

## METHODS OF SILICA EXTRACTION FROM HYDROTHERMAL HEAT CARRIERS

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### ABSTRACT

The analysis of methods of extraction of silica and other chemical compounds from hydrothermal heat carriers was done. There were a lot of methods developed for the extraction because of many types of chemical compositions of heat carriers at different hydrothermal fields. The follows methods of silica extraction were analysed: 1) by addition of lime; 2) by addition of other coagulants such as metal salts; 3) by electrochemical coagulation; 4) by ultrafiltration; 5) by using fluidized beds; 6) membrane filters. One can choose method fit for the heat carrier with definite characteristics. Silica extraction is carried out simultaneously with recovery of electrical and heat energy for increasing efficiency of heat carrier using. The examples of extraction of metals, iodine, bromine, sodium chloride, potash, boron, arsenic from the liquid phase of heat carriers and, besides, extraction of CO<sub>2</sub> and H<sub>2</sub>S from gaseous phase were also considered.

### INTRODUCTION

The analysis of chemical composition shows that compounds of such elements as I, Br, Zn, Li, Mn, Hg, Cu, B, Au, Ag, Pt, Si, etc. are present in hydrothermal heat carrier. Recovery of valuable components as mineral feed stock or semi-products from hydrothermal heat carrier excludes such expensive processes as deposit opening or mine construction, ore mining, its crushing and concentration and leaching processes that are typical for the traditional methods relating to the mining and re-working of hard useful minerals. The extraction of chemical compounds is carried out in addition to the production of heating and electric power and, thus, contributes to the increase in efficiency of heat carrier using (Potapov V.V., 2003). The physico-

chemical characteristics of heat carrier are different at various deposits, that is why it is necessary to use technological methods of extraction that correspond to the extracted compound and conditions of extraction. The analysis of available extraction methods at deposits of different kind is necessary.

Table 1 presents chemical composition of hydrothermal heat carriers of different type. Table 2 shows the technological methods of chemical compound extraction from liquid and gaseous phases of heat carrier. At the high-temperature geothermal fields concentration of silica in separate is always high: Wairakei, Kaweraw (New Zealand), Otake (Japan), Cerro Prieto (Mexico), Dixie Valley, Salton Sea (USA), Reykjanes (Iceland), Monte Amiato (Italy) and Mutnovskoe deposit (Southern Kamchatka, Russia). At these geothermal fields a preliminary silica removal is necessary in order to extract successfully chemical compounds. Silica litters surface of sorbents and prevents cooling of separate because of the risk of solid deposits growth in wells, pipe-lines, heat equipment, apparatuses of technological line of extraction. The development of bar membrane methods is one of the perspective way for extraction of colloidal silica.

The extraction of metals from separate solutions requires developing of such processes as sorption, extraction, electrolysis. Application of biotechnological methods using microorganisms can be one of the new ways for metal extraction. Microorganisms can also be applied for obtaining of sulphuric acid water solutions from hydrogen sulphide of gaseous phase of heat carriers. For extraction of NaCl, KCl salts it is necessary to develop evaporation and crystallization processes. The extraction of iodine and bromine from the liquid

phase of heat carriers is related to degassing, condensation and sorption. Using of selective sorbents is one of the possible approaches for boron extraction from both gaseous and liquid phase of heat carriers.

Table 1.

The chemical composition of liquid phase (separate) of heat carriers from different hydrothermal fields.

Components mg/l	Wairakei, New Zealand, mg/l	Otake, Japan mg/l	Sumikava, Japan, mg/l	Onuma, Japan, mg/l	Cerro Prieto, Mexico, mg/l	Dixie Valley, USA mg/l	Salton Sea, USA mg/l
pH	8,4	7,70	7,5	-	-	9,2-9,44	5,2
Al <sup>3+</sup>	0,35	0,31	2,4	1,3	-	-	-
Li <sup>+</sup>	11	-	-	-	26	2,95	245
K <sup>+</sup>	185	321	70	54,6	1863	87,3	14300
Na <sup>+</sup>	1190	1640	348	391	7777	578	-
NH <sub>4</sub> <sup>+</sup>	-	-	-	-	-	-	-
Ca <sup>2+</sup>	23	17,3	-	13,4	404	10,15	-
Mg <sup>2+</sup>	0,004	0,04	<0,1	0,77	-	0,028	68
Fe <sup>2+</sup>	-	0,02	-	-	-	-	1300
Fe <sup>3+</sup>	-	-	0,03	0,03	-	-	-
Cl <sup>-</sup>	2100	2710	550	566 + 3,4 (F)	14488	617	-
HCO <sub>3</sub> <sup>-</sup>	13	32,3	46	31,7	90	97	-
CO <sub>3</sub> <sup>2-</sup>	-	-	-	-	-	64	-
SO <sub>4</sub> <sup>2-</sup>	32	129	106	205	-	265	-
H <sub>2</sub> BO <sub>3</sub>	-	-	-	-	-	-	-
H <sub>3</sub> BO <sub>3</sub>	28 (B)	-	237 (B) + 14 (As)	-	-	-	300 (B)
SiO <sub>2</sub> (total)	560	977	860	512	1138	591	506

Table 1  
(continuation).

Components mg/l	Lakes, USA,	Reykjanes, Iceland mg/l	Kizildere, Turkey, mg/l	Monte Amiato, Italy mg/l	Cheleken, Turkmenistan, mg/l	Mutnovskoe field, Russia, mg/l	Pauzhetskoe field, Russia, mg/l
pH	-	7,6	8,9	6,0-8,5	6,0	8,5-9,3	8,0-8,3
Al <sup>3+</sup>	0,25	-	-	0,31-1,1	-	0,3	0,16
Li <sup>+</sup>	1,9	7,7	-	21,9-11,0	8,5	1,6	3
K <sup>+</sup>	33,0	2125	127,8	558	620	57,0	78
Na <sup>+</sup>	345,0	15300	1240,25	1977	73430	239,9	736,4
NH <sub>4</sub> <sup>+</sup>	-	1,6	3,95	439	-	0,7	0,4
Ca <sup>2+</sup>	2,1	2560	3,2	128	22942	4,0	45
Mg <sup>2+</sup>	0,21	3	0,95	<0,5	3232,5	0,24	1,8
Fe <sup>2+</sup>	-	-	-	1,6	18,3	0,1	0,6
Fe <sup>3+</sup>	-	-	-	-	1,17	0,1	-
Cl <sup>-</sup>	235,0	29800	107,17	4135	160000	291,1	1305
HCO <sub>3</sub> <sup>-</sup>	-	-	2246,75	-	17,0	43,9	37,64
CO <sub>3</sub> <sup>2-</sup>	-	-	-	-	0,0	18,6	-
SO <sub>4</sub> <sup>2-</sup>	116,0	62	769,75	25,8	370,0	124,9	102
H <sub>2</sub> BO <sub>3</sub>	-	-	-	-	265,0	-	15
H <sub>3</sub> BO <sub>3</sub>	As – 1,3, F – 12,0	12,4 (B)	24,48 (B)	41904	-	106,9	177
SiO <sub>2</sub> (total)	255,0	985	288,0	700-1040	-	650-900	300-350

Table 2.  
Technological methods for extraction of chemical compounds from hydrothermal heat carriers.

