DOI: 10.31897/PMI.2020.2.197

UDC 66.081.3+544.723.2

Research of lithium sorption by KU-2-8 cation exchanger from model solutions simulating geothermal fluids in the dynamic mode

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The extraction of chemical compounds from hydromineral raw materials is currently a promising objective. The geothermal deposits in the Kamchatka Territory should be considered as possible sources of lithium, boron and other chemical compounds. Their economic efficiency is justified by the complexity of the use of resources of geothermal fluids. The article presents data obtained as a result of experimental studies of lithium sorption by KU-2-8 cation exchanger from model solutions that simulate geothermal fluids in the dynamic mode. It was shown that in the first phase of sorption, ion exchange results in the absorption of lithium and sodium ions by the hydrogen form of cation exchanger up to the degree of cation exchanger saturation by 78 %. After that, the displacement of lithium ions by sodium ions is observed. The intermediate solutions were obtained in which the molar ratio of Li/Na is 80 times higher than in the initial solution. To separate sodium and lithium, it is proposed to use the lithium form of cation exchanger obtained using a portion of lithium chloride concentrate. The separation occurs due to the displacement of lithium ions by sodium ions. The effluent has a molar ratio of Li/Na = 10.4. The regeneration is carried out with 1 n hydrochloric acid, while the concentration coefficient of sodium chloride equals three.

Key words: *integrated use; geothermal fluids; extraction of valuable components; lithium; sorption; ion exchange; exchange capacity*

***How to cite this article*:** Belova T.P., Ratchina T.I. Research of lithium sorption by KU-2-8 cation exchanger from model solutions simulating geothermal fluids in the dynamic mode. Journal of Mining Institute. 2020. Vol. 242, p. 197-201. DOI: 10.31897/PMI.2020.2.197

Introduction. In the Kamchatka region, a promising direction of the mining industry is the extraction of lithium from geothermal resources. Considering geothermal deposits as possible sources of lithium, it should be noted that the extraction of lithium and other rare alkali metals is a by-product in the production of geothermal electricity, and therefore cost-effective due to the complexity of the use of energy and mineral resources [3, 4, 10]. The Research Geotechnological Center of the Far Eastern Branch of the Russian Academy of Sciences is conducting research on the development of technological schemes for the extraction of lithium from geothermal resources [3-5, 8-10]. The extraction of lithium is usually hindered by alkaline earth metals; there is data on the extraction of lithium from brines with high concentrations of magnesium [11, 12] and heavy metals [13]. In [11] the authors described the use of Amberlite IR-120, molecular sieve 13X, aluminosilicate MCM-41, and activated carbon as sorbent agents for the extraction of lithium from solutions. It is noted that under the experimental conditions, the best results were obtained for Amberlite IR-120 and molecular sieve 13X, the sorption capacity for lithium was 20-25 mg/g. To extract lithium from seawater, a synthesized sorbent HMnO was proposed [14], and the maximum achieved sorption capacity was 15.2 and 11.9 mg/g from the model solution and seawater, respectively. The advantage of technogenic solutions of the Pauzhetskaya and Mutnovskaya geothermal stations is the low content of alkaline earth elements, and the disadvantage is the high content of sodium ions and ortho-silicic acid. Silicic acid is removed by electrodialysis [1] or by membrane concentration [2], then lithium is removed by sorption. Sodium ions have a competing effect on lithium sorption. Based on previous studies, it was found that for the concentration of lithium from hydromineral raw materials, sorbents obtained by the targeted modification of silica extracted from the separated liquid of the Mutnovskaya GeoES and zeolites of the Yagodninsky deposit of the Kamchatka Territory can be used [8-10]. As a result of desorption with hydrochloric acid, the proposed scheme makes it possible to increase the concentration of lithium ions, to reduce the molar ratio $(Na^+ + K^+)/Li^+$

