Lithium recovery from separate of Pauzhetskaya geothermal station by sorbents on the basis of modified silicates and aluminosilicates of the deposits of Kamchatka krai

T P Belova, T I Ratchina and L S Ershova

Research Geotechnological Center, Far Eastern Branch of Russian Academy of Sciences, Russia. E-mail: tpbel@yandex.ru

Abstract. The question about rational use of electrical and thermal energy is sensitive today all over the world. The complex approach is necessary to improve work efficiency of geothermal stations. The recovery of silica and lithium from technogenic solutions of geothermal stations to obtain marketable products is one of the methods. The crude product namely amorphous silica was obtained by the method of electrodialysis. Amorphous silica is a valuable material to obtain selective sorbents. The sorbents to recovery lithium from technogenic geothermal materials were obtained by using direct modification of the silica and zeolites surfaces from Yagodinsky deposit of Kamchatka region. The dynamic exchange capacity of sorbent MSI-Li was 0.29 mg/g, the concentration factor was 3.44. The dynamic exchange capacity of sorbent ZEO-5Li was 0.44 mg/g, the concentration factor was 4.54 per one phase of sorption.

Key words: complex use, geothermal heat carries, recovery of valuable components, silica, lithium, sorption, exchange capacity.

1. Introduction

A lot of attention has been devoted to the questions of complex use of minerals and energy resources lately. The geothermal power-engineering develops in Kamchatka region. Two geothermal stations Mutnovskaya and Pauzhetskaya work at the moment. The high-temperature geothermal fluids are necessary to be considered as a source of thermal energy and chemical compounds.

The potential of geothermal heat carries is not entirely used. The steam-water mixture is injected into the separators from recovery well, where separation into a working steam and separate happens. The working steam is supplied into the turbines of geothermal station and the separate is escaped on to the relief or injected into rocks. The temperature of separate is 170°C. Thermal energy use of separate would let to increase the operational efficiency of geothermal station by 25–30%. Besides, the concurrent recovery of mineral components would provide complex approach to use natural resources.

The mineralization of geothermal fluids of different deposits widely varies. The chemical composition of geothermal fluids depends on mining-and-geological conditions in bedding regions. For example, the mineralization of technogenic solution of Pauzhetskaya geothermal deposit is approximately 2.25 g/l (Table 1). Such components as sodium (670 mg/l), boron (135 mg/l related to boric acid), lithium (3.1 mg/l) etc. are of interest. The total mineralization of separate of Mutnovskaya geothermal station-1 is 2.10 g/l. More than 50% of total mineralization is for silica. Among other components sodium (273 mg/l), H$_3$BO$_3$ (96 mg/l) and etc. should be noted. The composition of technogenic solutions is given in Table 1.

High concentration of silica in separate of Mutnovskaya geothermal station creates essential technological problems. The efficiency of geothermal station reduces considerably because of solid depo-
sits in heat and power equipment. On the other hand, mineral product like amorphous silica is a valuable material in chemical, paper, paint-and-vanish and other branches of industry. In some branches of industry the use of crude silica is possible. Particularly, the selective sorbents can be obtained on the basis of crude silica obtained by the method of electrodialysis. The lithium consumption has been increased lately, because of the development of such areas of industry as metallurgical, glass, ceramic, refractory, thermoplastics generation, pharmaceutics, synthetic rubbers, electronics and especially due to electromobile production, where it is a basis of accumulators. The nuclear engineering is the main application of lithium.