Field	Extracted chemical compounds	Extraction methods	Phase of the work
Kaweraw, Wairakei, Brodlands, New Zealand	SiO <sub>2</sub>	Addition of CaO into separate, ultrafiltration	Pilot plant
	As	Treatment by ferric sulfate for flocculation, sorption of arsenic with preliminary pre-oxidation of sodium hypochlorite	Pilot plant
Ohaaki (Brodlands), New Zealand	SiO <sub>2</sub>	Fluidized bed of close sand	Pilot plant
Wairakei, Brodlands, New Zealand	SiO <sub>2</sub>	Cation polymeric flocculants Zetag, anion polymeric flocculants, Magnafloc, FeCl <sub>3</sub> , Ca(OH) <sub>2</sub> , polyaluminium chloride, MgCl <sub>2</sub> , CaCl <sub>2</sub>	Laboratory plant
Sumikawa, North Japan	SiO <sub>2</sub>	Nitrogen-bearing cation surface-active reagents : Dimethyldiarilammoniumchloride Methacryldimethylaminoethyl methylchloride	Laboratory plant
Sumikawa, Onuma, Japan	SiO <sub>2</sub>	Entering the growth centres seeds – silica colloidal particles – by addition of silica gel or hydrothermal solution	Laboratory, pilot plant
Otake, Japan	H <sub>2</sub> S (from gaseous phase)	1) Adsorption by inorganic materials, hydrogen sulphide; 2) oxidation of hydrogen sulphide by thermophilic microorganisms; 3) biochemical reactor to obtain sulphuric acid	Pilot plants
Cerro Prieto, Mexico	SiO <sub>2</sub>	Addition of coagulant CaO into separate	Pilot plant
	KCl - NaCl	Evaporation, crystallization, flotation	Pilot plant
	SiO <sub>2</sub>	Flocculants of Magnifloc, Calgon, Separan, Purifloc series	Laboratory plant

Dixie Valley, CIIIA	SiO <sub>2</sub>	Addition of MgCl <sub>2</sub> into separate, then microfiltration by membranes with pore diameter 1 μm	laboratory, pilot plant
Salton Sea, CIIIA	Zn	Ion exchange, liquid extraction, electrolysis	Industrial production
	Fe, Mn, Pb, Ag, Cu, Sn	Precipitation of metal hydroxides after entering of CaO, precipitation of metal sulphide, cementation	Pilot plants
Mamos Lakes, USA	SiO <sub>2</sub> (colloidal solution)	Reverse osmosis, ultrafiltration, entering of coagulants (salts)	Pilot plants
	Cs, Rb, Li	Reverse osmosis, ultrafiltration, ion exchange	Pilot plants
Reykjanes, Iceland	SiO <sub>2</sub>	Recirculation of sludge after electromagnetic treatment	Industrial production
	NaCl	Evaporation, crystallization	
	CO <sub>2</sub> (from gaseous phase)	Gas separation, cooling, condensation,	
Kizildere, Turkey	SiO <sub>2</sub>	Entering of precipitants: Ca(OH) <sub>2</sub> , CaO, CaCO <sub>3</sub> , CaSiO <sub>3</sub>	Laboratory plant
Kizildere, Turkey	B	Using of selective materials – amberlite resine Amberlit IRA 743 for purification	Pilot plant
Kizildere, Turkey	CO <sub>2</sub> (from gaseous phase)	condensation	Industrial production
Monte Amiato, Italy	SiO <sub>2</sub>	Coagulation (Ca(OH) <sub>2</sub> , CaCl <sub>2</sub> ), flocculation	Laboratory plant
Lardarello, Italy (gaseous phase)	H <sub>3</sub> BO <sub>3</sub> (boric acid)	Vapor condensation, concentrating of condensate, filtration, crystallization, centrifuging	Industrial production
	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O (boral)	Vapor condensation, addition of sodium carbonate, concentrating of condensate, filtering, crystallization, centrifuging	Industrial production

	NH <sub>4</sub> HCO <sub>3</sub> (sodium bicarbonate)	Evaporation of vapor condensate and obtaining of gases saturated with ammonium; gas condensation and obtaining of ammonium solution; evaporation of CO <sub>2</sub> from vapor condensate, its purification from H <sub>2</sub> S in absorption towers by solutions of sodium and potassium permanganate; bubbling of CO <sub>2</sub> through ammonium solution to carry out a reaction resulting in obtaining of sodium bicarbonate.	Industrial production
	S	Obtaining of permanent gases by evaporation of vapor condensate; mixing with air and air oxidation up to elemental sulfur in absorption towers over a catalyst – ferric oxides; washing with ammonium solution to purify from sulphates; extraction of sulfur by organic solution and obtaining of sulfur flakes in the flocculator	Industrial production
Cheleken Turkmenistan	Br, J	Degassing, condensation, sorption	Industrial production
Mutnovskoe field, Kamchatka, Russia	SiO <sub>2</sub>	Coagulation, flocculation, electro coagulation, low-temperature concentrating, membrane filtration	Laboratory plant
Pauzhetskoe field, Kamchatka, Russia	SiO <sub>2</sub>	Using of coagulation (lime), membrane filtration	Laboratory plant

### **EXTRACTION OF CHEMICAL COMPOUNDS FROM HYDROTHERMAL HEAT CARRIERS**

The example of boric acid extraction from the heat carrier of Lardarello field (Italy) is well known (Dvorov I.M.; 1976, Allegrini, G., Luccioli, F., Trivella, A., 1992.). In the 30-s of XIX century Lardarello Company started drilling of steam-hydrothermal deposits aimed at the industrial production of boric acid and borax. In the 70-s at Toskana steam-hydrothermae they extracted up to 15 thousand of tons a year of various chemical raw materials, including 4400 tons of boric acid, 4000 – 5000 tons of borax, 620 tons of salmiac and other compounds. The content of boric acid and ammonia in vapor condensate from Lardarello deposit is the following: H<sub>3</sub>BO<sub>3</sub> – 0.15 – 0.4 g/kg of vapor, NH<sub>3</sub> – 0.15 – 0.6 g/kg of vapor. Although the content of boric acid in vapor is insignificant it

is extracted in large amounts owing to the vapor discharge.

Until 60-s of XX century a chemical plant operated at Lardarello deposit aimed at the production of boric acid, borax, sodium bicarbonate and elemental sulfur. The chemical composition of the original vapor is the following: H<sub>3</sub>BO<sub>3</sub> – 0.25 g/kg, NH<sub>3</sub> – 0.1-0.3 g/kg, permanent gases – 4.7 mass %, from them CO<sub>2</sub> – 94 %, H<sub>2</sub>S – 2.5 %. The system of preparation of process solutions and gases included coiled or shelf-tubular heat exchanger-separator (4.5 bar, 200 °C) where geothermal vapor that had come from wells was partially condensed. Clean vapor at a pressure about 2.0 bar was directed to the turbine for the electricity production and vapor condensate with a concentration H<sub>3</sub>BO<sub>3</sub> 8-10 % was directed to the tank for degassing (4.0 bar, 126 °C) through the opening in the upper part of which permanent gases- CO<sub>2</sub> и H<sub>2</sub>S were taken off. The aqueous solution from the low part of the degassing tank came to the dilator (1.65 бар, 113 °C) where vapor saturated with NH<sub>3</sub> – 1.5 g/kg was obtained. The process solution of boric acid and gases obtained were used according to the following schemes. The production of boric acid H<sub>3</sub>BO<sub>3</sub>: concentrating of condensate, filtration, crystallization, centrifuging and obtaining of different types of products like powder, transparent granules of high purity. The production of borax Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O (in various forms also): addition of sodium carbonate, concentrating of condensate, crystallization, centrifuging. The production of sodium bicarbonate NH<sub>4</sub>HCO<sub>3</sub>: condensation of vapor saturated with ammonia and obtaining of ammonia solution; evaporation of CO<sub>2</sub> from vapor condensate, its purification from H<sub>2</sub>S in absorption towers by solutions of sodium and potassium permanganate; bubbling of CO<sub>2</sub> through ammonia solution to carry out a reaction resulting in obtaining of sodium bicarbonate. The production of elemental sulfur S: obtaining of permanent gases; mixture of gases with air and air oxidation up to the elemental sulfur in the absorption towers over a catalyst – ferric oxides; washing of solid mass with ammonium solution to purify from sulphates; sulfur extraction by the organic solution and obtaining of sulfur flakes in the machine-flocculator.

At the hydrothermal deposit Kizildere (Turkey) tests for the laboratory and pilot plants to purify heat carrier from boron compounds were successfully conducted (Recepoglu O., Beker U., 1992). The extraction was done using selective material – amberlite resine Amberlit IRA 743. Evident boron contents are present at two more geothermal fields in Turkey: Idin-Jermensik with a concentration of H<sub>3</sub>BO<sub>3</sub> 71 mg/l and Salvatari with a concentration of

H<sub>3</sub>BO<sub>3</sub> 62 mg/l. At all these deposits CO<sub>2</sub> contents in a heat carrier are rather high – from 1.5 to 2.0 mass %. At the geothermal power plant of Kizildere deposit CO<sub>2</sub> extracted provides 80 % of the local soft drink industry.

