

SILICA EXTRACTION FROM HYDROTHERMAL HEAT CARRIER BY MEMBRANE FILTERS

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ABSTRACT

The experiments on silica extraction by membrane filters were carried out. Three types of membranes were tested. The first were ceramic membrane filters with diameters of pores 0.1-0.3 μm and average pores diameter 0.2 μm . The second type were filters with pores sizes in the range of ultrafiltration – 0.01-0.001 μm . The third was filter with reverse osmosis membrane with diameters of pores in the range 0.001-0.0001 μm . Addition of coagulant aluminium sulphate was used in the experiments with ceramic filters. Temperature of solution was varied from 20 to 90 $^{\circ}\text{C}$, mass rate of filtrate was from 5 to 720 liters per hour. Concentration of Al^{3+} cation added with coagulant in the experiments with ceramic filters was from 2 to 10 mg/liter. Selectivity of membrane layers with respect to colloidal silica particles and molecules of orthosilicic acid was determined in the experiments. Concentrated solutions with SiO_2 content about 27 g/liter were obtained by reverse osmosis filtration. Results of our work can be applied for developing of technology of silica extraction from hydrothermal heat carriers.

INTRODUCTION

A hydrothermal heat carrier is a renewable source of electric and thermal energy and mineral stock (Potapov V.V. et al., 2003). The dissolved salt content of a heat carrier that goes into heat equipment of a geothermal power station straight after contact with rocks of hydrothermal fields without primary purification is much higher than the heat carrier of typical thermoelectric power stations. This results in solids formation in wells and equipment of the geothermal power station and a decrease of efficiency of heat carrier using.

There are a number of examples of using filtration facilities for silica extraction: ultramembranes (Brown K.L., Bacon L.G., 2000), fluidized bed (Axtmann R.C., Grant-Taylor D., 1986), and microfilters (Lin M.S., Premuzic E.T., Zhou W.M., Johnson S.D., 2001). Use of such facilities is one of the ways of silica extraction. The presence of colloidal silica in a hydrothermal solution is potential associated with a nucleation and polycondensation of orthosilicic acid molecules that were introduced into water solution during its chemical interaction with aluminosilicate minerals in the rocks of hydrothermal fields at increased temperatures of 250-300 $^{\circ}\text{C}$.

KINETICS OF COLLOIDAL SILICA FORMATION IN HYDROTHERMAL SOLUTION

Kinetics of nucleation and polymerisation of orthosilicic acid. The residence time of presence of a solution in a tank volume must be sufficient to complete a nucleation of silicic acid and growth of silica particles to the given size. A rate of nucleation and particle growth, finite size of particles and their concentration can be varied by change of temperature, pH of a solution and dimensions. The rate of nucleation depends on a total content of silica that had initially come into solution at chemical interaction with rocks at 250-300 $^{\circ}\text{C}$. It can be estimated according to solubility C_{qu} (mole/kg) of α -quartz in pure water (Crerar D.A., Anderson G.M., 1971) at temperature $T(\text{K})$:

$$\lg C_{\text{qu}} = -1.468 + 252.9/T - 3.217 \cdot 10^5/T^2, \quad (1)$$

The rate of nucleation depends also on oversaturation of water solution relative to amorphous silica solubility C_e (mole/kg). Its dependence upon temperature $T(\text{K})$ for pure water follows from equation (Marshall W.L., 1980):

$$\lg C_e = -0.1185 - 1.126 \cdot 10^3/T + 2.3305 \cdot 10^5/T^2 - 3.6784 \cdot 10^7/T^3, \quad (2)$$

A part of silica after completion of polymerization process stays as orthosilicic acid molecules H_4SiO_4 for which C_s is close to the solubility of amorphous silica $C_e(T)$. Besides colloidal particles and silicic acid molecules a small amount of silicic acid ions ($H_3SiO_4^-$, $H_2SiO_4^{2-}$, $HSiO_3^-$, etc.) and macromolecules of polysilicic acids are present in the solution. A sum of concentrations of colloidal silica C_{col} , soluble silicic acid C_s and silicic acid ions C_{in} equals a total content C_t of silica in the solution:

$$C_t = C_{col} + C_s + C_{in} \quad (3)$$

An oversaturation $S_N(T)$ that is equal to a ratio C_s/C_e and pH are the main factors that determine a nucleation rate I_N^0 of silicic acid in a water solution (Weres O., Yee A., Tsao L., 1981):

$$I_N^0 = Q_{LP} \cdot Z \cdot (R_{md} \cdot A_{cr} \cdot N_A \cdot M_{Si}^{-1}) \cdot \exp(-\Delta F_{cr}/k \cdot T), \quad (4)$$