**Table 1. Technogenic solutions composition.**

| Components | Separate of Mutnovskaya geothermal station | Separate of Pauzhetskaya geothermal station |
|------------|-------------------------------------------|------------------------------------------|
| pH (units, pH) | 9.20 | 8.32 |
| Li^+ | 0.10 | 0.014 | 3.10 | 0.447 |
| K^+ | 53.0 | 1.355 | 44.0 | 1.125 |
| Na^+ | 273 | 11.875 | 670 | 29.143 |
| NH_4^+ | 0.80 | 0.044 | 1.0 | 0.055 |
| Ca^{2+} | 3.80 | 0.190 | 46.0 | 2.295 |
| Mg^{2+} | 0.10 | 0.008 | 1.22 | 0.100 |
| Fe (total) | 0.30 | 0.016 | 0.30 | 0.016 |
| Σ cations | 331 | **13.503** | **763** | **32.736** |
| Cl^- | 234 | 6.601 | 1078 | 30.409 |
| HCO_3^- | 42.0 | 0.688 | 12.3 | 0.202 |
| CO_3^{2-} | 5.20 | 0.173 | 0.186 | 0.006 |
| SO_4^{2-} | 210 | 4.372 | 76.8 | 1.599 |
| H_4SiO_4^- | 79.8 | 0.839 | 7.32 | 0.077 |
| H_2BO_3^- | 51.0 | 0.838 | 19.2 | 0.316 |
| Σ anions | 622 | **13.512** | **1194** | **32.608** |
| H_3BO_3 (total) | 96.0 | 1.552 | 135 | 2.183 |
| H_2SiO_4 (dissolved, total) | 275 | 2.891 | 183 | 1.924 |
| H_2SiO_4 (total) | 1180 | 12.404 | 183 | 1.924 |
| Mineralization | 2098 | – | 2248 | – |
The world lithium resources are evaluated as 35 tons; approximately 60% of them occur at salt brines of saline lakes, about 26% concentrate at the lithium pegmatites and the rest part is in geothermal and oil fields and sedimentary rocks [2]. In the South America (Chile, Argentina), China, Bolivia lithium is produced from the salar and salt brines of saline lakes. The works of many scientists on recovery of lithium from salt brines by the method of liquid extraction, practically without reagent expenses are known [3]. In China for processing lithium saline brines of magnesian type the devices of centrifugally-planetary type developed in Russia are used, where the sorbent LiCl·2Al(OH)3·H2O (DGAL-Cl) from chloride lithium and defective forms of aluminum hydroxide is formed. There are ion-exchange technologies, based on the use of selective nonorganic ion-exchangers on basis of titanium dioxide in which manganese dioxide is injected on the stage of synthesis. The dioxides gels are saturated with solutions of lithium hydroxide under thermal synthesis; as a result they have selective activity relative to lithium [5]. In the USA at the factory «Simbol» after obtaining electricity geothermal waters are cleaned of silicates and passed through chemical resin, where the sorption of lithium and other valuable components happens, after that the water is reinjected into the layers [6]. Kimura K. recovered lithium from geothermal water through membranes [7].

The RGC FEB RAS studies the development of technological schemes to recover lithium from geothermal heat carries [8, 9]. The low concentration of alkaline-earth elements is an advantage; the high concentration of orthosilicic acid is disadvantage. Orthosilicic acid is deleted with electrodialysis [10] or membrane concentration [11]. Then lithium is recovered by the sorption method.

Earlier we have shown [10] that amorphous silica can be precipitated in a dynamic mode by the method of electrodialysis with aluminum or zinc electrodes using porous membrane. The precipitation occurs in an anodal part of electrodialysis cell at solution speeds from 0.005 to 0.02 m/min. Silica, extracted in the same way, is a polluted material of electrodes and mineral components of separate. The crude product is a colloidal solution containing SiO2 – 2.35%, Al3+ – 0.2%, Na+ – 0.05%, less than 0.02% is for other mineral components of separate.

Fig. 1. Scheme of installation for silica removal from separate of the Mutnovskaya geothermal heat carry: 1 – sedimentation chamber; 2 – line of separate discharge from electrodialysis cell; 3 – valve; 4 – cathodic plate; 5 – porous membrane; 6 – power supply; 7 – direct-current power source supply of model “Instek” (1) with regulation of voltage and current strength; 8 – line of separate supply from heat exchanger in to electrodialysis cell; 9 – heat exchanger; 10 – line of separate supply from separatory of GeoPlant; 11 – cooling water inlet; 12 – cooling water outlet from heat exchanger; 13 – anode plate; 14 – branch pipe from anode chamber of electrodialysis cell; 15 – precipitated suspended solid substances of colloidal silica with different chemical compounds; 16 – branch pipe from cathode chamber of electrodialysis cell; 17 – outlet of clarified separate from the system [10].

