

EXPERIMENTS ON SILICA SOLS PRODUCTION FROM HYDROTHERMAL SOLUTIONS BY MEMBRANE FILTERS

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ABSTRACT

The experiments on concentration of hydrothermal solutions by membrane filters for silica sols production were carried out. Three types of membranes were tested. The first type was ceramic membrane filters with diameters of pores 0.1-0.3 μm and average pores diameter 0.2 μm . The second type was filters with pores sizes in the range of ultrafiltration – 0.01-0.001 μm . The third one 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 varied from 20 to 90 $^{\circ}\text{C}$, mass rate of filtrate through membrane filter was from 5 to 1200 liters per hour. Cations Al^{3+} were used in the experiments with ceramic filters prior filtration for colloidal silica particles aggregation. No cations were added in the experiments with ultrafiltration and reverse osmosis. Selectivity of membrane layers with respect to colloidal silica particles and molecules of orthosilicic acid was determined in the experiments. Concentrated silica sols with SiO_2 content from 5 up to 150 g/liter were obtained in our experiments by ultrafiltration and reverse osmosis. Silica sols can be utilized in the chemical industry, for example, for production of catalysts, ceramics and zeolites.

INTRODUCTION

A hydrothermal heat carrier is a renewable source of electric and thermal energy and mineral stock (Potapov V.V. et al., 2002, 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 $^{\circ}\text{C}$.

Searching of new silica sources is provided by increasing of amorphous silica utilization in current industry including high-tech branches connected with nanostructured material production. Hydrothermal solutions are untraditional source of mineral including amorphous silica. A possibility of extraction of silica-containing material with different physicochemical characteristics from hydrothermal solutions of considerable volumes was shown in a number of works. An extraction can be carried out by addition of coagulants, flocculants, by electrochemical coagulation and other methods.

There is an approach to extract of useful components of hydrothermal solutions on basis of their membrane concentration. Stable monodisperse water silica sols are one of the products of membrane concentration. Economic expediency of the projects of silica extraction from hydrothermal solutions is provided by multiple use of these solutions for energy and mineral production. Solution purification from colloidal silica must give an additional quantity of electric and thermal energy due to temperature

reduction of solution reverse pumping and mineral as amorphous silica at the same time. There are large reserves of high-temperature hydrothermal resources in Russia. Total power potential of the single Mutnovsky field (the South Kamchatka) is 300 MW. During using of this potential the flow of separated water heat carrier of the Mutnovskaya GeoPP will be about 300 liter/s with average silica content 700 mg/liter. When extraction rate is 45-60 % the quantity of amorphous silica will be about 3-5 thousand tons per year.

Silica comes into natural solution as molecules of orthosilicic acid (OSA) as a result of its chemical interaction with aluminosilicate minerals of the rocks of hydrothermal fields. When the solution raises to the surface along producing wells and the temperature reduces the solution becomes supersaturated and polycondensation and nucleation of OSA molecules take place and lead to the forming of silica spherical nanoparticles with radii 5-30 nm. To develop of the technology of membrane silica concentration the main stages must be worked out.

The stages are the following: nucleation and polycondensation of OSA, sol filtering in membrane facilities and sol cleaning from electrolytes, sol stabilization (addition of stabilizing additives).

The paper represents the results of experiments which allow to determine the characteristics of the main stages of membrane concentration technology. The experiments on obtaining of concentrated water silica hydrosols were carried out with the separate of wells of the Mutnovskaya Geothermal power plants (GeoPP). Measurement range pH of the initial separate was 8,0-9,4, silica concentration was $C_i=500-1000$ mg/kg, solution temperature varied from 20 to 90 °C. Mean radius of silica nanoparticles was 5-30 nm. Concentrations of the main components of initial separate solution have values (mg/liter): Na^+ - 282, K^+ - 48,1, Li^+ - 1,5, Ca^{2+} - 2,8, Mg^{2+} - 4,7, $Fe^{2+, 3+}$ - <0,1, Al^{3+} - <0,1, Cl^- - 251,8, SO_4^{2-} - 220,9, HCO_3^- - 45,2, CO_3^{2-} - 61,8, H_3BO_3 - 91,8, SiO_{2t} - 780, SiO_{2s} - 200.

