75-2) \cdot 10^{-5}$ g/cm²·min, can be reached with dimension of particles of 5-15 Å and proper concentration N_{\max} $3.8 \cdot 10^{17} - 1.4 \cdot 10^{16}$ cm⁻³. Using such model of silica scaling in test conditions at the geothermal field Wairakei showed a range of particle dimensions of 10-30 Å and concentrations $10^{15} - 10^{16}$ cm⁻³ (Jamieson R.K., (1994)).

For the flow of solution in one of the reinjection wells 024 under the temperature of 100°C, mass rate 18 kg/s and diameter 0.2 m the rate of deposition in the range of particle dimensions 5-15 Å is $(2.0-5.3) \cdot 10^{-5}$ g/cm²·min. Such value R_p corresponds to the growth of the scales height on the surface of the pipes at a rate of 4.3-11.5 mm/month. As a result, it should be expected that the inner section of the reinjection well will considerably decrease (by 1-2 cm) during the first 1-3 month and this will lead to the loss of capacity.

If the reinjection is carried out under higher temperature (>140°C) dimensions of particles can reach 100 Å and rate of scales growth will be about $4.0 \cdot 10^{-6}$ g/cm²·min = 0.86 mm/month = 11 mm/year. In this case decrease in the inner section of the well will occur during the 1st year of exploitation.

Thus, it is necessary to evaluate the feasibility and efficiency of measures on prevention or control for the process of amorphous silica scaling in conditions of the Verkhne-Mutnovskaya geothermal power station.

MODELING STUDY RESULTS OF THE HYDROTHERMAL FLUID CHEMICAL COMPOSITION

Comparing to the experimental data on silicium solubility obtained by other investigators was necessary for appreciation of the results obtained during the numerical modeling study. Data on silica solubility in pure water are well-known by papers of Marshall W.L. (1980), Fournier R.O. and Rowe J.J. (1977), Crerar D.A. and Anderson G.M. (1971), their review is presented in the paper of Chan S.H. (1989).

In a temperature range of 150-250°C calculation results obtained by authors with the accuracy satisfactory for this work coincide with the data given in the paper of S.Arnorsson, S.Sigurdsson and H.Svavarsson (1982): discrepancy value for quartz is within 20%, for amorphous quartz-glass – 3-15%, for α -cristobalite – 1-5%. Temperature is the basic factor that determines silica solubility in poorly dilute water solution. Pressure influences solubility less considerably. Constants of ionization of basic reactions determining the composition of water solution coincide to within 1% with experimental data presented in paper [14].

Results of the modeling study of two-phase fluid composition were compared to the data of the wells tests: wells 4E, 016, 26, Mutnovskoe hydrothermal field. Tests were done with the purpose of determining pressure, mass rate, enthalpy and chemical composition of geothermal fluid. Test equipment included the separator CC-45 of the Kaluzhsky turbine factory, diaphragms and diphmanometers to determine steam and water mass rates, pipes for collecting samples for chemical analysis. Separator CC-45 consists of the battery of cyclones, washing panel, gravitation separator that provide wetness of separated steam up to 0.05 wt.%.

Well 4E drained the lower water part of the reservoir. Vapor content x of the flow was about 0.3, the temperature at the well bottom was 285-286°C (quartz geothermometer). Wells 26 and 016 drained the upper vapor-water zone and they are vapor dominated: wetness $y = 0.001-0.035$. Gas content of well 4E changed during the tests within 0.009-0.015 mole %, well 26 – 0.049-0.068 mole %, well 016 – 0.073-0.119 mole %.

According to the tests data of the well 4E (12.11.98) chemical composition of water brine was the following (mg/kg): SiO₂ – 821, Na⁺ – 272, K⁺ – 54.5, Cl⁻ – 244.9, Ca²⁺ – 3, Mg²⁺ – <0.24, Fe²⁺ – <0.3, Al³⁺ – <0.27, Li⁺ – 1.42, As – 4.2, F⁻ – 4.24, H₃BO₃ – 109.5, NH₄⁺ – 0.55, SO₄²⁻ – 249.7, HCO₃⁻ – 79.3, CO₃²⁻ – 7.2. With the total gas content of 0.014 mole % the composition of non-condensing gases is the following (mole %): CO₂ – $1.023 \cdot 10^{-2}$, H₂S – $2.01 \cdot 10^{-3}$, H₂ – $1.12 \cdot 10^{-4}$, CH₄ – $2.52 \cdot 10^{-5}$, N₂ – $1.58 \cdot 10^{-3}$, Ar – $3.08 \cdot 10^{-5}$, He – $2.94 \cdot 10^{-7}$.

Analyses data were used as the entrance data for the program modeling the chemical equilibrium in two-phase state. Pressure and temperature were taken as equal to ones measured in the separator. Specific volume of two-phase fluid was changed so that to satisfy the values x and y . Results of calculating the concentrations of water solution components and gases compounds were compared to the data of analyses for wells 4E, 016, 26.