where ΔF_{cr} is a change in free energy concerned with a formation of nucleus of critical radius R_{cr} , A_{cr} is a surface area of critical radius nucleus, $A_{cr} = 4 \cdot \pi \cdot R_{cr}^2$, R_{md} (pH, T) is a rate of molecular precipitation of SiO_2 on solid surface, $g \cdot (cm^2 \cdot min)^{-1}$, k – Boltzmann constant, M_{Si} – molecular mass SiO_2 , N_A – Avogadro constant, Q_{LP} – Lose-Paund's factor, $Q_{LP} = 3.34 \cdot 10^{25} kg^{-1}$, Z – Zeldovich's factor. The dependencies of ΔF_{cr} , R_{md} and Z upon temperature and pH of a solution are determined by a set of analytic functions or their integrals given in the paper of Weres O., 1981. A maximum nucleation rate I_N^0 expressed by equation (4) is reached after some time that exceeds induction time τ_{in} which is necessary for growth and forming of a stable population of particles with dimensions close to the critical one. A value I_N^0 corresponds to a nucleation rate of particles having radius that slightly exceeds a critical one and amount of molecules SiO_2 which equals $n = n_{cr} + 0.5/Z$. Time dependence of $I_N(\tau)$ is the following (Weres O., Yee A., Tsao L., 1981):

$$I_N(\tau) = I_N^0 \cdot (1 - e^{-\tau/\tau_{in}}), \quad (5)$$

An induction time is expressed by the following formula (Weres O., Yee A., Tsao L., 1981):

$$\tau_{in} = 1.08 \cdot 10^{-6} \cdot (Q_{LP} \cdot Z \cdot R_{cr}^2 \cdot \exp(-\Delta F_{cr}/k \cdot T))^{-0.25} \cdot (6 \cdot R_{md})^{-1} \quad (6)$$

The characteristics of one of the separate samples from wells of the Verkhn-Mutnovskaya geothermal power station are the following: 1) a concentration of the main components (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; 2) pH = 9.2; 3) mineralization $M_h = 1638.9$ mg/kg; 4) ionic strength of a solution $I_s = 0.014$ mole/kg; 5) specific electric conductivity – 1.2-1.3 mSm·cm⁻¹. The total silica content in a separate from Mutnovskoe field wells is 500-965 mg/kg, pH is

within 8.0-9.5. The calculations have shown that values of a critical radius R_{cr} increase from 0.3 to 2.3 nm as temperatures increase from 20 to 153°C under conditions typical for a hydrothermal solution from Mutnovskoe field: pH=8.7, $C_t = 700$ mg/kg. An increase in temperature and reduction of pH of solution affect equally induction time, concentration and finite size of particles: with an increase in temperature a nucleation rate I_N decreases and induction time τ_{in} increases, a concentration of particles N_p decreases and a finite average radius of particles R_f increases. In this general, computational method can be used to determine the influence of various factors such as temperature, pH of a solution, total silica content, dimensions and amount of nuclei that were introduced into solution before nucleation on the rate of nucleation processes, the finite size of particles and their concentration.

THE SIZES OF COLLOIDAL SILICA PARTICLES

Experiments studying the kinetics of silicic acid polymerization reaction that showed how quickly monomeric silicic acid passed into colloidal silica revealed an influence of the main factors: temperature, pH, ionic strength of solution. During the experiments with a solution with pH within a range of 8.2-9.4 the following dependence of oversaturation S_m (mg/kg) equal to $(C_s - C_e)$ at the beginning of polymerization τ_p was obtained (20°C, pH = 8.4): $\tau_p = 0$ h - $S_m = 229.9$ mg/kg, 1.0 h - 139.3 mg/kg, 2.0 h - 73.7 mg/kg, 3.0 h - 41.2 mg/kg, 4.0 h - 29.9 mg/kg, 5.0 h - 22.4 mg/kg, 24.0 h - 6.8 mg/kg. To determine the dimensions of colloidal silica particles that had formed in a hydrothermal solution at ageing stage, a photon correlation spectroscopy (PCS) was used. An average radius r_p for particles of the solution sample mentioned above was 11.1 ± 0.2 nm. A diffusion constant corresponding to a such radius is equal to $D = (1.92 \pm 0.03) \cdot 10^{-7} cm^2/s$. The amount of particles with radii over 100 – 300 nm is relatively small. According to the photon correlation spectroscopy data the average radius of silica particles in various hydrothermal solution samples has values from 7.0 to 53.0 nm. If the temperature of silicic acid polymerization was 20 °C the average radius of particles was 7.0-12.0 nm, at the temperatures 60-70 °C the average radius was 30-50 nm.