A plant for membrane concentration of hydrothermal solution included a cartridge(cartridges) with membrane filters, pump, flowmeter, manometer, lock and control valves, vessels for initial solution, concentrate and filtrate. The possibility of the main membrane processes such as microfiltration, ultrafiltration, nanofiltration and reverse osmosis for concentration of hydrothermal solutions were studied during the experiments.

Tables 1 a,b show the characteristic of membrane processes: pore diameters of membrane layer d_p , volume density of membrane surface D_{MS} in filters, penetrability of membrane layer - G , selectivity of membrane layer on colloidal silica φ_{cs} and ions of dissolved salts φ_{TDS} , pressure drop on membrane layer ΔP (transmembrane pressure), electric power consumption for silica concentration: per unit mass SiO_2 in water sol E_{SM} and per unit sol volume E_{SV} . Total charge of electric power A (kW·h) was estimated according to pressure drop ΔP on membrane layer and filtrate volume V_f passed through membrane layer:

$$A = \Delta P \cdot V_f \quad (1)$$

Specific consumption of electric power E_{SM} (kW·h/kg) and E_{SV} (kW·h/l) was estimated by division of total consumption A by silica mass m_s in obtained sol or by sol volume V_s :

$$E_{SM} = A/m_s, \quad (2)$$

$$E_{SV} = A/V_s \quad (3)$$

The rate of water flow Q_f (m³/s) through membrane layer (filtrate charge) and membrane penetrability G at that pressure drop ΔP are connected by:

$$G = Q_{GW}/S_m, \quad (4)$$

where S_m is a total surface of membrane layer in the cartridge, m².

Table 1a.

The characteristic of membrane processes used for silica extraction from hydrothermal solution. MF means microfiltration on ceramic filters, UF means ultrafiltration, NF means nanofiltration, ROF means reverse osmosis filtering. The temperature is 20 °C. φ_{cs} is the selectivity on colloidal silica; φ_{TDS} is the selectivity on salts (electrolytes); G , m³/m²·h is membrane penetrability; D_{MS} , m²/m³ is volume density of a placing of membrane surface; ΔP , MPa is pressure drop; d_p is diameter of membrane pores, micrometer.

| Type | d_p , micro meter | ΔP , MPa | D_{MS} , m ² /m ³ | G , m ³ /m ² · hx10 ⁻³ | φ_{cs} | φ_{TDS} |
|------|---------------------------|---------------------|----------------------------------------------|-----------------------------------------------------------------|----------------|-----------------|
| MF | 0,1- 0,3 | 0,078 | 154,0 | 115,0 -51,0 | 0,6- 0,89 | 0,0 |
| UF | 0,01- 0,001 | 0,18- 0,22 | 20000- 30000 | 1,35- 1,53 | 1,0 | 0,071 5 |
| NF | 0,0006 -0,008 | 0,30 | 425,0 | 31,74 -3,03 | 1,0 | 0,79- 0,88 |
| ROF | 0,001- 0,0001 | 0,45- 0,55 | 425,0 | 11,6- 1,0 | 1,0 | 0,83- 0,94 |

Different constructions of membrane filters were used during the experiments. Microfiltrational membranes of tubular type had membrane layer applied on outside surface of ceramic pipes. Ultrafiltrational membranes were made as capillars. Capillaries beam had U-shaped form. Concentrated

medium was supplied into capillaries. Reverse-osmosis and nanofiltration membranes had roll spiral placing of membrane layer. Concentrated medium moved along axis of cartridge-filter. The filtrate was supplied into axis drain channel in radial direction on spiral trajectory.