The experiments on silica precipitation with entering of Ca(OH)<sub>2</sub>, CaO, CaCO<sub>3</sub>, CaSiO<sub>3</sub> had been carried out with the model aqueous solutions which were close by characteristics to separate from Kizildere wells (Badruka M., Matsunagab I., 2001).

Potentially lithium is one of the most considerable elements of hydrothermal solution. Kimura K. had carried out successfully the experiments on extraction of lithium from hydrothermal solution using membranes immobilizing lithium (Kimura K., Sakamoto H., Kitazawa S., Shono T., 1995). The successful tests for a pilot plant for extraction of lithium from large amounts of solution had also been conducted at the American deposit.

Increasing demand for lithium metal is expected to rise above the current production levels. Most lithium production is currently from mining and recovery of pegmatite ores. Recent research has emphasized recovery from brine sources such as geothermal water and seawater. A novel liquid-membrane-extraction process is investigated for the recovery of lithium metal from these natural resources by Ma P., Chen X. D. and Hossain M. M. (2000). Different carriers and combinations of carriers were tried for lithium selectivity. A carrier combination of LIX54 (main component is  $\alpha$ -acetyl-*m*-dodecylacetophenone) and TOPO (tri-octyl phosphine oxide) had a synergistic effect for lithium extraction and was found to be most effective. This combination was used to extract lithium in a supported liquid membrane (SLM) process. Variables considered were pH, carrier concentrations, initial lithium concentration, type of organic solvent and stripping phase, and presence of sodium and potassium ions in the feed and flow rates of both aqueous phases. The optimal extraction efficiency of the system was higher than 95% for a model feed solution containing Na<sup>+</sup>, K<sup>+</sup>, and Li<sup>+</sup> at pH greater than 12.5. The permeability of the system was maintained at a constant value for a maximum period of 2 days and dropped below 50% after 4 days. Empirical mathematical models for lithium extraction were derived from the results of SLM experiments.

Arsenic is the most problem element of hydrothermal solution because of its influence on the environmental ecology. A removal of As from a solution must be done in that way so the final product to be utilized. Otherwise it will be expensive and

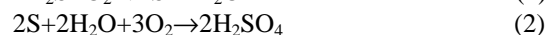
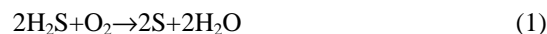
inexpedient. After removal of arsenic in some cases it is possible to discharge spent heat carrier to the local reservoirs and rivers. This excludes expensive measures for reinjection. Buisson D.X. made considerable efforts on the development of technique of arsenic removal from hydrothermal separate. Buisson D.X. and his colleagues tested a pilot plant for removal of arsenic from separate at the fields Brodlands and (Wairakei Buisson D.H., Rothbaum H.P., Shannon W.T., 1979). The water was treated firstly by ferric sulfate to form flakes which sorbed arsenic and at the same time by sodium hypochlorite to oxidize trivalent arsenic and to convert it in quinquivalent one. The last one coprecipitated better. Nonionic flocculant was added to improve flake formation. The water was saturated with air in special tanker and transferred into another tanker with smaller pressure where air bubbles evolved from water and flake flotation of the material precipitated to the surface occurred. Flotation contributed to the better separation of flakes from water and their dehydration. Fe consumption necessary for complete precipitation of quinquivalent arsenic was 11 mg/l. Arsenic could be extracted from flakes that have precipitated. Silica coprecipitation stopped when water had been acidified up to pH 4-5.

In 1977 in geothermal region of Iceland, southwestern part of Reykjanes peninsula a pilot plant for NaCl production was launched. In 1983 a commercial plant for salt discharge began to work with a capacity of 8000 tons/year (Kristiansson I., 1992; Gudmundsson S.R., Einarsson E., 1989) In 1986 a plant for extraction of carbon dioxide CO<sub>2</sub> from vapor condensate with a capacity of 1500 tons/year was also put into operation. A possibility of extraction of silica slurry used for medical purposes from the solution flow was studied. The hydrothermal solution was treated by the following way. Two-phase flow at the temperature 250<sup>0</sup> C and pressure 4.4 MPa was fed to a separator. There pressure was decreased to 1.0 MPa and temperature – to 180<sup>0</sup> C. Then water solution was directed to the evaporator with forced circulation where a part of solution had been evaporated and its density increased. A separate from Reykjanes field had the following chemical composition (mg/kg) after evaporation stage: SiO<sub>2</sub> - 985, Cl - 29800, Ca - 2560, Mg - 3, Na - 15300, K - 2125, Li - 7.7, SO<sub>4</sub> - 62, NH<sub>4</sub> - 1.6, Br - 108, B - 12.4, Mn - 0.05, As - 0.10, I - 0.6, NO<sub>2</sub> - 0.07, NO<sub>3</sub> - 0.03, PO<sub>4</sub> - 0.18, pH = 7.6. At the first stage a water in the evaporator was acidified up to pH = 3.5, at the second stage – up to pH = 2.4 to decrease silica precipitation growth in heat exchangers. Then a separation of silica with adding of caustic soda was done in an open sedimentation tank in order to increase pH up to 8.2 and speed up

adhesion of colloidal particles. After that a solution was directed through a flat-bottomed evaporator into flat-bottom vessels (plates) for crystallization. Before this an abundance of silica was removed from the flow in a cyclone-settling system. Before a solution was fed to the crystallization plates it had been acidified again up to pH = 6.5 and NaCl salt had isolated during the subsequent evaporation. A separated steam was used for acidification. A condensate from heat exchangers was collected in liquid gas separator. Pure CO<sub>2</sub> was evolved from gas containing up to 95% of CO<sub>2</sub> and after compression liquid CO<sub>2</sub> and dry ice were produced.

In Japan at the geothermal power station Otake experimental plants were tested for extraction and use of hydrogen sulphide which was a part of geothermal gas composition (Hirowatari K., Syunji K., Izumi J., Takeuchi K., 1995). The tests were carried out on acidifying separate in order to slow down rate of solids formation. The sulphuric acid H<sub>2</sub>SO<sub>4</sub> was produced from hydrogen sulphide and it was used at the geothermal power station to acidify separate before reinjection. Acidification corresponds to the efficiency of geothermal solution and reduction in hydrogen sulphide emission to the environment. The silica content in separate is within 425-665 mg/kg. Silica concentration in a solution which requires acidification up to pH = 5-5.5 reaches 850 mg/kg. The chemical composition of a heat carrier at Japanese field Hatchobaru is the following (well H-15, 276<sup>0</sup>C): 1. separate (mg/kg)-SiO<sub>2</sub> - 977, Na<sup>+</sup> - 1640, K<sup>+</sup> - 321, Ca<sup>2+</sup> - 17.3, Mg<sup>2+</sup> - 0.04, Cl<sup>-</sup> - 2710, SO<sub>4</sub><sup>2-</sup> - 129, HCO<sub>3</sub><sup>-</sup> - 32.3, Fe<sup>2+</sup> - 0.02, Al<sup>3+</sup> - 0.31, pH = 7.70; 2. gases (volume percentage)- CO<sub>2</sub> - 92.5, H<sub>2</sub>S - 5.8, N<sub>2</sub> - 1.2, gas content - 0.096 volume percent (vol.%). In the experimental plants sulphuric acid was produced by three different methods: 1. combustion of hydrogen sulphide; 2. thermophilic oxidation of hydrogen sulphide; 3. hydrogen sulphide oxidation in a biochemical reactor. A plant for hydrogen sulphide combustion consisted of adsorption – desorption chambers (PSA), combustion chamber, converter and gas washing chamber. An initial gas mixture contained 0.7-1.3 vol.% H<sub>2</sub>S, 30-50 vol.% CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>. hydrogen sulphide in PSA chambers was adsorbed by inorganic material (zeolite, alumina), reactivated after pressure had been decreased and fed to the combustion chamber where it was oxidized up to SO<sub>2</sub>. The duration of adsorption – desorption cycle was about 100 seconds. In a converter with vanadium catalyst SO<sub>2</sub> was converted into SO<sub>3</sub> which then was absorbed by water solution in the gas washing chamber and changed into H<sub>2</sub>SO<sub>4</sub> acid. The initial H<sub>2</sub>S content in a mixture was 0.94 vol.%, rate of mixture feed – 12.25 Nm<sup>3</sup>/h, H<sub>2</sub>S concentration after adsorption – desorption - 6.0-16.8