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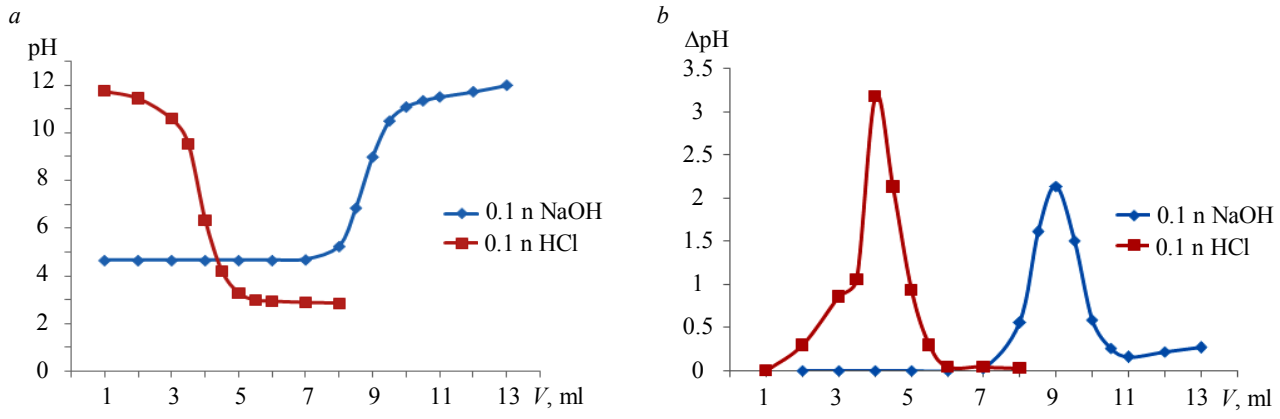


Fig.1. Titration curves of the H-form of KU-2-8 cation exchanger with sodium hydroxide and hydrochloric acid: *a* – integral form; *b* – differential form

but it does not allow the separation of lithium and sodium. The aim of this research is to study the possibility of separation of lithium and sodium using industrial cation exchangers.

Methods and materials. The industrial strongly acidic cation exchanger KU-2-8, which is a copolymer of styrene and divinylbenzene containing sulfo groups bound to the benzene nucleus, was used as a sorbent. To study sorption processes, in the presence of lithium and sodium, we prepared the columns with KU-2-8 cation exchanger in two different forms – two columns in hydrogen and one in lithium form.

Model solutions were prepared by dissolving lithium chloride $LiCl \cdot H_2O$ (p) and sodium chloride NaCl (c.p.) in distilled water. To bring the pH to the desired level, sodium hydroxide NaOH (chemical grade) was used. In total, two model solutions were prepared, differing in the content of lithium and sodium ions by five times, and having the same pH value of 8.5 units, corresponding to the pH value of the technogenic solution.

The solutions with a flow rate of 1 ml/min were passed through columns with a layer height of 200 mm and diameter of 10 mm. We monitored the contents of lithium and sodium ions and solution PH level at the outlet of the columns.

The chemical analysis of the column effluents was carried out by ion chromatography on an LC-20 liquid chromatograph (Shimadzu) using a Shodex IC YK-421 chromatography column (Japan); the eluate was a mixture containing 5 mmol/l of tartaric acid, 1 mmol/l of dipicolinic acid, 24 mmol/l of boric acid, with a conductometric sensor.

Discussion of results. To establish the number of exchange centers of cation exchanger, potentiometric titration with a NaOH solution was carried out. For this, 30 ml of distilled water was added to a sample of the cation exchanger in the hydrogen form. In this case, the pH of the solution was 4.85 units, which corresponds to a concentration of hydrogen ions of $1.4 \cdot 10^{-5}$ mol/l. Taking into account the weight of the resin and the volume of distilled water added, the concentration of exchange centers in the cation exchanger is $8.4 \cdot 10^{-7}$ mol/g. Then the 0.1 n sodium hydroxide solution was added from the burette and the pH values were recorded. Then the 0.1 n hydrochloric acid solution was added to the same system to neutralize the excess amount of sodium hydroxide and convert the cation exchanger to the H-form, the titration curves are shown in Fig.1. The KU-2-8 cation exchanger has a gel structure, the effective grain size of a spherical shape is 0.4-0.55 mm.

The equivalence points are established by the differential form of the curve. It is noted that when titrating with sodium hydroxide at the equivalence point, a value of 1.8 mmol/g was obtained, it corresponds to the sorption capacity of the cation exchanger declared by the manufacturer and equals to 1.9 mmol/g. When titrated with hydrochloric acid, only the excess part of the added sodium hydroxide and some of it located on the surface of spherical granules, are neutralized. Thus, the complete regeneration of the resin KU-2-8 cannot be carried out with the 0.1 n hydrochloric acid solution.