As the experiments have shown, colloidal silica particles are unstable when metal cations are introduced into solution by adding coagulants (Potapov V.V., Podverbny V.M., Povarov K.O., 2003). Table 1 gives data on a critical concentration of every coagulant and coagulating cation. An introduction of metal cations in amount which is less

than a critical one leads to a formation of aggregates of colloidal silica particles and increase in their average size without flocculation. Ca^{2+} cations were introduced by adding of slaked lime, Al^{3+} cations – by adding of hydrolyzing salt aluminium sulphate $\text{Al}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$. After Ca^{2+} cations had been introduced an average radius of particles increased up to 172.4 nm, after introduction of Al^{3+} cations it increased up to 73.4-100.2 nm.

Table 1. Data on the experiments on coagulation and precipitation of colloidal silica in a hydrothermal solution by cations of various metals at a temperature of 20°C. ECA – electrochemical coagulation on aluminium electrodes.

Coagulant	Coagulating cation	Critical concentration of coagulant, mg/kg	Critical concentration of cation, mg/kg	Cost of treatment, \$ U.S./m ³
CaO	Ca^{2+}	80.0	57.1	0.05
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	Al^{3+}	250.0	20.2	1.121
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	Fe^{3+}	250.0	55.66	1.02
ECA	Al^{3+}	90.0	90.0	0.428

EXPERIMENTS ON COLLOIDAL SILICA EXTRACTION BY CERAMIC MEMBRANE FILTERS

In our experiments we used filter constructed at the Mendeleev Russian Chemical-Technological University (Terpugov G.V., Mynin V.N., 2005) (Fig. 1a,b). The main technical characteristics of a ceramic filter are presented in Table 2. Testing was carried out in the laboratory at a temperature of 20°C and in a working module of the Verkhne-Mutnovskaya geothermal power station. In the test at the Verkhne-Mutnovsky GeoPP, drainages with temperature 80 °C from separators were used.

A plant for baromembrane filtering included a ceramic filter, manometers, flowmeters, adjusting valves and vessels for concentrate and filtrate collection (Fig. 2). Water was fed to the plant from a vessel of 50 l in volume by a pump with a capacity of 220 W. A flow of source water came to the filter through a connecting pipe, passed along central perforated pipe and then went to the tube space. Under the action of working pressure water passed through a porous ceramic element forming at the same time a filtrate that was removed through a filtrate connecting pipe. A water (concentrate) that had not passed through ceramic elements came from the filter through a connecting pipe. There was flexible conductor for a separate supply to the central input of filter, flexible conductor for taking of a concentrate from the output and metal-plastic pipe for taking of filtrate. Manometers were set at the input

connecting pipe and output connecting pipes. This allowed measurement a pressure difference in the membrane layer and filter casing at different flows of filtrate and concentrate. A total water flow pumped over the plant with a pump and filtrate flow was measured by flowmeters. A filtrate and concentrate flow rate was changed by adjusting valves. A concentrate recycling to the initial vessel was done by a valve switching.

Table 2. Technical characteristics of a ceramic filter.

length of filtering cartridge	270±2 mm
diameter of filtering cartridge	65 mm
mass	1.03 kg
amount of cartridges in a plant	1
material	stainless steel, polypropylene
output for distilled water	0.2-0.01 m ³ /hour/ cartridge
average diameter of pores	0.2 μm = 200 nm
area of filtering surface	0.0873 m ² /cartridge
length of ceramic tubes	180 mm
wall thickness of ceramic tubes	1 mm
thickness of layer of membrane lay	0.1 mm
amount of ceramic tubes	20/cartridge
working pressure	0.2-0.5 MPa
range of working temperatures	5-110 °C
regeneration	using method of reversed air blowing under pressure of 0.6 MPa or washing with cleaning solutions

An initial separate from the Verkhne-Mutnovskaya power station had a total silica content $C_t^0 = 800.0$ mg/kg and a concentration of dissolved orthosilicic acid $C_s^0 = 165.6$ mg/kg. During a test run on silica extraction at a temperature of 20°C and initial concentration of Al^{3+} cations of 1-2 mg/kg, the total silica content in a filtrate was reduced to $C_t^f = 219$ mg/kg, and the concentration of dissolved silicic acid was $C_s^f = 153$ mg/kg. Thus, a concentration of colloidal silica C_{col} that is equal to a difference $C_t - C_s$ decreased from 634.0 to 66.0 mg/kg. The fraction ϕ_s of extracted silica in a filtrate, that is membrane selectivity on colloidal silica and silicic acid, calculated according to:

$$\phi_s = (C_t^0 - C_t^f) / C_t^0 \quad (7)$$

was 0.726. The fraction of extracted colloidal silica in a filtrate φ_{cs} , that is membrane selectivity on colloidal silica, calculated according to the equation:

$$\varphi_{cs} = (C_{col}^0 - C_{col}^f) / C_{col}^0, \quad (8)$$

was 0.896.