vol.% and mixture volume - 0.6 Nm<sup>3</sup>/h. A hydrogen sulphide concentration in the gases decreased to 500 ml/m<sup>3</sup>. A production rate of H<sub>2</sub>SO<sub>4</sub> by the first method was 280-320 g/hour, efficiency of H<sub>2</sub>S combustion up to SO<sub>2</sub> was almost 100% (at a temperature over 550<sup>0</sup>C), efficiency of SO<sub>2</sub>/SO<sub>3</sub> converting and SO<sub>3</sub> absorption was not more than 90%. During thermophilic oxidation sulfur-oxidizing bacteria (*Sulfolobus*) were used, in a third method – bacteria-oxidants *Thiobacillus thioparus*. The first method is the most perspective method for usage of geothermal gases at the Otake field. It is closer to the traditional method of sulphuric acid production. Nevertheless, a biochemical method of obtaining of sulphuric acid using *Thiobacillus thioparus* was substantially developed in papers. At Japanese field Otake a pilot aqueous bioreactor was tested. Noncondensable hydrothermal gases from the geothermal power station were fed to the lower part of reactor. The bacteria completed oxidation reactions for hydrogen sulphide dissolved in water according to the following equations:



The extraction ratio for hydrogen sulphide in such bioreactor was more than 90%, acidified water corresponded to 0.1 H solution of sulphuric acid. The H<sub>2</sub>SO<sub>4</sub> solution obtained biochemically from hydrothermal hydrogen sulphide was then used to acidify separate from the station in order to slow down rate of solids growth.

Among 20 – 30 chemical elements which could be profitable to be extracted from thermal waters. Currently, only iodine and bromine are extracted industrially. In Russia useful resources of 9 deposits of thermal iodide-bromine water are explored and proved (Dvorov I.M., 1976). A considerable part of thermal fields with a high percentage of iodine is not used because of their high alkalinity. Naphthenic acids, alkaline salts of organic acids and oil admixture also adversely effect processes of iodine and bromine obtaining from thermal waters. Usually, the iodide-bromine waters are enriched in strontium. Having an available technology it is possible to organize industrial production of this element from cheap mineral stock – wastes after iodine and bromine extraction. For many years a plant operates in Western Turkmenistan based on thermal brines from Cheleken iodine-bromine field where 12 water-bearing horizons are exploited. At present, 150 wells bring thermal brines to the surface. Some of them work based on well-spring but the most part of them were converted for pumping. Besides a high content of iodine (26.3 mg/l) and bromine (578.7 mg/l)

thermal brines contain a number of other components. Lebedev L.M. and Nikitina I.B. made a chemical analysis of brines from the Cheleken field for 11 horizons and detected a high content of microcomponents (mg/l) in them [9]: lithium — 7.8, rubidium — 0.65, lead — 3.24, zink — 3.7, copper — 2.4, cadmium — 1.48, arsenic — 0.36, strontium — 715. If to take into account the average annual well production, then according to the preliminary data the following elements are thrown to the sea for one year (t): lithium — more than 100, rubidium — about 10, lead — 300 - 350, zink — 48 - 50, copper — 24 - 35, cadmium — 18 - 24, arsenic — 6 - 8, strontium — 7200. The Cheleken thermal waters are an example of manifestation of present-day large ore-forming hydrothermal system.

Table 3

*An estimation of the mineral potential of the Salton Sea field. 1 - chemical compound; 2 - extraction potential, thou. t/year; 3 - consumption in USA, thou. t/year, 1980; 4 - market value of a potential product, US\$ million/year, 1981; n.d. (not determined) - market opportunities in USA for this very compound are not determined.*

1	SiO <sub>2</sub>	NH <sub>3</sub>	Li	Mn	Fe	Cu	Zn	Sn	Pb	Se
2	135	117	65	335	346	0.8	133	6	24	0.7
3	n.d.	15800	4.7	1061	69400	3902	920	53	1100	0.4
4	4.6	27.1	1075	648	97	n.d.	135	90	19	6

The geothermal field Salton Sea (USA) has unique potentials for mineral extraction. In the Imperial Valley carbon thermal brines (more than 400 g/l) with a temperature of 270°C, high content of potassium, lithium and heavy metals were revealed by a deep well. During trial pumping a brine had a precipitate in drain-pipes with a substantial concentration of silver, copper, gold and some other scattered elements. During pumping they needed to clean pipes from thick layers of precipitates every month. The precipitates consisted mainly of amorphous substance with a high background ferrum. According to the analysis data, silver content was 9277 g/t of brine, or almost 1.2%, and gold content — 3.12 g/t. A potential of the field is about 2.5 ton per second. Several companies became interested in geothermal brines. Their attention was attracted by a question of electricity generation and simultaneous extraction of potassium and lithium for the initial period. It had been calculated that only one well could yield 1 thou. of tons of potassium salts per day. In their papers Maimoni A. (1982) and Werner H.H. (1970) gave an estimation of the productivity of a combined power-mineral factory with a capacity of 1000 MWt based on resources of the field. A cost of valuable compounds in case of extraction from a brine can exceed considerably benefit from electricity sale. Such a factory is able to meet from 14 to 31% of

needs in manganese in USA and give substantial amounts of zink, lead, lithium and valuable metals.

At the Salton Sea field a supermineralized solution has the following chemical composition (well Sinclair No.4, mg/kg) [29]: SiO<sub>2</sub> - 506, NH<sub>3</sub> - 440, Li - 245, K - 14300, Rb - 25, Mg - 68, Sr - 600, Mn - 1260, Fe - 1300, Cu - 3, Zn - 500, B - 300, Pb - 90, As - 7, Ag - 0.5, Au - 0.1, Pt - 0.06, total salt content - 294 g/kg, pH = 5.2. With electricity price of 6 cents/kWt-year cost of the energy sold will be US\$ 394 million/year, and potential profit from a sale of mineral components (without taking lithium into account) – US\$ 500-1500 million/year. Table 3 contains the calculation results for potential opportunities of an energy-mineral factory at Salton Sea field. For valuable metals calculations gave the following results (extraction – t/year, consumption in USA – t/year, market value of the product US\$ million/year): Ag - 4.2, 99, 38; Au - 0.8, 3.0, 341; Pt - 0.5, 2.2, 206.

At Salton Sea field pilot plants were tested and laboratory experiments were carried out on mineral extraction from geothermal solution. The following extraction methods were studied: 1. separate precipitation of hydrated ferric oxides and oxides of manganese, zinc, lead after adding of lime; 2. treatment of a solution with hydrogen sulphide and separate precipitation of sulfides according to the increase in solubility in a line Ag, Pb, Zn, Fe and Mn; 3. using cementation during electrolysis to obtain Ag, Cu, Pb, Sn. Based on the analysis of Salton Sea field it have been concluded that it is necessary to use combined approach for extraction of compounds and gain advantages of each method. The CalEnergy Company with a project in the value of US\$ 200 millions in 1999 planned to produce at Salton Sea field up to 30000 tons of pure zink every year (99.99% - Zn) (Clutter T.J., 2000). A plant for zink production began to work in 2002, it needs 20 MW energy from a power unit (49 MW) at the cost of US\$ 150 millions. The equipment for zink extraction includes a combination of available technologies which were modified for the given task: ion exchange, liquid extraction and electrolysis. A technology is the following: separate with a temperature not less than 116 °C firstly passes through ion exchanger (the similar one is used for water softening) modified with organic molecules which are meant for zinking on necessary conditions. After this stage a solution is directed to the apparatuses of the next stage. Here during a liquid extraction process it transforms a resulting zink chloride into zink sulphate. Further metal is melted into bars and then realized. A special high-quality zink of more than 99-% purity is a final product of

the firm-producer. At Salton Sea field they continue to search other extraction products which are potentially profitable. They include manganese, lithium, boron and small amounts of noble metals. But silica is the most abundant. In its latest research effort company is looking for the economically sound methods of transformation of silica precipitated into marketed product.