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The sorption of lithium and sodium by various forms of KU-2-8 cation exchanger was carried out from model solutions with the following composition:

Solution number	$C(Li^+)$, mol/l	$C(Na^+)$, mol/l	Ionic strength I, mol/g	Activity factor γ(±)	pH
1	0.00049	0.0347	0.0352	0.838	8.5
2	0.00246	0.174	0.1765	0.736	8.5

The first solution was passed through the first column with the KU-2-8 cation exchanger in the H-form; its composition copies the composition of the technogenic solution of the Pauzhetskaya GeoES:

Components	Content, mg/l	Content, mmol/l
pH,(units, pH)	8.32	
Li	3.10	0.447
K^+	44.0	1.125
Na^+	670	29.143
NH_4^+	1.0	0.055
Ca^{2+}	46.0	2.295
Mg^{2+}	1.22	0.100
Fe (total)	0.30	0.016
Σ cations	763	32.736
Cl^-	1078	30.409
HCO_3^-	12.3	0.202
CO_3^{2-}	0.186	0.006
SO_4^{2-}	76.8	1.599
$H_3SiO_4^-$	7.32	0.077
$H_2BO_3^-$	19.2	0.316
Σ anions	1194	32.608
H_3BO_3	135	2.183
H_4SiO_4 (total)	183	1.924
Mineralization	2248	–

Figure 2 shows the output curves of the sorption of lithium and sodium from model solution 1. The slip of lithium ions in the effluent occurs when the column is filled by 49 %, while 22 column volumes of the model solution pass through the column, the slip of sodium occurs in 6 column volumes, but its content in the effluent remains at the level of 1-2 mg/l up to the filling degree of 67 %. The absorption of lithium ions by cation exchanger was observed at the filling degree of 73 %, then lithium is displaced by sodium. Ion exchange occurs according to the scheme:

$$R - H + \mathrm{Me}^+ \rightarrow R - \mathrm{Me} + H^+,$$

where $R - H$ – cation exchanger KU-2-8 in the H-form; Me^+ – singly charged metal cation; R – Me – metal in the cation exchanger phase.

Solution 2, in which the content of lithium and sodium ions is five times higher than in solution 1, was passed through a second column with KU-2-8 cation exchanger in the H-form; such solutions can be obtained by concentrating the initial technogenic solution, for example, by evaporation [7].

The output curves of sorption dynamics are presented in Fig.3. At the filling degree of 42 %, the lithium concentration reaches its content in the initial model solution, after which it continues to increase due to competitive sorption and

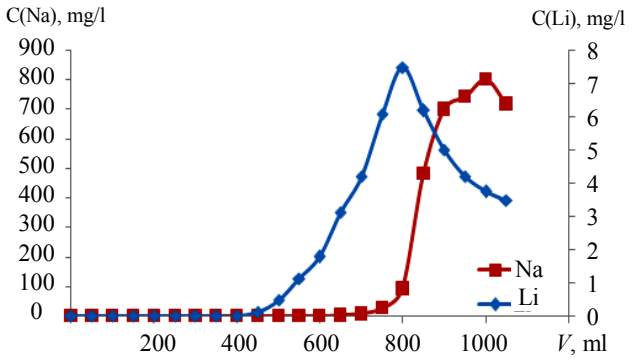


Fig.2. Dynamics of lithium sorption from the model solution 1

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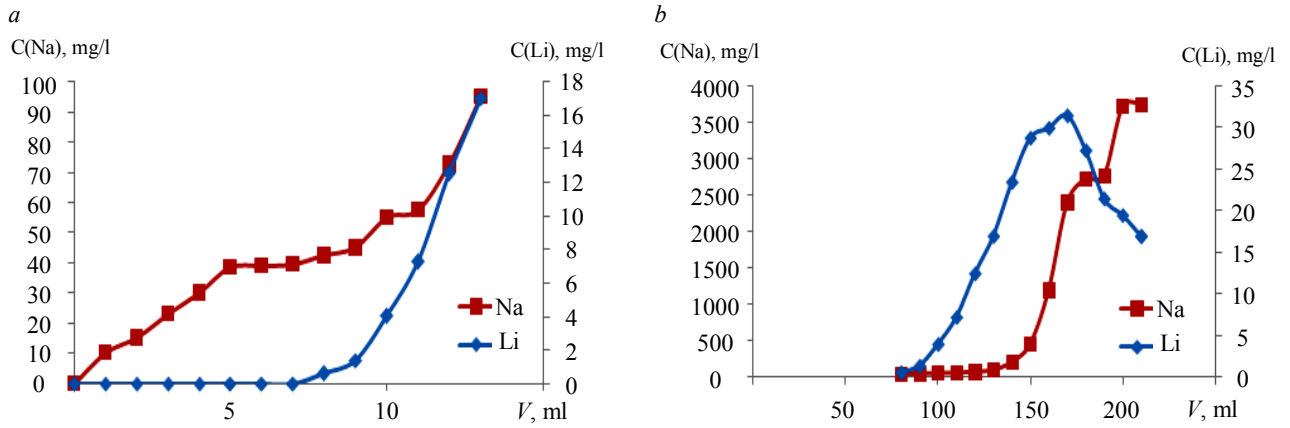