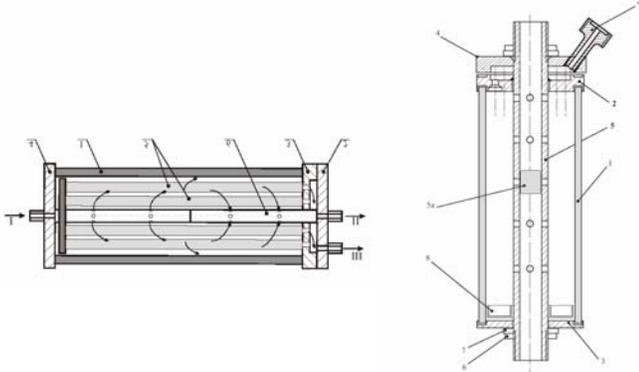


Fig. 1a.

Fig. 1b.

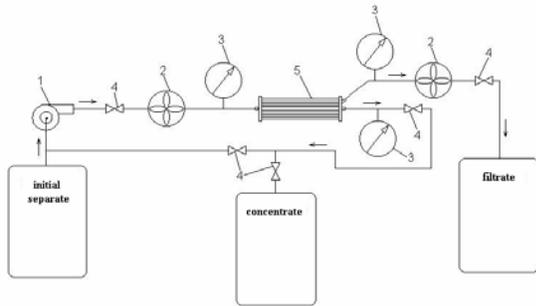


Fig. 2.

Fig. 1a. Slit of filter section with main flows of liquid medium directed inside filter. 1 – plastic body (polypropylene), 2 – filtrate covers, 3 – tube plate, 4 – bottom, 5 – ceramic tubular filtering elements with outer selective layer (membrane), 6 – central pipe. I – main flow of medium, II – concentrate, III – filtrate.

Fig. 1b. Filter assembly drawing. 1 – body, 2 – tube plate, 3 – cover, 4 – filtrate cover, 5 – central spreader pipe, 5a – bush, 6 – screw, 7 – washer, 8 – glass, 9 – connecting pipe for filtrate yield.

Fig. 2. Installation diagram for baromembrane filtering. 1 – pump; 2 – flowmeter; 3 – manometer; 4 – ball valve; 5 – ceramic membrane filter.

During various test runs at 20°C membrane selectivity on colloidal silica φ_{cs} was ranged from 0.20 to 0.97 at different concentrations of added Al^{3+} in the range 2-8 mg/kg. Pressure drop ΔP on membrane layer needed for filtering a volume

$Q_{GW}(m^3/s)$ of solution through a membrane layer was $\Delta P = 0.078$ MPa. The rate of water flow $Q_{GW}(m^3/s)$ through membrane layer and membrane penetrability G at that pressure drop ΔP were determined in the experiments:

$$G = Q_{GW} / S_m, \quad (9)$$

where S_m is total surface of membrane layer in the cartridge, m^2 .

During filtration after coagulant's addition membrane penetrability G decreased and selectivity φ_{cs} increased with the time of filtration due to gel's formation on membrane pipes. The values of G and φ_{cs} at different concentrations of added cations Al^{3+} are shown in the Table 3.

Table 3. Penetrability and selectivity of membrane in the experiments with ceramic filters.

Al^{3+} , mg/kg	G , $m^3/m^2 \cdot hour$	φ_{cs}
2.0	0.515-0.274	0.22
4.0	0.515-0.210	0.19-0.21
6.0	0.198	0.22
	0.0845	0.45
	0.0661	0.62
	0.0598	0.74
	0.0517	0.84
8.0	0.115	0.68
	0.093	0.89

During a test run with separate recycled flow carried out at a temperature of 20°C, hydrosols with a total silica content SiO_2 of about 1500 and 5100 mg/kg were obtained. These concentrations are approximately 2 and 6 times higher than in the initial solution. Average radius of colloidal silica particles in these hydrosols was about 70 nm.

The characteristics of initial separate that was used during tests at temperatures of 80°C were the following (20°C): $pH=9.50$, $C_t^0=713-744$ mg/kg, $C_s^0=177$ mg/kg. A temperature of a separate sampling was 88.3°C. After sampling separate was cooled to 80°C and aged for 40 minutes in order to complete nucleation and polymerization of orthosilicic acid and form colloidal particles. After ageing and before filtering a coagulant – aluminum sulfate $Al_2(SO_4) \cdot 18H_2O$ – was introduced into separate. After coagulant had been added, the solution was strongly mixed. The amount of coagulant that had been introduced was $3400 \text{ mg}/49 \text{ kg} = 69.4 \text{ mg/kg}$, corresponding to a concentration $Al^{3+} = 5.6 \text{ mg/kg}$.