#### **METHODS FOR EXTRACTION OF SILICA**

At the Sumikawa and Onuma fields they used seed colloidal particles of different gels to purify from silica: Wakogel C-100, Wakogel C-200, Wakogel C-300, Kaseigel 60-75, Kaseigel 120-75, Kaseigel 300-75 (Sugita H., Matsunaga I., Yamaguchi T., Kato K., Ueda A., 2003). At the Onuma field the experiments were made using seed silica particles that had been obtained by the evaporation of separate from Onuma wells, disintegration of water into drops (100  $\mu\text{m}$ ), drying at 110  $^{\circ}\text{C}$  after preliminary washing with distillate.

Researchers of the Central Research Institute of Mitsubishi Corporation together with Daido Chemical Corporation made series of experiments on extraction of silica using cation reagents (Kato K., Mogi K., Ueda A., Ishumi K., 2000). Two types of nitrogen-bearing cation surface-active reagents were tested to extract silica from oversaturated separate from geothermal power station Sumikawa (North Japan): dimethyldiarilammoniumchloride and methacryldimethylaminoethylmethylchloride

The most important research works on development of the extraction and application method for geothermal silica were conducted at the fields of New Zealand, Mexico, Iceland and USA. At geothermal power stations Wairakei and Kaweraw in New Zealand there is an experience of obtaining of geothermal silica on a commercial basis. According to its physicochemical characteristics it approaches to the synthetic silica applied in the production of top-quality paper and is quite competitive to it (Harper R.T., Thain I.A., Johnston J.H., 1992, 1995). The silica content  $\text{SiO}_2$  in separate from wells in New Zealand is up to 1000 mg/kg. A capacity of the geothermal power station at Kaweraw field is 157 MW. The extraction of silica according to the project calculations will make it possible to obtain additionally up to 16 MW of electric energy and up to 180 MW of heat energy due to a decrease in rejection temperature from 130 to 40 $^{\circ}\text{C}$ . For this purpose a separate flow with a discharge of 3500 t/hour = 972.2 kg/s is directed to a system of primary heat exchangers of a binary plant where its temperature is decreased from 130 to 87 $^{\circ}\text{C}$  and heat is passed to the working body of a gas turbine with a

16 MW capacity. At the next stage silica is extracted with a decrease in its total content up to a solubility of amorphous silica. At the same time decrease in a separate temperature is supposed to be insignificant – from 87 to 85 $^{\circ}\text{C}$ . A silica is extracted in a valuable form and its physicochemical characteristics satisfy the requirements for silicate additions at the top-quality paper production. A silica precipitated has a sufficient purity. A chemical composition of dried silica from Wairakey field was the following (wt.%):  $\text{SiO}_2$  - 98.7,  $\text{Al}_2\text{O}_3$  - 0.33,  $\text{Fe}_2\text{O}_3$  - 0.01,  $\text{CaO}$  - 0.32,  $\text{Na}_2\text{O}$  - 0.37,  $\text{K}_2\text{O}$  - 0.19, As - 0.00041. A silica particle size is within a range of 15.0-20.0 nm, a specific surface area – 54-155  $\text{m}^2/\text{g}$ . A potential capacity for the geothermal silica production at Wairakei field is 7500 t/year, at Kaweraw field – 3000 t/year. All this will ensure the following profit: at Wairakei field - US\$9750000/year and at Kaweraw field - US\$3900000/year. According to the project at Wairakei field after extraction of silica a separate passes 180 MW of heat to a river water flow with a discharge of 12600 t/h through a system of secondary heat exchangers and warms it up to 38 $^{\circ}\text{C}$ . Warm river water is used then to hold temperature in ponds with shrimps. As a result a separate is cooled to a temperature of 40 $^{\circ}\text{C}$  and injected into reservoir through reinjection wells. The similar scheme of obtaining of additional electric and thermal power by decrease in reinjection temperature with a silica extraction method can be realized at any high-temperature hydrothermal field.

A valuable mineral stuff – lithium Li becomes available. Its obtaining before silica extraction is difficult because of clogging of immobilization materials by which lithium is adsorbed. A potential profit from lithium production at Wairakey field is \$18000000/year. The amount of lithium which is planned to be extracted is 300 t/year. At Wairakei field after reduction of a concentration of arsenic poison a separate can be thrown into the river instead of reinjection. The pilot plants for extraction of lithium and arsenic were tested successfully. Taking this into account, a complex (integrated) approach for using of geothermal heat carrier extracted will be developed. All this increases its cost.

In the paper of Hurtado R., Mercado S. and Gamino H. (1989) a scheme of a pilot plant for a treatment of hydrothermal separate with lime in order to precipitate colloid silica is given. Also its testing results are presented there. It worked under conditions of the geothermal power station at Cerro Prieto (Mexico) in a flow mode with a discharge of 1 kg/s. A total power for electricity production at stations Cerro Prieto is 620 MW, a summary discharge of separate flow is 1667 kg/s = 6000 t/h, a



total silica content in separate solution reaches 1000-1200 mg/kg.

A chemical composition of a hydrothermal solution forms as a result of mixing of sea water with Colorado river water and interaction with high-temperature rocks of a geothermal system. A typical chemical composition of separate is the following (well M-25, mg/l): Na - 7777, K - 1863, Ca - 404, Li - 26, Cl - 14488, B - 21,  $\text{HCO}_3$  - 90,  $\text{SiO}_2$  - 1138, total mineralization- 23588. The separate flow entire goes to a natural reservoir with a square of 16 km<sup>2</sup> where part of water evaporates. At Cerro Prietto field reinjection is not carried out because of a high risk of precipitation in wells, though there is a necessity for reinjection to maintain pressure in the reservoir. The results of laboratory tests have shown that addition of lime and organic flocculants into a separate solution leads to the more rapid precipitation of silica in case if a solution was aged for 10-15 minutes before treatment. During this time a polymerization reaction took place in a solution. At the same time a concentration of monomeric silica decreased and colloidal silica particles which could be coagulated appeared. A treatment scheme on a pilot plant included the following stages: 1. evaporation of a separate extracted at atmospheric pressure; 2. ageing of a solution until colloidal particles will appear; 3. addition of lime and quick mixing; 4. silica precipitation and clarification of a solution. The equipment used in this scheme had the following construction parameters. A separator: pressure 0.1 MPa, a vessel of cylindrical form (0.508 m in diameter), 1.1 m in height, installed upright, made of carbon steel. A tank for ageing of a solution: closed, of squared shape, made of carbon steel, length - 3.00 m, width - 0.8 m, height - 1.0 m, volume 2.4 m<sup>3</sup>, covered with fiber-glass insulation. Within a tank partitions are placed to direct solution according to "S"-pattern in order to avoid stagnation. There were three outlets for sampling in a tank which were evenly distributed along the length. A mixing tank had a cylindrical form, diameter - 0.6 m, height - 0.85 m, volume - 0.24 m<sup>3</sup>. It was made of carbon steel, covered with fiber-glass insulation, equipped with a mixer with a variable speed of rotation (300-1000 turn/min). A precipitation tank (clarifier) made of carbon steel consisted of two sections. The upper section had a cylindrical form, lower part - conical form. The cylindrical section had an outer diameter of 1.85 m and it was 1.55 m in height. A cylindrical inset was placed inside it (0.45 m in diameter, 1.35 m in height) through which a solution entered from a tank for mixing. The lower part of a cylindrical inset had a conical section with an outer diameter of 1.45 m. The upper section with a ring section was a solution clarification zone which was filled with a

solution refined. Near to the upper face of a tank there was an outlet through which a solution refined flew from a tank. A tank had 5 ports for sampling that allowed to obtain characteristics of a solution in the inner zones such as zone of a solution clarification, zone of precipitation concentration, etc.. A tank for lime was of a cylindrical form, made of carbon steel, equipped with a mixer with a steady speed of rotation 1750 turn/min.