2. Materials and methods
Silica extracted from separate of Mutnovskaya geothermal heat carry and zeolite of Yagodinsky deposit of Kamchatka region with modified surface were used as sorbents for lithium recovery. Zeolite tuffs of Yagodinsky deposit of Kamchatka are clinoptilolite (up to 70%) and mordenite (up to 10%).
Up to 20% are for cristobalite, crystalline silica, mica and clay materials. Siliceous module SiO₂/Al₂O₃ varies within 5.0–6.0. Silica modification was carried using microwave radiation of capacity equaled 1000 W and frequency equaled 2450 MHz within 5 minutes. The fraction with particles size from 0.25 to 0.50 mm was separated by the method of dry sieving. Chemical modification of silica (MSIₐ) and zeolite (ZEO-5₁₄) was made in a dynamic mode. Solution, representing the mixture of aluminum and lithium chlorides with concentration of aluminum 5.4 g/l, the lithium 0.7 g/l and solution speed 4 ml/min was passed through columns with sorbents. Then columns were shut and kept within 24 hours at a room temperature. In 24 hours 2% solution of ammonium hydroxide was passed through columns. Columns were shut and kept within 24 hours again and washed by water up to a stable value of pH and aluminium and lithium ions absence in washing waters. The double hydroxide aluminum and lithium precipitated in sorbent phase. Before the sorption sorbents were washed with 0.01 M hydrochloric acid and then with water.

3. Results and discussion

Sorption from model and natural solutions was carried out by the method of down flow with the speed 1 ml/min. The experimental data are presented in Table 2 and on graph (Fig.1). Desorption of MSIₐ and ZEO-5₁₄ was made with 0.01 M hydrochloric acid (Fig.2). Sorption from technogenic solution of Pauzhetskaya geothermal deposit was carried out by the method of down flow, too. The experimental data are presented on graph (Fig.3). The content of alkaline and alkaline-earth metals in eluate was simultaneously controlled.

The dynamic of lithium sorption is presented on graph (Fig.1). Lithium is not discovered in the first 25 of columns volumes using modified silica (MSIₐ). Then breakthrough fraction comes, the lithium concentration quickly increases and becomes equal to original value after 50 columns volumes. 0.22 mg/l lithium concentration is detected in the first volumes of eluate at the sorption on (ZEO-5₁₄). The lithium concentration slowly increases and does not equal to original value even after passing 70 columns volumes.

On the graph three zones connected with different mechanisms of sorption process can be distinguished. The first zone (from 0 to 25 of column volumes) is possibly characterized by external diffusion mechanism. The second zone (varies within 25–50 of columns volumes) is characterized by mixed diffusion mechanism and the third one (more than 50 of columns volumes) is characterized by inside diffusion mechanism. Such tendency is detected in the second and next cycles. Only four cycles of sorption were carried out. The sorption capacity is 0.29 mg/l in the first cycle under sorption on MSIₐ. The second cycle of sorption capacity decreases almost thrice and becomes equal to 0.11 mg/g, after that it stabilizes. 98.9% of lithium are recovered at the first cycle under desorption. The lithium recovery decreases to the fourth cycle up to 95.7%. The concentration factor (k) is equaled to 3.44±0.30. The sorption capacity is higher at the sorption on the ZEO-5₁₄. It is equaled to 0.44 mg/l at the first cycle, it decreases up to 0.34 mg/l at the second cycle and begins to rise and then it stabilizes on the level 0.38 mg/g at the third cycle. The lithium recovery from sorbent ZEO-5₁₄ remains on the level 95.7%. The concentration factor increases by 22% and it is equaled to k₁₄ = 3.71–4.54 to the four cycles.

The data on lithium sorption from technogenic solution are presented on graph (Fig. 4). Sorbent was washed by hydrochloric acid of 0.01 M concentration before sorption. Lithium ions included in double aluminium hydroxide were removed from phase of sorbent completely. The exchange centers containing sodium, potassium and alkaline-earth metals cations were decationized only partially. From phase of sorbents alkaline metals cations are removed fullest, it is confirmed by the analysis of washing waters and next sorption.