A total silica content in a filtrate reduced to $C_t^f = 284$ mg/kg. The characteristics of a filtrate obtained at 78°C were the following: $pH= 6.42$, $C_s^f = 246$ mg/kg. Al^{3+} concentration in filtrate was not higher than 0.27

mg/kg. Membrane selectivity on total silica was $\phi_s = 0.600$. If taking into account a solubility of amorphous silica at 78°C $C_e = 312$ mg/kg membrane selectivity on colloidal silica ϕ_{CS} was practically equal to 1.0.

EXPERIMENTS ON COLLOIDAL SILICA EXTRACTION BY ULTRAFILTRATION

The experiments were carried with ultrafiltration plant (UF plant) at 20 °C. Plant included UF membrane filter, pump, manometers, vessels for initial solution and for filtrate. Cartridge of UF filter was filled with thin fibre pipes the walls of which were coated by membrane layer. The diameters of pores of membrane layer were in the range of 0.01 – 0.001 $\mu\text{m} = 10.0 - 1.0$ nm. Packet of thin fibre pipes in the cartridge have U-form with one end for solution entrance and another dead end so there was one exit in the cartridge for filtrate only. Density of membrane surface in the cartridge volume was $D_{MS} = 20000$ m^2/m^3 . Initial pressure drop ΔP needed for filtration of hydrothermal separate through membrane layer was about 0.18-0.22 MPa, the flow rate was 27.0-30.6 liters per hour, penetrability $G = 0.003128 - 0.002453$ $\text{m}^3/\text{m}^2\cdot\text{hour}$. Pressure drop increased during filtration to 0.30-0.42 MPa.

Concentration of silica in filtrate was $C_t^f = 150.0$ mg/kg. Thus UF membrane selectivity on colloidal silica ϕ_{CS} was about 1.0 and all colloidal particles of silica were retained. Total dissolved salts TDS in solution was 922 mg/kg before filtration. TDS in filtrate was 856 mg/kg and only a small part of cations and anions were retained by membrane: $\phi_{TDS} = 0.0715$. Thus it is possible to get solution with high concentration of SiO_2 and low concentrations of impurities – Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+,3+}$, Al^{3+} , SO_4^{2-} , Cl^- - by ultrafiltration. Parameter (TDS/C_t) in the initial hydrothermal solution was 805 (mg/kg)/709 (mg/kg) = 1.135. This parameter in the solution concentrated by ultrafiltration was about 0.01, SiO_2 content was 82500 mg/kg.

EXPERIMENTS ON SILICA EXTRACTION BY REVERSE OSMOSIS

The experiments on silica extraction by reverse osmosis (RO) were carried out in the laboratory at 20 °C and in Mutnovsky GeoPP at 50-80 °C. RO plant included cartridge with RO membrane filter, pump RO-900 with the pressure up to 1.0 MPa, device for automatic regulation of flow rate of pumped water, adapter for transformation of electric voltage to constant 24 V, manometer, vessels for hydrothermal solution, filtrate and concentrate. RO membrane made of thin film of composite material was rolled in the cartridge in spiral form. The total surface of membrane was 0.3 m^2 , diameters of pores of

membrane layer were in the range of 0.001-0.0001 $\mu\text{m} = 1.0 - 0.1$ nm. Density of membrane surface in the cartridge volume was $D_{MS} = 468.75$ m^2/m^3 .

At the laboratory experiments carried out at 20 °C filtrate rate was 3.5-4.5 liters per hour, concentrate rate – 20 l/h, pressure drop on membrane layer $\Delta P = 0.45-0.55$ MPa. RO membrane penetrability was $G = 0.0116-0.0115$ $\text{m}^3/\text{m}^2\cdot\text{hour}$. Membrane selectivity on total silica ϕ_s was 0.96, membrane selectivity on colloidal silica $\phi_{CS} = 1.0$, selectivity on cations and anions retained by RO membrane - $\phi_{TDS} = 0.89$. The experiments on second stage filtration at 20 °C shown that molecules of silicic acid were extracted by RO membrane. RO membrane selectivity on silicic acid was $\phi_s = 0.78-0.90$, fraction of cations and anions - $\phi_{TDS} = 0.83-0.94$. Thus reverse osmosis can be used for extraction of silicic acid molecules when nucleation and polymerisation of silicic acid is not over and silica colloidal particles are not formed.