Coincidence of the data on silica solubility, constants of ionization and wells tests with the calculation results makes it possible to expect a sufficient accuracy when modeling the two-phase flow within well 048. Equilibrium composition of the system was modeled with various vapor contents x and volumes of steam-water mixture. Concen-

tration of silica SiO_2 in a liquid phase increased considerably with the growth of x until the solubility under given temperature in water was reached. This rule works accurately under the temperatures from 100 to 250°C and gives the possibility to determine vapor content x at which a solid phase begins to appear in the system.

Supersaturation of solution with silica concentration 830 mg/kg is reached at the sections of geothermal power station at the temperature of less than 188°C.

SEARCHING FOR MEASURES FOR SILICA SCALING CONTROL (ASIDIFICATION, ALKALIZATION)

Silica solubility was calculated under the elevated pH values reached by alkalization (NaOH). Content of silica in a separated water before reinjection will be 850 mg/kg. To increase the solubility up to 850 mg/kg under the temperature of 143.62°C and well debit of 50 kg/sec it is necessary to spend up to 380 (240 mg/kg) tons of alkali a year.

To increase quartz solubility up to 850 mg/kg under the reservoir temperature of 272°C it is necessary to add 363 t/year (231 mg/kg) NaOH. There will not be quartz deposition with any ratios of mixing the alkalined solution with and reservoir fluid.

Kinetics of polymerization can be slowed down considerably by increasing the equilibrium solubility of amorphous silica so that the silica concentration does not exceed the solubility by 2-2.5 times. It required to add 165.5 t/year (105 mg/kg) NaOH under the temperature of 100°C. After alkalization pH of solution changes inconsiderably: from 7.47 to 8.37 at 100°C.

Modeling study of water composition with lowered pH was done by adding hydrochloric acid HCl. Using acid to increase the quartz solubility needs more expenditures than alkalization. Besides, deposition of quartz is possible when the proportion of mixing with reservoir fluid is high. Acid is an effective inhibitor of polymerization reaction and can eliminate solids in the surface technical equipment and wells. To inhibit reaction it is necessary to decrease pH up to 5-5.5. According to the calculations it is required up to 60 t/year of hydrochloric acid with the concentration of 36-38 mg/kg.

Expenditures for acidification can be reduced by using non-condensing gases (like carbon dioxide CO_2). Weight percent of carbon dioxide in the steam-water mixture is about 0.01. Dilution of 500 mg/kg CO_2 decreases pH to 5.5 that can inhibit kinetics of polymerization. Using separated carbon dioxide will make it possible to reduce the amount of acid necessary for the water treatment in conditions of the Verkhne-Mutnovskaya geothermal power station by 10%.

ELECTROCHEMICAL TREATMENT RESULTS FOR HYDROTHERMAL SOLUTIONS

Silica extraction from the separated geothermal water is necessary for decrease in supersaturation, elimination of the risk of solids deposition, lowering the temperature of reinjection and obtaining silica gel as a by-product. Tests on treatment the samples of water brine from well 014 (Mutnovskoe geothermal field) were done by direct electric current in order to try to find the effective technology of silica extraction.

Sampling was done from the separator, temperature of the sampling was 72°C. Tests on the treatment by the electric current were done in field conditions near well 014 with hot solution and in the laboratory with cooled solution. During the tests the following processes have been observed: change in water colour, bubbling, coagulation and silica deposition.

Electric scheme of the tests included a source of direct current, an amperemeter, metallic electrodes lowered in a vessel with solution. Voltage ranged within 4-30 V, amperage- 0.5-3.0 A, distance between electrodes- 10-15 mm, electric field strength- 80-200 V/m, temperature of solution varied from 20° to 60°C. Electrodes made of aluminium, steel and copper were used.

When carrying out a series of tests in field conditions the vessel with solution sample was placed in a capacity of much greater volume with the hot water (72°C). This provided slow cooling of water in the vessel. Average temperature of the solution during the treatment was 60°C. Five solution samples of 1 litre volume were sampled and five tests were done. After treatment precipitate was separated by rough filter. Then silica content of solution was analyzed in the laboratory.

Total silica content SiO_2 of untreated solution from well 014 is 800 mg/kg, pH= 8.73, concentrations of the other components are the follows (mg/kg): NH_4^+ -0.7, Na^+ -239.9, K^+ -57.0, Ca^{2+} -4.0, Mg^{2+} -<0.24, Cl^- -291.1, SO_4^{2-} -124.9, HCO_3^- -43.9, CO_3^{2-} -18.6, F^- -1.6, H_3BO_3 -65.3, Li-1.3.

In test 1 electrodes made of aluminium were used, treatment time were 30 minutes, supersaturation decreased unconsiderably. In tests 2-5 steel electrodes with zink covering were used. Total silica content SiO_2 after treatment during 15 minutes in test 2 was 638 mg/kg, in test 3 (30 minutes)- 613 mg/kg, in test 4 (with add of alkali NaOH, 100 mg/kg)- 578 mg/kg, in test 5 (with add of acid HCl, 40 mg/kg)- 569 mg/kg.

Sizes of particles complexes after aggregation has the values in the following range: from 2-5.5 to 10-24 microns. Weight portion of silicium dioxide in dried solid precipitate samples reached 80 wt%. As X-Ray analyse showed all samples have amorphous structure.