Two tests were done at Cerro Prietto field: the first one with duration of 50 hours, second - 70 hours. A discharge of lime CaO necessary for colloidal silica precipitation and reduction of a total content up to the solubility of amorphous silica was 30 mg/l. This discharge was sufficient to ensure reduction of colloidal silica content to a level of 10-30 mg/l. For a separate flow at Cerro Prietto field with a total discharge of 1800 kg/s at duration of solution ageing of 15 minutes two ageing tanks are required with the following dimensions: height - 2.0 m, length - 5.0 m, width - 37.5 m. According to the test data for a pilot plant at Cerro Prietto field at a density of separate flow 40 l/min·m<sup>2</sup> two precipitation tanks with a diameter of 30.5 m and height of 5.5 m are required. A silica precipitation from separate of wells at Cerro Prietto was carried out in the laboratory using flocculants of Magnifloc, Calgon, Separan, Purifloc series (Weres O., Yee A., Tsao L., 1980, 1981). In comparison with lime silica precipitation requires less concentrations of flocculants. However, the cost of flocculants is high and as a result of this in some cases a treatment of separate with lime can be cheaper. At Cerro Prietto field a pilot plant for potash KCl extraction with a productivity of 1 t per day was tested (Mercado, S., Hurtado, R., 1992). To extract potash such process as evaporation, crystallization and flotation were used.

In New Zealand Rothbaum H.P. and Anderton B.H. (1975) tested a pilot plant for silica precipitation from hydrothermal separate. This plant was analogous to such that had been tested in Mexico. At Wairakei and Brodlands fields a removal of colloidal and monomeric silica from a solution was studied with addition of slack-lime: up to 400 mg/kg CaO at Wairakei and up to 700 mg/kg at Brodlands. A silica content in separate from Wairakei field was about 550-650 mg/kg, in separate from Brodlands field - up to 1000 mg/kg. In this case silica precipitated as a hydrated calcium silicate gel with a weight content of solid phase up to 30%. During drying gel converted to fine amorphous powder with a density of 0.2 g/cm<sup>3</sup> and  $\text{SiO}_2/\text{CaO}$  ratio about 1.7. A treatment by a pilot plant included ageing of a solution at a temperature of 90°C, addition of slack-lime and gel separation in precipitation tank.

A chemical composition of a separate from the fields in New Zealand differs greatly from one of Cerro Prieto field: calcium content in it is 15-30 times less, total mineralization is much lower. Therefore, for effective silica precipitation a considerably greater amount of lime than at Cerro Prieto field was required. An addition of lime led to coprecipitation of arsenic As, its concentration in separate from Wairakei and Brodlands fields was 3-5 mg/kg. Preoxidation of arsenic to quinquivalent state contributed to its, almost complete, removal from separate.

Initially tests were carried out with separate samples of a separate from Wairakei and Brodlands fields. They were carried out in a laboratory and at fields using newly warmed solution. The preliminary tests confirmed the fact that silica precipitation from a separate that was subjected to ageing required a considerably less amount of lime in comparison with a treatment of fresh solution. It is connected with the fact that during ageing a polymerization reaction and formation of colloidal particles take place and colloidal silica precipitates in considerably greater amounts than monomeric silica. The time necessary for a polymerization reaction to be completed for solutions from Brodlands and Wairakei fields was within 0.5-2.0 h and decreased with increasing of total silica content. A dependence between the amount of lime CaO added to a solution and residual total silica SiO<sub>2</sub> content C<sub>i</sub> in a solution subjected to warming up to 90<sup>0</sup>C and ageing was the following (mg/kg): 0 mg/kg CaO - 660 mg/kg SiO<sub>2</sub>, 50 - 655, 100 - 448, 200 - 310, 400 - 110, 700 - 41, 1000 - 7. Arsenic coprecipitated together with silica. A complete removal of arsenic required addition of 1000 mg/kg CaO. During preoxidation of trivalent arsenic to quinquivalent state a necessary amount of lime decreased to 400 mg/kg. During tests by a pilot plant oxidation of arsenic to quinquivalent state was carried out by adding of sodium hypochlorite into solution. To a pilot plant separate came under gravitational head. The plant consisted of two large tanks 5 m<sup>3</sup> in volume, the first tank was for ageing and the second one – for flake separation. Besides, it included a small mixing tank divided into three sections: first section served to add organic high-molecular flocculant Polyflok 90 AP, second section – to add lime, and third section – for precipitation. All surfaces that were in contact with water or lime had an epoxy resin cover to inhibit corrosion. Sodium hypochlorite was added into the first tank to oxidize arsenic. A separate refined overflowed from the upper part of second tank and sludge of the material precipitated was taken off from a tank bottom to vacuum filter. The duration of separate ageing during

the tests at Wairakei field was 2.5 h. At the same time a temperature of separate decreased from 90 to 75<sup>0</sup>C. The duration of ageing at Brodlands field was 0.5 h, and temperature of separate decreased from 92 to 86<sup>0</sup>C. Two grillages of pipes were installed at the top and bottom of the first tank. They provided a laminar flow regime of a separate in vertical direction. After addition of lime calcium silicate precipitated as small frail flakes. A permanent precipitation of these flakes required a low-velocity flow in horizontal direction with a small turbulence. For this purpose a distributing chute with a special construction was placed in the second tank at the input of a feed chute. This chute made a barrier. It caused water to flow under it until a flow crossed the tank and water flew into effluent chute. With such a construction a removal of 95% of flakes from water was reached. The chemical analysis results for a separate treated and material precipitated have shown that an addition of lime CaO into separate from Wairakei field in the amount of 410 mg/kg at a pilot plant led to a reduction of silica SiO<sub>2</sub> concentration in a separate from 560 to 100-87 mg/kg. pH of a separate increased considerably: from 7.6 to 11.4. The CaO concentration in a separate after treatment was 216 mg/kg. The SiO<sub>2</sub>/CaO ratio in a dried precipitate at a lime discharge of 410 mg/kg was 1.55, density of a dried precipitate was 0.16 g/cm<sup>3</sup>. At Brodlands field a silica SiO<sub>2</sub> concentration in a separate decreased from the value of 910 mg/kg by the following way: at a discharge of CaO 460 mg/kg – up to 263-230 mg/kg, 605 mg/kg CaO - up to 165 mg/kg, 685 mg/kg CaO - 126-93 mg/kg, 815 mg/kg CaO – up to 70 mg/kg, 1120 mg/kg CaO – up to 7 mg/kg. pH of a solution changed considerably during treatment: with addition of 685 mg/kg CaO a pH value increased from 8.6 to 11.3-11.4. The SiO<sub>2</sub>/CaO ratio and density of a dried precipitate depended upon the amount of lime that had been added: with addition of 460 mg/kg CaO a SiO<sub>2</sub>/CaO ratio was 2.14, density – 0.43 g/cm<sup>3</sup>, 605 mg/kg CaO - 1.90, density – 0.40 g/cm<sup>3</sup>, 685 mg/kg CaO - 1.68, density – 0.20 g/cm<sup>3</sup>, 815 mg/kg CaO - 1.40, density – 0.20 g/cm<sup>3</sup>, 1120 mg/kg CaO - 0.74, density – 1.00 g/cm<sup>3</sup>. At Brodlands field at a lime discharge of 685 mg/kg arsenic content decreased from 4.3 to 2.0 mg/kg. In this case preoxidation of arsenic to a quinquivalent state by sodium hypochlorite increased an amount of arsenic precipitated: at a hypochlorite discharge of 10 mg/kg arsenic concentration decreased to 1.7 mg/kg, at a hypochlorite discharge of 20 mg/kg a residual As concentration was 0.9 mg/kg. At a discharge of lime CaO 1100 mg/kg at Brodlands field almost absolute precipitation of arsenic to a residual concentration 0.1 mg/kg was reached without its preoxidation by hypochlorite. For the commercial variant of the plant for SiO<sub>2</sub> and As coprecipitation using of chlorine

instead of hypochlorite for arsenic oxidation is preferred.