Table 16.

Electric power rate to obtain silica water sols by membrane concentration for different membrane processes. K_C is concentration rate that is equal the ratio of total silica in concentrated sol and initial hydrothermal solution. E_{SM} is electric power rate per mass unit of SiO_2 in obtained sol; E_{SV} is electric power rate per volume unit of obtained sol.

| Type of membrane process | K_C | E_{SM} , kilowatt ·h/kg | E_{SV} , kilowatt ·h/liter |
|--------------------------|-------|---------------------------|------------------------------|
| MF | 6,8 | 0,098 | 0,0005 |
| UF | 17,25 | 0,426 | 0,0055 |
| | 110,0 | 0,252 | 0,0208 |
| NF | 60,0 | 0,511 | 0,0132 |
| RO | 20,8 | 0,560 | 0,00875 |
| | 35,82 | 0,521 | 0,0140 |

When microfiltration membranes were used SiO_2 content in concentrates was 3,0-5,5 g/liter, in experiments with reverse-osmosis membranes – 27,0 g/liter, with nanofiltration membranes – 45,0 g/liter. Maximum rate of concentration of stable water sols was obtained on ultrafiltration membranes. SiO_2 content was brought up to 82,5 g/liter using ultrafiltration membranes, and it is not the end.

The experiments with microfiltration membranes were carried out with simultaneous addition of cations-coagulants Al^{3+} to enlarge silica nanoparticles. Without coagulant addition the selectivity of membrane layer on silica nanoparticles was low.

The fraction ϕ_s of extracted silica in a filtrate, that is membrane selectivity on colloidal silica and silicic acid, calculated according to:

$$\phi_s = (C_t^0 - C_t^f) / C_t^0, \quad (5)$$

C_t^0, C_t^f are total silica in initial solution and filtrate.

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

$$\phi_{cs} = (C_{col}^0 - C_{col}^f) / C_{col}^0, \quad (6)$$

C_{col}^0, C_{col}^f are the concentration of colloidal silica in initial solution and filtrate.

During various tests with microfiltration membranes ϕ_s run at 20°C the selectivity on colloidal silica ranged from 0,20 to 0,97 at different concentrations of added Al^{3+} in the range 2-8 mg/kg. Silica selectivity was up to 0,726.

During filtration after coagulant's addition membrane penetrability G decreased and selectivity ϕ_{cs} increased due to gel's formation on membrane pipes. Values of G and ϕ_{cs} at different concentrations of added cations Al^{3+} are shown in the Table 2.

Table 2.

Membrane productivity and selectivity in the experiments with ceramic filters.

| Al^{3+} , mg/kg | G , $m^3/m^2 \cdot h$ | 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 |

Reverse-osmosis membranes in addition to a high selectivity ϕ_{cs} on colloidal silica had considerable selectivity ϕ_{ms} on dissolved orthosilicic acid (OSA) reached up to 0,7-0,9. This result gives the possibility to change process flowsheet of concentration fundamentally, if the stage of ageing of initial hydrothermal solution is eliminated when nucleation of orthosilicic acid (OSA) and colloidal particles growth occur. Reverse-osmosis membranes give the possibility to concentrate molecules of OSA without their preliminary transformation in silica nanoparticles. Use reverse-osmosis provides with deeper cleaning of water heat carrier of GeoPP from silica, it increases the effectiveness of utilization of heat carrier power budget. The selectivity ϕ_{cs} on colloidal silica of nanofiltration membranes was close to 1,0, the selectivity on molecules of OSA was too much lower than reverse-osmosis membranes had. The imperfection of reverse osmosis concentration as well as nanofiltration concentration is salts accumulation in a concentrated medium due to this type of membranes have high selectivity on ions of dissolved salts: reverse-osmosis membranes have $\phi_{TDS} = 0,83-0,94$, nanofiltration membranes have $\phi_{TDS} = 0,79-0,88$.