The colour of solution and precipitate after treatment depend on electrodes material: treatment by steel electrodes with zinc covering leads to green-brown colour, stainless steel- to brown colour, copper electrodes- to green-blue colour.

Tests were made using aluminium electrodes in order to research how supersaturation of silica depends on treatment time. Amperage of direct current was 1.5 A, voltage- 10.7 V, distance between electrode plates- 10 mm, electric field strength- about 100 V/m. Dependence of silica SiO₂ concentration on treatment time turned out to be the following (mg/kg): at the beginning- 819, after 5 minutes- 631, 10 minutes- 340.6, 12.5 minutes- 251, 15 minutes- 114, 20 minutes- 46. After 30 minutes of treatment pH of solution increased from 8.6 to 9.33.

In order to decrease silica concentration from 819 to 250 mg/kg it is necessary to treat hydrothermal solution by direct current with amperage 1.0-1.5 during 10-15 minutes, with capacity of current supply 16 W (12 kJ/kg= 0.0033 kWh/kg). Amount of electric charge passed through the solution is about 1100 coulomb/kg. We assume that electrochemical treatment with such parameters is a perspective way of extracting silica from hydrothermal heat-carrier.

CONCLUSIONS

1. Weight portion of silicium dioxide in samples of solids from the Mutnovskaya geothermal system is 70-90%. The bulk of silica has the amorphous structure mainly. Weight portion of quartz in various types of scales is 1-4%. In samples composition the following mineral phases are revealed: pyrite, hematite, quartz, halite, thenardite, gypsum, opal.
2. Rate of the scales growth at the Mutnovskoe hydrothermal field was determined during the test on observation for the process of amorphous silica scaling on the surface of the heat exchanger pipes. The range of dimensions (5-15 Å) and concentrations of colloidal particles (10¹⁶⁻¹⁷ cm⁻³) in the geothermal solution was revealed and a prediction on rate of the scales growth in the reinjected wells was made.
3. Modeling study results of the chemical composition of two-phase flows were compared with test data for the geothermal wells. An approximate rule for determining the start point of the solid phase deposition was proposed.
4. Calculations show the necessity of adding 100-200 t/year of alkali with the concentration of 100 mg/kg to the separated geothermal water as an inhibitor to reduce the risk of appearing of amorphous silica in the reinjection wells (per debit of 50 kg/sec).
5. Acidification is admissible as a control measure for scaling in wells and surface technical equipment but it does not eliminate the risk of silica deposition in res-

ervoir. Alkalinization is more reliable method of water treatment before reinjection on the long-term basis.

6. Electrochemical treatment of geothermal solution by direct current influences the processes of silica polymerization and aggregation of colloidal particles by speeding up these processes. Owing to this, deposition of amorphous silica occurs in the treated solution more quickly and on larger scales. Thus, electrochemical treatment is a prospective method of the geothermal silica precipitation from the separated water solution under production conditions of geothermal electric power station.

REFERENCES

- Chan S.H. (1989). A review on solubility and polymerization of silica. *Geothermics*, vol. 18, №1/2, pp.49-56.
- Crerar D.A., Anderson G.M. (1971). Solubility and solvation reactions of quartz in dilute hydrothermal solutions. *Chem. Geol.*, 8, pp.107-122.
- Fleming B.A., Crerar D.A. (1982). Silicic acid ionization and calculation of silica solubility at elevated temperature and pH (application to geothermal fluid processing and reinjection). *Geothermics*, vol. 11, № 11, pp.15-29.
- Fournier R.O., Rowe J.J. (1977). The solubility of amorphous silica in water at high temperatures and pressure. *American Mineralogist*, 62, pp.1052-1056.
- Harper R.T., Thain I.A., Johnston J.H. (1995). An integrated approach to realise greater value from high temperature geothermal resources: a New Zealand example. *Proceedings of the World Geothermal Congress, Florence, Italy*, pp.2853-2858.
- Iler R.K. (1979). *The chemistry of silica- Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*. John Wiley & Sons, Inc., New York, 866p.
- Jamieson R.E. (1984). Simulation of the silica scaling process. *Proc. 6th NZ Geothermal Workshop*, pp. 135-140.
- Karpov I.K., Chudnenko K.V., Kulik D.A. (1997). Modeling chemical mass transfer in geochemical processes: thermodynamic relations, conditions of equilibria, and numerical algorithms. *American Journal of Science*, vol.297, October, pp.767-806.
- Marshall W.L. (1980). Amorphous silica solubilities I. Behavior in aqueous sodium nitrate solutions; 25 -300°C, 0-6 molal. *Geochimica et Cosmochimica Acta*, vol.44, pp.907-913.
- S.Arnorsson, S.Sigurðsson, H.Svavarsson (1982). The chemistry of geothermal waters in Iceland. I. Calculation of aqueous speciation from 0^o to 300^o C. *Geochimica et Cosmochimica Acta*. V.46, pp.1513-1532.

Thomas, D.M., Gudmundsson J.S. (1989). Advances in the study of solids deposition in geothermal systems. *Geothermics*, v.18, No.1/2, pp.5-15.