It has been determined that an optimal discharge of lime for a separate treatment at Wairakei field was 400 mg/kg with arsenic preoxidation. A treatment under such conditions led to the removal of 90% arsenic from a solution and cessation of formation of the solid silica precipitations from separate. It makes possible to use it as a heat source. At Brodlands field an optimal discharge of lime CaO with a preoxidation by hypochlorite was 700 mg/kg, this provided the removal of 80% arsenic and stabilization of solids growth in wells and heat equipment. A typical chemical analysis of a dried precipitate at a discharge of lime CaO 685 mg/kg was the following (weight percent after gel drying at a temperature of 105°C): SiO<sub>2</sub> - 47.0, CaO - 28.0, As - 0.19, CO<sub>2</sub> - 6.7, NaCl - 2.3, Mg - 0.3, Fe - 0.04, SO<sub>4</sub> - 0.18. A specific surface area of powder was 110 m<sup>2</sup>/g. As an X-ray phase analysis had shown, powder was amorphous with a small portion of crystalline calcium carbonate. An ignition at 900°C led to a transition of amorphous structure into crystalline wollastonite CaSiO<sub>3</sub>. An ignition of other amorphous samples of calcium silicate at 900°C also led to a transition into wollastonite. Samples with a large portion of SiO<sub>2</sub> after ignition contained a some part of cristobalite, samples with a small portion of SiO<sub>2</sub> – calcium silicate. A gel of calcium silicate is a material of a potential value. Gel obtained by the pilot plant at Wairakei field contained from 5 to 15 weight percent of solid phase. Such a range is the most difficult to be used: with a content of less than 5 wt.% gel can be passed by pipes, but with a content of more than 15% gel becomes hard enough for usual flow. Therefore, the tests were carried out on a filtration under high pressure from 1.4 to 14.0 MPa using a hand hydraulic press. The tests have shown that filtration at a pressure of 1.4 MPa increases content of a solid phase in gel from 7 to 16 wt.% for a short period of time. However, a long-term filtration at this pressure and short-term filtration at much more higher pressures did not increase substantially content of a solid phase. Besides, gel was dehydrated in a filtration centrifuge during 20 minutes at a frequency of 2000 turns/min. At the same time a chalk-type material with a solid phase content of 17 wt.% was obtained which was difficult to be removed from a centrifuge. Based on this it has been concluded that an optimal result is obtained by a short-term filtration at a pressure of 1.3 MPa.

Further the tests with gel samples obtained by vacuum and pressure filtration were carried out on a drying rate using hot air warmed up to 90°C from hydrothermal separate. After pressure filtration

samples were dried better and more quickly. The tests have shown that after pressure filtration a gel can be initially dried quite satisfactorily with air warmed by geothermal heat. After that it becomes hard enough to be easily converted into powder which is then dried with air at a comparatively low temperature. The dried calcium-silicate can be used in making wall-papers and other coverings. In this case rather small amount of arsenic in the material (0.2 wt.%) will not be an obstacle for such a production. Using of calcium silicate precipitated as an addition in the production of dyes and rubber will be, probably, difficult because of the presence of As. A calcium silicate can also be slightly applied in ceramics production after its ignition up to 900°C and transition to wollastonite. Besides, calcium-silicate can be used in a construction industry as a raw material for cement making and for fertilizers production also.

In the paper of Gudmundsson S.R. and Einarsson E. (1989) a working scheme of the geochemicals plant in Reykjanes (Iceland) is given with extraction of NaCl salt and silica from hydrothermal separate. An application of the electromagnetic field is a peculiarity of the silica extraction method in this very scheme. The electromagnetic field makes it possible to reduce a consumption of alkali NaOH for a separate treatment before silica precipitation, increase its precipitation rate after treatment and increase amount of the material precipitated. A hydrothermal solution passes through several stages of evaporation in separator and then in two-effect evaporator so that a density of the solution increases to 1.09 g/cm<sup>3</sup> and total silica content after evaporator is 2700 mg/l. A solution is directed to an open precipitation tank to which a recirculated flow of freshly precipitated silica sludge alkalinized with NaOH enters. In the precipitation tank after mixing with recirculating sludge pH of a solution increases to 8.2. From the precipitation tank solution is fed to a flat-bottomed evaporator and then to the flat vessels for NaCl extraction where some amount of silica also precipitates. At the plant in Reykjanes in 1985 and 1986 the tests have been carried out with a connection of an electromagnetic apparatus to recirculating flow of silica sludge. In addition to alkalization sludge was treated in the electrostatic and magnetic fields directed transversely to each other. An electromagnetic apparatus was connected to a recirculating sludge flow in the open precipitation tank and cyclone precipitation system. It has been established that at the use of the electromagnetic field a pH value necessary for rapid silica precipitation becomes lower and reaches 7.3-7.8 instead of 8.2. Alkali consumption decreased two times correspondingly. The amount of silica extracted did

not increase in this case. Using of the electromagnetic field led to the increase in a rate of silica particles precipitation. In the precipitation tank a rate of precipitation increased from 1.3 cm/min to 7.1-7.9 cm/min at 100°C and to 3.4-4.6 cm/min at 40°C if to compare with a solution that had been alkalified only. A growth of the precipitation rate of particles allows to miniaturize equipment. Besides, in a solution treated in the electric and magnetic fields a rate of polymerization increased. To explain the results obtained Gudmundsson S.R. and Einarsson E. supposed that electric and magnetic fields could destroy a double electric layer around colloidal silica particles and, thus, diminish influence of a negative surface charge that was responsible for low polymerization rate.

A separate discharge at the pilot plant for silica precipitation using electromagnetic field was 100-300 l/min. A silica concentration in a separate flow at the input of the plant was 2200-2300 mg/l. The incoming acid separate was firstly cooled in a heat exchanger; this provided decrease in a growth rate of deposits in a system. A mixing tank was placed under cyclone. Silica sludge came from the bottom part of a cyclone into the tank. It was added with NaOH. Acidified sludge flow was then mixed with an acid separate flow and a mixture with pH = 6.2-7.8 came to an electromagnetic reactor. Further a mixture of separate and sludge treated in the electromagnetic field came to a cyclone where silica precipitated. A clarified separate was then directed to the evaporation vessels and sludge precipitated – from the bottom part of a cyclone to recirculating flow. A part of sludge was taken off to a separate vessel for further silica concentrating. A temperature in a system varied from 100 to 20°C. A concentration of silica in a clarified separate changed according a temperature. A concentration of monomeric silica SiO<sub>2</sub> was within 191-256 mg/l, this corresponded to a solubility of amorphous silica 80-270 mg/l in a temperature range 20-100°C. A total silica content in a sludge flow coming from the bottom part of a cyclone and in a mixture separate-sludge also depended upon a temperature and varied within the following range: for sludge - 2900 mg/l at 20°C, 5900-9000 mg/l at 40°C, 14000-20000 mg/l at 86-97°C, for a mixture - 2600 mg/l at 20°C, 3900-4200 mg/l at 40°C, 4400-6000 mg/l at 90-97°C. A silica content in sludge after concentrating was 40000-44600 mg/l. A ratio between a discharge of separate and sludge at mixing also changed depending on the temperature. The optimal mixing proportions sludge/separate for the effective silica precipitation were the following: 1:1 - at 20°C, 1:3-1:5 - at 40°C, 1:7 - at 95°C. An alkali NaOH discharge was 90-91 mg/l at a temperature of 95-97°C and 155-174 mg/l at a temperature of 20°C.

A scheme for a colloidal silica extraction developed at a geochemicals plant in Iceland was tested only for a strongly oversaturated highly mineralized solution from Reykjanes field that passed preliminary stages of evaporation with obtaining of SiO<sub>2</sub> concentration up to 2200-2300 mg/l. Using of such scheme at another field with a solution having another initial concentration of silica and another chemical composition will require a change of parameters and, possibly, after further investigation only.