The selectivity ϕ_{TDS} on ions of dissolved salts of ultrafiltration membranes is low. So electrolytes accumulation doesn't occur when SiO_2 content increases in concentrated sols. It profitably distinguishes ultrafiltration membranes as a method of obtaining of stable water sols with the highest SiO_2 contents and low impurities concentration. Data on physicochemical characteristics of sols obtained during the experiments with ultrafiltration membranes are shown in the table 3. Sizes of sols nanoparticles just after concentration are shown in the table 3.

Table 3.
Physical and chemical characteristic of silica water sols obtained by ultrafiltration.

| | |
|--------------------------------------------------------------------------|-------------------------------------------|
| pH | 8,5-9,2 |
| Total content of SiO ₂ , g/dm ³ | 4,0-152,5 |
| Sol density ρ _s , g/dm ³ | 998-1109 |
| Salt content TDS, mg/dm ³ | 873-1070 |
| Nanoparticles mean radius, nm | 5-12 |
| Coefficients of nanoparticles diffusion | (4-2)·10 ⁻¹¹ m ² /s |
| Mean zeta-potential ξ of nanoparticles surface, mV | -32,4 ... - 42,5 |
| Sol dynamic viscosity μ, Pa·s (20 ⁰ C) | (1,00 –1,15)·10 ⁻³ |
| conductivity σ, mS/sm | 1,065-1,361 |
| SiO ₂ content in the material precipitated from a sol, mass % | 99,72 |

When silica concentration in sols is rather high nanoparticles are unstable and aggregate forming complexes which sizes reach 30-50 nm just in the first hours after obtaining. Aggregates sizes are increased during the first 24 hours with further sols ageing up to 80-100 nm, during the first weeks up to 500 nm, at the same time sol coagulation or gelatinization take place. In sols obtained by reverse-osmosis concentration nanoparticles' aggregation, coagulation and gelatinization are happened quicker than in sols obtained by ultrafiltration. It is obvious that process flowsheet of concentration must provide with stabilizers addition (long-chain surfactant species and macromolecules of high-molecular compounds) to prevent coagulation and gelatinization independently of type of membrane process used for concentration. Stabilizers addition must be carried out after finishing of nucleation and growth of silica nanoparticles but before solution filtering in membrane facilities because nanoparticles aggregation starts during the process of concentration.

Table 4
Impurities content in the material obtained from a sol concentrated by ultrafiltration.

| compound | mass % |
|--------------------------------|--------|
| SiO ₂ | 99,72 |
| TiO ₂ | 0,00 |
| Al ₂ O ₃ | 0,173 |
| FeO | 0,00 |
| Cr ₂ O ₃ | 0,00 |
| MgO | 0,00 |
| CaO | 0,034 |
| Na ₂ O | 0,034 |
| K ₂ O | 0,069 |
| MnO | 0,00 |
| NiO | 0,00 |
| ZnO | 0,00 |
| total | 100,0 |

Silica content in filtrates after ultrafiltration can be reduced up to the values which correspond to

amorphous silica solubility, i.e. colloidal phase in filtrates will be completely absent. At the same time metals' ions of the initial solution are weakly delayed by ultrafiltration membranes and come in filtrate in considerable quantity. If the filtrate is concentrated by reverse osmosis after ultrafiltration facilities water with high content of lithium, rubidium, caesium and other useful chemical compounds presenting in initial solution in ionic or molecular form will be obtained.