In the experiments with recirculation of concentrate solutions were received with silica content SiO_2 15600-27300 mg/kg, that is 20-36 times higher than in the initial hydrothermal separate. Parameter (TDS/C_t) in the solution concentrated by reverse osmosis was = 0.374.

During the experiments at Mutnovsky GeoPP the vessel for filtrate was put into the thermos to get a little decline of the filtrate temperature at the second stage of filtration. Two experiments with hot solution were carried out.

At the first experiment the temperature of filtrate on the 1-st stage was 62 °C, on the 2-nd - 55 °C. Filtrate flow rate was 10.19 l/h, pressure drop $\Delta P = 0.32-0.34$ MPa, RO membrane penetrability $G = 0.0339$ $\text{m}^3/\text{m}^2\cdot\text{hour}$. Silica content SiO_2 in the initial hydrothermal separate was $C_t = 718.75$ mg/kg, $C_s = 200.0$ mg/kg, total dissolved salts TDS = 750 mg/kg. Silica content in the filtrate of the 1-st stage was $C_t = 156.25$ mg/kg, $C_s = 150.0$ mg/kg, TDS = 110 mg/kg. Only soluble silicic acid was in filtrate after 1-st stage of filtration, all colloidal silica was retained by RO membrane. Silica content in the filtrate of the 2-st stage was $C_t = 50$ mg/kg, $C_s = 50.0$ mg/kg, TDS = 30 mg/kg. Thus the characteristics of RO membrane on the 1-st stage of filtration were: $\phi_s = 0.782$, $\phi_{TDS} = 0.853$. On the 2-nd stage of filtration $\phi_s = 0.720$, $\phi_{TDS} = 0.727$.

At the second experiment the temperature of filtrate on the 1-st stage was 72.0-68.8 °C, on the 2-nd - 58 °C. Filtrate flow rate was 8.18-7.49 l/h, pressure drop $\Delta P = 0.30-0.34$ MPa, RO membrane penetrability $G = 0.272-0.249$ $\text{m}^3/\text{m}^2\cdot\text{hour}$. Silica content SiO_2 in the

initial hydrothermal separate was $C_t = 781.25$ mg/kg, $C_s = 200.0$ mg/kg, total dissolved salts TDS= 750 mg/kg. Silica content in the filtrate of the 1-st stage was $C_t = 192.2$ mg/kg, $C_s = 186.9$ mg/kg, TDS = 130 mg/kg. Silica content in the filtrate of the 2-st stage was $C_t = 60.0$ mg/kg, $C_s = 59.4$ mg/kg, TDS = 30 mg/kg. Thus the characteristics of RO membrane on the 1-st stage of filtration were: $\varphi_s = 0.753$, $\varphi_{TDS} = 0.826$. On the 2-nd stage of filtration $\varphi_s = 0.687$, $\varphi_{TDS} = 0.769$.

TECHNOLOGY OF SILICA EXTRACTION

With the increase along producing wells pressure and temperature of heat carrier decrease, from some depth pressure can be lower than pressure of saturated vapor. Therefore, a part of a liquid heat carrier converts to a vapor phase. The producing wells of the geothermal power station bring the heat carrier to the surface as a water-vapor mixture. In a separation system water-vapor mixture is separated into vapor phase and liquid phase. The vapor phase is fed to the vapor turbines of condensation type to generate electric energy. The liquid phase (separate) is reinjected into the subsurface in order to avert a depletion of the reservoir and ecological disturbances. Due to the risk of amorphous silica solid deposits in the wells, pipelines, heat equipment and apparatuses, pumping of a separate is carried out at an increased temperature of 140-160⁰C. This decreases the efficiency of a heat carrier for energy production and makes difficult the extraction of useful chemical components.

If silica is extracted from separate it is possible to obtain electric energy in the binary power units (BP) of the geothermal power station. A process flow sheet for colloidal silica extraction includes the following main stages:

- 1) an ageing of a solution of hydrothermal separate that comes out from the heat exchangers of the binary power unit, to induce nucleation and polymerisation of silicic acid molecules and to form colloidal silica particles of the given size and concentration;
- 2) addition of cations-coagulants Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} that are sorbed by the surface of colloidal silica particles and form bridges between the particles; thus cations aggregate silica particles up to the sizes that are larger than a diameter of filter pores: if silica particle sizes are larger than filter pores then there is no need to add metal cations.
- 3) filtering of a solution through the membrane filter that have pore diameters little enough to extract silica particles or it's aggregates;
- 4) accumulation of concentrated solution with high SiO_2 content to obtain monodispersed silica sol which can be used in industry or for precipitation silica from sol, dehydration and drying precipitated material to obtain of a fine powder of amorphous silica with a

low concentration of admixtures (less than 0.1 mass %) and specific surface area 300-500 m²/g that can be used commercially.