The experiments on a silica precipitation from hydrothermal solution samples from the different wells of Monte Amiato field (Italy) were carried out for samples from wells PC-33, PC-34 и PC-35 (Vitolo S., Cialdella L., 1995). A silica precipitated by adding lime and calcium chloride CaCl<sub>2</sub> at 20 and at 90°C. The aim of the experiments was to study an influence of the chemical composition of a solution upon coagulation and silica precipitation. A treatment of a solution from well PC-33 by lime was less effective than treatment of a solution from wells PC-34 and PC-35. For coagulation and silica precipitation in a solution from well PC-33 it was necessary to add not less than 2000 mg/l Ca(OH)<sub>2</sub> and for a solution from two other wells 500 mg/l Ca(OH)<sub>2</sub> was enough. The authors explained this result by the fact that pH of a solution from well PC-33 was substantially lower than in wells PC-34 and PC-35. Only after addition of 2000 mg/l Ca(OH)<sub>2</sub> pH of a solution from well PC-33 increased from 6.0 to 6.8. At pH = 6.8 a colloidal particle surface could be sufficiently saturated with the negative hydroxyl groups and a calcium cation could perform a coagulation function on formation of bridge bonds between particles. Another behavior of colloidal and monomeric silica was observed at a treatment with calcium chloride CaCl<sub>2</sub>. After a treatment with CaCl<sub>2</sub> only colloid silica precipitated, and monomeric silica was stable at the largest consumptions of coagulant right up to 20000 mg/l. A treatment with calcium chloride led to a decrease in pH of a solution and suppression of coagulation influence of a cation Ca<sup>2+</sup>.

In Russia a number of methods for silica extraction was developed based on the experiments with a separate from the Mutnovskaya and Pauzhetskaya geothermal power stations (Southern Kamchatka): with addition of coagulants, flocculants, low-temperature concentrating and using of membrane filters (Potapov V.V. et al, 2003, 2005). Slack-lime, calcium chloride, aluminium sulphate, chloride of ferrum, sea water, mixtures of slack-lime and sea water were used as coagulants. Polydimethylammonium chloride, Multifloc-231, high-molecular cation polyacrylamides Zetag 7689,

Zetag 7623 and Praestol 854BC were used as flocculants. A method of silica precipitation by an electrochemical coagulation was developed. It offers to bring metal cations into a water solution by a dilution of aluminium or ferric anode at passing of continuous electric current through. The utilization methods for the material extracted were developed to produce sorbents for a gas chromatography and purification of natural waters and sewage from oil products, metal silicates, additions to Portland cement for fortification of concrete, liquid glass.

A considerable success in development of a silica extraction technology was achieved by a group of specialists from a Brookhaven National Laboratory (USA) headed by Mow Lin (Lin M.S., Bohenek M., Premuzic E.T., Johnson S.D., 2000; Lin M.S., Premuzic E.T., Zhou W.M., Johnson S.D., 2001). The investigations were oriented at an extraction of silica from the low-mineralized hydrothermal solutions of Dixie Valley field. In this case an amount of silica extracted was less but its purity was much higher if to compare with a supermineralized solution from Salton Sea field. Mow Lin's group succeeded in obtaining of geothermal silica of a record purity, and a technology that had been offered gained award and was included in a list of 100 best technologies of USA.

From a flow of separate with a discharge of 630.8 l/s at the Dixie Valley geothermal power station (50 MW capacity) it is possible to obtain up to 6000 t/year of silica. Its cost can reach from \$2 to \$110 per kilogram depending on its physicochemical properties. Market requirement in USA amounts to 190000 t/year of silica and up to 68000 t/year of colloidal silica with an increase in a consumption of 4% per year. A geothermal silica from Dixie Valley field can satisfy an annual increase in need of USA market. The main stages of a separate treatment according to the technology that has been offered are the following. The main stages of a separate treatment according to the technology that has been offered are the following. A separate goes from a reinjection line to a reactor through a heat exchanger by which a temperature of a separate is adjusted before a treatment. A  $MgCl_2$  solution is fed from a tank for reagents into reactor by a batcher pump. A discharge of  $MgCl_2$  is rather small and has a range of several ppm (mg/kg). A temperature of a separate treatment is maintained at a level of 90°C. A reactor is equipped with a mixer. From a reactor separate goes to a microfiltering system where membranes with a pore dimension of 1 mkm are placed. A silica precipitated is separated from a separate in a filtering arrangement. At the same time a weight content of water in silica sludge is 30 %. Further sludge is

washed with a lean HCl solution to remove ions sorbed by a colloidal particle surface. A clarified separate goes for reinjection. In accordance with the given technological scheme it is possible to extract up to 60% of silica that is contained in a solution. Using an electron microscope dimensions of particles were studied. A concentration of admixtures in the material precipitated was determined by X-ray spectroscopy and ICP-spectroscopy methods. A specific surface area (BET-square), volume and pore diameter were changed using adsorption method for nitrogen absorption. According to its physicochemical properties material obtained at a pilot plant corresponded to the laboratory samples. A portion of silicon dioxide in the material obtained was 99.9 wt.%. Thus, a concentration of admixtures (Mg, Al, Ca, Fe, Hg, etc.) was record low for geothermal silica – less than 0.1 wt.%. A specific surface area of silica obtained was within a range of 200-500 m<sup>2</sup>/g, a summary pore volume – 0.9-1.0 cm<sup>3</sup>/g, a pore diameter, when a pore volume was highest possible, – 30.0 nm. A dimension of particles that formed material was within 20-30 mkm. Aggregates with a dimension up to 100 mkm made a small part. A dimension of primary particles that formed particles of a final product was not bigger than 10 nm.

At Mamos Lakes (USA) a preconcentration by reverse osmosis was used for colloidal silica extraction. An initial SiO<sub>2</sub> concentration was not more than 250 mg/kg. At the geothermal power station there is a necessity for pure water for a cooling in turbine condensers, therefore, a problem of separate purification appeared. After concentrating water with SiO<sub>2</sub> content 800-1000 mg/kg is directed to the vessels equipped with mixers where a coagulant (metal salt) comes and silica precipitates. A part of a concentrated water flow passes through ultramembranes, thus the second product is obtained – concentrated silica sol. Cs, Rb, Li are extracted from a filtrate that passed through ultramembranes using ion exchange.

The methods based on a filtration process were used earlier at Kaweraw and Brodlands fields (New Zealand). In one case, a surface of close sand in a fluidized state was used to extract dissolved silicic acid (Axtmann R.C., Grant-Taylor D., 1986). In the other case, a hydrosol of colloidal silica concentrated up to 30 mass % was obtained by filtering through three stages of ultramembranes (Brown K.L., Bacon L.G., 2000).

## **CONCLUSIONS**

1. Extraction of chemical compounds is one of the methods to increase the efficiency of hydrothermal

carriers. An analysis shows a necessity for a development of the following methods of chemical technology for a profitable extraction of chemical compounds from heat carriers of different type: metals - sorption, ion exchange, extraction, electrolysis, cementation, biotechnological methods using microorganisms; H<sub>2</sub>S (gas phase) – microorganisms to solve the tasks of obtaining of sulphuric acid water solutions; NaCl, KCl – evaporation, crystallization; I, Br - degassing, condensation, sorption; B - selective sorbents; As – coagulation and coprecipitation, flotation, sorption; Si –coagulation, flocculation, electrochemical coagulation, membrane methods.

2. An extraction of colloidal silica particles that appear as a result of nucleation and polycondensation of orthosilicic acid molecules is one of the main tasks concerning use of a high-temperature heat carrier. Silica pollutes a surface of sorbent and inner surface of the technological equipment used for extraction. Nonreagent membrane extraction of silica nanoparticles is a perspective method.

3. Membrane methods have some advantages:

- a) decrease in amount of reagents for water treatment;
- б) reduction of quantity and dimension of tanks-mixers, batchers, mixers;
- в) obtaining of silica of higher purity is possible;
- г) in most cases effluents from membrane apparatuses do not pollute the environment.

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