Table 5.
The results of filtrates concentration by reverse osmosis method. K is an amount on cations, A is an amount on anions. n/r means not revealed.

| Index | Initial | | Φ-1 | | Φ - 2 | | K - 1 | | K - 2 | |
|--------------------------------|----------|---------|----------|---------|----------|---------|----------|---------|----------|---------|
| | mg/liter | mgequ/l | mg/liter | mgequ/l | mg/liter | mgequ/l | mg/liter | mgequ/l | mg/liter | mgequ/l |
| pH | 8,12 | | 7,88 | | 8,06 | | 8,53 | | n/r | |
| Na ⁺ | 286,5 | 12,46 | 46,6 | 2,03 | 268,0 | 11,65 | 1657,8 | 72,08 | 4426,3 | 192,45 |
| K ⁺ | 47,1 | 1,2 | 7,68 | 0,2 | 47,8 | 1,22 | 281 | 7,2 | 496 | 12,7 |
| Li ⁺ | 1,5 | 0,22 | 0,26 | 0,04 | 1,47 | 0,21 | 7,44 | 1,07 | 27,78 | 4,0 |
| Ca ²⁺ | 3,6 | 0,18 | <0,4 | | 0,4 | 0,02 | 26,0 | 1,3 | 115,2 | 5,75 |
| Mg ²⁺ | 1,2 | 0,1 | <0,2 | | 0,7 | 0,06 | 7,6 | 0,63 | <0,2 | |
| Fe ³⁺ | n/r | | n/r | | n/r | | n/r | | n/r | |
| Fe ²⁺ | n/r | | n/r | | n/r | | n/r | | n/r | |
| Al ³⁺ | <0,6 | | <0,6 | | <0,6 | | <0,6 | | <0,6 | |
| K | 338,7 | 14,16 | 54,54 | 2,27 | 318,37 | 13,16 | 1979,8 | 82,28 | 5065,3 | 214,9 |
| Cl ⁻ | 251,8 | 7,1 | 49,6 | 1,4 | 391,8 | 11,3 | 1397,1 | 39,4 | 3368,7 | 95,0 |
| SO ₄ ²⁻ | 201,7 | 4,2 | 6,7 | 0,14 | 38,4 | 0,8 | 1585,0 | 33,0 | 8261,2 | 172,0 |
| HCO ₃ ⁻ | 146,4 | 2,4 | 48,8 | 0,8 | 128,1 | 2,1 | 759,7 | 12,45 | n/r | |
| CO ₃ ²⁻ | 0,0 | | 0,0 | | 0,0 | | 29,4 | 0,98 | n/r | |
| A | 599,9 | 13,7 | | 2,34 | 558,3 | 14,2 | 3771,2 | 85,83 | 11630 | 267,0 |
| H ₃ BO ₃ | 104,6 | | 84,6 | | 100,1 | | 104,6 | | n/r | |
| SiO _{2s} | 127,5 | | 16,9 | | 46,3 | | 165 | | 210 | |
| SiO _{2t} | 127,5 | | 46,9 | | 39,7 | | 1321,9 | | 3296,9 | |

Nanodispersed silica can be precipitated from the sol by flocculants or other methods. Impurities concentration in the material obtained by silica precipitation from the sol is shown in table 4. Before silica precipitation sol was subjected to H-cation exchange (cation polishing) by passing through ion-exchange column to reduce of metal cations concentration in it. Then we precipitated silica, cleaned the precipitate by weak acid solution and dried at 120⁰C during 8 hours. In table 4 data for the sample with the least impurities content among all samples obtained for this time is shown. SiO₂ content in the sample has reached up to 99,72 mass %, it isn't the limit for the developed process.

Table 5 presents the experiments' results on reverse osmosis concentration of filtrate obtained in ultrafiltration facilities after several stages of filtering. The concentration of cation Li⁺ on the first concentration stage has increased from 1,5 up to 7,44 mg/liter, on the second stage up to 27,78 mg/liter. Selectivity of reverse osmosis membrane on cations of lithium φ_{Li} on the 1-st

concentration stage was not less than 0,833, on the 2-nd stage was not less than 0,802.