Process flowsheet equipment for extraction of silica from a liquid phase of hydrothermal heat carrier is as follows. After separation from a water-steam mixture in a separation system a liquid phase is directed into heat exchangers of a binary power unit (BPU) where it is significantly cooled. At the same time it gives heat to a low-boiling organic working fluid (OWF) which is fed to the gas turbine to generate electric power. The residence time of hydrothermal solution in the pipes of BPU heat exchanger is small and nucleation and polymerization processes have no time to develop. When hydrothermal solution goes out of BPU heat exchanger it goes to an ageing tank to complete nucleation and polymerization and to form colloidal silica particles of the given size. Then an introduction of metal cations by adding a coagulants solution and mixing are carried out. After that a solution is directed into membrane filters with a pump. A pressure level ΔP created with a pump must be sufficient for filtering of the given consumption of a solution $Q_{GW}(m^3/s)$ through a membrane layer.

If reverse osmosis is used hydrothermal solution can be filtered through membrane filters with out ageing because RO membranes have high selectivity on silicic acid molecules.

Electric power and chemical reagents (coagulants) are necessary for purification of hydrothermal heat carrier according to the process flowsheet. Electricity charges E_{XEP} for electric power spent for pumping at duration of a plant working τ (c) are the following:
 $E_{XEP} = 2.777 \cdot 10^{-7} \cdot \eta_p^{-1} \cdot \Delta P_{MF} \cdot Q_{GW} \cdot \tau \cdot \alpha_E$, (10)
 η_p – efficiency of a pump, α_E – a cost of 1 kilowatt of electric power, \$ U.S./kW.

Table 4. Effectiveness of the binary power modules of Ormat production. N_{BE} – power unit capacity. OWF in units 1-4 is freon-11, OWF in units 5-7 is freon-114. (-) – temperature is not indicated.

Characteristic	Unit 1	Unit 2	Unit 3	Unit 4	Unit 5	Unit 6	Unit 7
Q_{GW} , kg/s	613.9	622.2	393.0	236.1	48.8-51.3	53.0	54.9
t_1 , ⁰ C	160	115	130	120	105	105	105
t_2 , ⁰ C	85	85	100	80	90	90	90
Q_{CW} , kg/s	3958.3	1458.3	1041.6	750.0	137.5	135.8	134.36
t_{1e} , ⁰ C	20	18	18	5	12	14.4	18.3
t_{2e} , ⁰ C	30	29	28	16	-	-	-
N_{BE} , MW	21	8,4	6,0	3.6	0.821-0.852	0.755	0.647
η_{BE} , %	10.7	10.6	12.0	9.0	8.9-9.4	7.4	6.5

Electric power consumption that is necessary for pumping depends upon thickness and permeability of membrane layer and filtration rate. A consumption of electric power which is necessary for pump depends upon a viscosity μ of water (Pa·s), a temperature dependence of which is:

$$\mu(t_s)=10^{-7} \cdot 241.4 \cdot 10^{-247.8/(t-140)} \quad (11)$$

The cost of chemical reagents T_R used for colloidal particles coagulation depends on a specific reagent discharge Q_R (kg/m³) and their cost α_R (\$U.S./kg):

$$EX_R = Q_{GW} \cdot \tau \cdot Q_R \cdot \alpha_R \quad (12)$$

A profitable aspect of a working plant assumes the following factors.

1) A profit Pr_{BE} on selling of additional electric power generated by a binary energy unit:

$$Pr_{BE} = 2.777 \cdot 10^{-7} \cdot \eta_{BE} \cdot C_p \cdot Q_{GW} \cdot (t_1 - t_2) \cdot \tau \cdot \alpha_E, \quad (13)$$

where η_{BE} – is an efficiency of a binary energy unit, C_p – is a volumetric heat capacity of water solution, J/m³, t_1 – is a temperature at the input to a heat exchanger of binary energy unit, t_2 – is a temperature at the output from a heat exchanger of binary energy unit. An efficiency of binary energy units which use a hydrothermal separate depends upon a water flow rate Q_{GW} , water temperature at the input and output of heat exchangers, properties of an organic working fluid, and cooling water temperatures t_{1c} and t_{2c} . It is within a range of 6.0-12.0 %. Table 4 gives values of efficiency-net η_{BE} for standard power converters of Ormat model that are based on organic Rankine cycle (G. Culver, 1984; Ormat energy converter).