Table 2. The degree of recovery and the concentration factors under lithium desorption by hydrochloric acid of C=0.01 M

| № cycle | MSIₐ | ZEO-5₁₄ |
|---------|-----|---------|
|         | Recovery, % | k | Recovery, % | k |

doi:10.1088/1755-1315/249/1/012032
In the process of sorption it was determined that alkaline metals of lithium, sodium and potassium presenting in technogenic solution are absorbed by sorbent and alkaline-earth metals of calcium and magnesium are displaced out of sorbent. Two types of exchange take place: at first, exchange of lithium ions for hydrogen ions in a structure of double aluminum lithium hydroxide $H^+\rightarrow Li^+$ and exchange of sodium and potassium ions for hydrogen ions in a structure of zeolite $H^+\rightarrow Me^+$, secondly, potassium and magnesium ions remaining in a structure of zeolite under acid processing, exchange for sodium and potassium ions $Me^{2+}\rightarrow 2Me^+$. Sorption capacity ZEO-5$_{Li}$ under sorption from technogenic solution in dynamic terms on lithium decreases in comparison with sorption from model solution, not only due to lower lithium concentration in technogenic solution, but due to competing sorption. Total volume is 0.31 mmol/g.
Lithium recovery is 71.1% as a result of desorption of hydrochloric acid solution of 0.01 M. The concentration factor on lithium is equaled to 2.02, but mole ratio (Na⁺+K⁺)/Li⁺ decreases up to 15.8, while in original solution (Na⁺+K⁺)/Li⁺ it is 67.8.

Conclusion
The sorbents obtaining by directional modification of silica from separate of Mutnovskaya geothermal station and zeolites of Yagodninsky deposit of Kamchatka can be used for lithium concentrating from hydromineral materials on basis of laboratory studies.

Acknowledgements
The authors would like to appreciate science officers of RGC FEB RAS for carrying out chemical analyses and I V Maslovskaya for correcting English.

References
[1] Morachevsky Yu V and Tserkovitskaya I A 1980 Principles of analytical chemistry of rare elements. L: LGU 207 p.
[2] Volkova N I, Vladimirov A G, Isupov V P and Moroz Ye N 2012 Lithium salt lakes of the South America and Central Asia Chemistry for sustainable development no 20 pp 21–26.
[3] Kuzmin V I, Pashkov G L, Kuzmina V N, Gudkova N V, Kuzmin D V and Rasputin S N 2010 Estimation of possibilities of extraction salts recovery from chloride-calcium salt brines of the Krasnoyarsk Region Chemistry for sustainable development no 18 pp 321–329.
[4] Manzheres L T, Ryabtsev A D and Mamylova Ye V 2004 Selective sorbent for lithium recovery from chloride highly mineralized salt brines News of Tomsk Polytechnical University V 307 no 7 pp 76–80.
[5] Rozhdestvenskaya L N, Tretyak M A, Palchik A V and Belyakov V N 2013 Lithium recovery from liquid mediums of composition materials based on titanium and manganese dioxides Scientific notes of Tavrida National University called by V I Vernadsky. «Biology, Chemistry» Series V 26 (65) no 4 pp 372–376.
[6] The geothermal power plants can be used for lithium production. [Electronic resource]. URL: http://www.energyland.info/analic SHOW-39114 (Date of reference 28.12.17).
[7] Kimura K, Sakamoto H, Kitazawa S and Shono T 1995 Novel lithium-selective ionofores bearing an easily ionizable moiety Chem. Comm., 4 pp 669–670.
[8] Belova T P 2013 Using sorption methods for purification of waste thermal waters Natural and technical sciences no 6(68) pp 212–216.
[9] Belova T P 2017 Experimental studies in the sorptive extraction of boron and lithium from thermal waters Journal of Volcanology and Seismology Vol 11 no 2 pp 136–142.
[10] Patent. 2323889 RF. MPK С 02, С01В33/12. The method of silica recovery from geothermal heat carrier / Latkin A S, Luzin V Ye, Parshin B Ye, Morgun V M, Basmanov O L and Belova T P Declared 04.07.2006. Published 10.05.2008. Bulletin no 13.
[11] Potapov V V, Zelenkov V N, Gorbach V A, Kashpura V N and Min G M 2006 Colloidal silica recovery from hydrothermal solutions by the method of membranes. M: RANS 228 p.