Taking into account the obtained experimental data the main stages of production of concentration water sols according to the process flowsheet are:

- 1) ageing of initial hydrothermal solution under the definite temperature regime, nucleation and polycondensation of orthosilicic acid, silica nanoparticles growth;
- 2) stabilizer adding to prevent nanoparticles aggregation;
- 3) membrane concentration made in several stages (2-3 stages);
- 4) ions removal (ions Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+,3+}$, Al^{3+} , SO_4^{2-} , Cl^-) out off the sol by the method of ion exchange (ion-exchange columns, filters) to increase chemical purity of sol and stabilize it;
- 5) filtrates concentration after ultrafiltration facilities by the method of reverse osmosis to obtain aqueous mediums with increased content of lithium, rubidium, caesium and other useful chemical compounds.

Periodical reverse cleanings of filtration facilities must be done in process flowsheet of silica concentration. It reduces rate of membranes degradation and increases their working life.

Sols production by membrane concentration of hydrothermal solutions is characterized by low expenses of chemical reagents in comparison with traditional sols production. For instance, sols production on the base of water solution of liquid glass (alkali silicate) needs the expenses of sodium silicate, cationite to purify initial water solution from sodium, and electric energy for membrane concentration. Suggested technology deletes the expense of liquid glass and high expense of H-cationite.

The cost of water sols depending to their physical and chemical characteristics reaches \$1000-4000 per a ton. The cost of silica mass unit in nanodispersed condition in water sol is higher than silica powders.

Silica water sol can be used to produce the materials with a controlled structure and defined properties. On basis of sol-gel method a large quantity of catalysts and adsorbents, zeolites, glasses, thermo-and-antidrumming compounds, porous materials, ceramics, composite and paintwork material, drilling fluids, etc. are produced. Sol-gel technology allows to carry out the process in optimal conditions with respect to management efficiency of properties of a final product, expenses of energy and process

productivity. Sol-gel transformation is the base of the obtaining nanomaterials: optical conductors, ceramic ultrafiltration membranes, anticorrosive coats, photomaterials, fibres, high-dispersed abrasives and other materials. Thanks to binding properties colloidal silica is successfully used as inorganic binder in materials with different filling material: inorganic powders, fibres, polymers, metals, etc. The character of such materials is their durability and heat resistance. Ceramic forms obtaining during the founding on smelted models, the production of refractory ceramics, insulating material can be the example of it.

CONCLUSIONS

1. Ultrafiltration membranes have selectivity on colloidal silica about 1.0 without preliminary addition any coagulants and low selectivity on silicic acid molecules and ions. Therefore it is possible to get by ultrafiltration the solution with high SiO_2 concentration and low concentration of impurity ions – Na^+ , K^+ , Ca^{2+} , Mg^{2+} , $\text{Fe}^{2+,3+}$, Al^{3+} , SO_4^{2-} , Cl^- . Thus, ultrafiltration has got advantages before other membrane processes when the problem of obtaining of silica concentrated water sols is solved.

2. Reverse osmosis membranes have selectivity on colloidal silica about 1.0 and high selectivity on silicic acid molecules. Thus, reverse osmosis can be used for extraction of silicic acid molecules without solution ageing when nucleation and polymerization of silicic acid are not over and colloidal silica particles are not formed. Moreover reverse osmosis can be used to obtain metal salts concentrates and other useful chemical compounds from filtrates purified from silica in ultrafiltration facilities.

3. For economic substantiation of process flowsheet of membrane concentration it is necessary to consider the following factors: 1) principal cost of membrane facilities that includes the cost of membrane surface taking into account definite quantity of cycles of membranes regeneration till their degradation, the cost of pumps, fittings, armature, storage tanks, control equipment, automated mechanisms; 2) the cost of electric power for membrane filtering of hydrothermal solution and periodical reverse cleaning of membranes; 3) the cost of cations and anionites in ion-exchange columns and solutions cost for their periodical regeneration; 4) the cost of final product namely concentrated water sol utilized in different industrial branches.

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