2) A profit Pr_{AS} on selling of amorphous silica:

$$Pr_{AS} = (1 - \beta_{CS}) \cdot Q_{GW} \cdot (C_{t1} - C_{t2}) \cdot \tau \cdot \alpha_{AS}, \quad (13)$$

where C_{t1} – is a concentration at the input of a plant for silica extraction, kg/m³, C_{t2} – is a concentration at the output of a plant, kg/m³; α_{AS} – is a cost of amorphous silica powder, \$ U.S./kg. A profit Pr_{GS} on selling of aqueous silica hydrosol that can be obtained by a concentrating of a hydrothermal solution in the membrane equipment:

$$Pr_{GS} = \beta_{CS} \cdot Q_{GW} \cdot C_{GS} \cdot \tau \cdot \alpha_{GS}, \quad (14)$$

where β_{CS} – is a portion of a hydrothermal solution volume which is directed to a concentrating for hydrosol obtaining; C_{GS} – is a concentration of silica in a hydrosol obtained, (kg/m³); α_{GS} – is a cost of aqueous hydrosol based on 1 kg of SiO₂, \$ U.S./kg.

A cost of silica extracted and aqueous hydrosol depends upon their physical and chemical characteristics and field of industry where an extracted material can be used. Amorphous silica powders are used in the production of paper, rubber, glue, paints, glass, in ceramics and chromatography (Potapov V.V., Guseva O.V., 2004). Aqueous silica hydrosols are materials for catalyst and synthetic

zeolite production, for production of polysilicates solutions.

3) A profit Pr_S on selling of additional electric power by elimination of idle times at the geothermal power station that are caused by a necessity to remove solid silica deposits out of the equipment:

$$Pr_S = 0.2777 \cdot N_{GP} \cdot \Delta\tau \cdot \alpha_E, \quad (15)$$

where N_{GP} – is a capacity of the geothermal power station, MW, $\Delta\tau$ – is a duration of idle times at the geothermal power station, s.

Costs for electric power used for pumps that move a separate through a membrane filter can be reduced by increase in pore diameter d_p of membrane layer. At the same time in order to keep a portion of extracted colloidal silica it is necessary to increase discharge of a coagulant as colloidal particles must be enlarged up to the sizes that are larger than filter pore sizes. An increase in coagulant concentration will also lead to the performance degradation of a silica-containing material and loss of a part of its selling value. A pore diameter must be chosen in such a way to minimize sum of costs for electric power and chemical reagents and initial cost of plant with membrane filters. The initial cost of plant depends on the cost of unit membrane layer (U.S.\$/m²) and membrane surface S_m (m²) needed for water flow rate Q_{GW} (m³/s).

In the Table 5 experimental data for different membrane processes are summarized. These data can be used for membrane plant project.

Table 5. Parameters of membrane processes used for silica extraction from hydrothermal solution. MF – microfiltration on ceramic filters, UF – ultrafiltration, RO – reverse osmosis. Temperature – 20 °C.

Type of membrane process	$d_p, \mu\text{m}$	$\Delta P, \text{MPa}$	$D_{MS}, \text{m}^2/\text{m}^3$	$G, \text{m}^3/\text{m}^2 \cdot \text{h}$	Φ_{cs}	Φ_{TDS}
MF	0.1-0.3	0.078	182.8	0.115-0.051	0.62-0.89	0.10-0.4
UF	0.01-0.001	0.18-0.22-0.30-0.42	20000	0.00313-0.00245	1.0	0.0715
RO	0.001-0.0001	0.45-0.55	468.75	0.0116-0.0115	1.0	0.83-0.9

CONCLUSIONS

1. The experiments with ceramic membrane filters have shown a possibility of extraction of silica colloidal particles from a liquid phase flow of hydrothermal heat carrier. The fraction of colloidal silica extracted depends on diameter of filter pores, temperature of a solution, amount of metal cations that have been introduced into solution to enlarge silica particles, and it can change from 0.05 to 1.0

depending on these factors. Selectivity of ceramic filters on silicic acid molecules is low.

2. UF filters have selectivity on colloidal silica about 1.0 without addition any coagulants and a low selectivity on silicic acid molecules and ions. Therefore it is possible to get by ultrafiltration solution with high concentration of SiO_2 and low concentrations of impurities – Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+,3+}$, Al^{3+} , SO_4^{2-} , Cl^- .

3. RO membranes have selectivity on colloidal silica about 1.0 and a high selectivity on silicic acid molecules. Thus reverse osmosis can be used for extraction of silicic acid molecules without solution ageing when nucleation and polymerisation of silicic acid is not over and silica colloidal particles are not formed.

4. An optimum mode of operation for membrane filtration plant is determined by a diameter of filter pores with which minimum costs are required. These are: 1) costs for electric power necessary for pumping; 2) for coagulants and other chemicals needed for plant operation; 3) initial cost of membrane plant.

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