Fig.3. Dynamics of sorption of lithium and sodium from model solution 2 with the hydrogen form of KU-2-8 cation exchanger: *a* – output curves at filling degrees of sorbent from the beginning of sorption to 78 %; *b* – from 42 % to full saturation

displacement by sodium ions. The maximum lithium content in the effluent of 30.2 mg/l is achieved with the filling degree of cation exchange resin of 95.3 %, then it gradually decreases. As a result, 90 ml of the effluent with a molar ratio Li/Na = 1.12 was obtained in the sorption phase, while in the initial model solution this ratio is 0.014. With an increase in the volume of the solution to 100 ml, the molar ratio of Li/Na decreases by 26.3 % and becomes equal to 0.83. In the selected effluent phase, only 30 % of lithium absorbed by cation exchanger is recovered from the column at the sorption stage; nevertheless, the proposed method for processing technogenic solutions can be recommended to increase the molar ratio of alkali metals of lithium to sodium in intermediate solutions.

The column regeneration should be carried out in two stages:

• with a solution of sodium chloride in concentrations greater than or equal to its content in the technogenic solution;

• with a 1 n hydrochloric acid solution to convert the cation exchanger to hydrogen form.

The third column was prepared as follows: first, the cation exchanger was converted to the hydrogen form, then a solution of lithium chloride was passed through it until the concentration of inlet and outlet was equal. In this case, the exchange capacity of the cation exchanger was realized only by 56 %, the capacity of KU-2-8 for lithium from an individual solution was 1.06 mmol/g. When passing through the column of a model solution 2, displacement of lithium ions and hydrogen ions by sodium ions was observed (Fig.4).

The column regeneration should be carried out in three stages: first, the column is washed with a sodium chloride solution to displace the residual amount of lithium ions, then it is converted to the hydrogen form and the lithium form using part of the obtained concentrate in the form of a lithium chloride solution. The proposed processing scheme will increase the molar ratio of Li/Na to 10.4. Thus, the separation of sodium and lithium takes place in the sorption phase. During regeneration, two solutions will be obtained. The first solution is obtained by displacing the residual amount of lithium from the column with sodium chloride, and the second by transferring the cation exchanger from the sodium form to lithium. The first solution must be returned to the technological cycle to reduce the loss of valuable components. In the second solution, the concentration of sodium chloride was noted to be three times higher than the initial one; a crude product of NaCl can be separated from it.

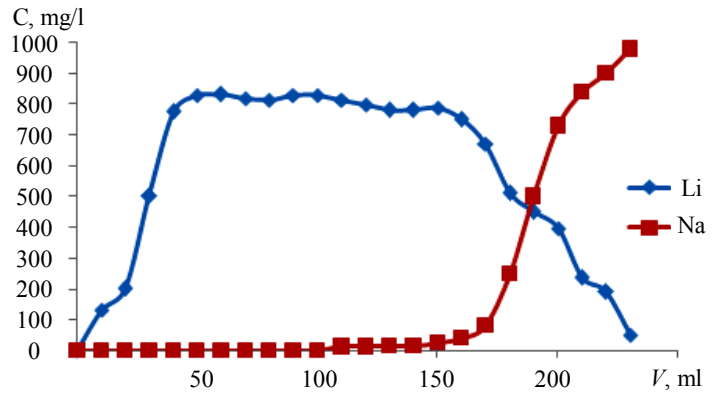


Fig.4. Dynamics of sorption of lithium and sodium from model solution 2 with lithium sorbent

DOI: *10.31897/PMI.2020.2.197*

Conclusion. The industrial cation exchanger KU-2-8 can be used for processing technogenic solutions of geothermal stations for the extraction of lithium and other alkali metals.

During sorption by the hydrogen form of cation exchanger, an increase in the molar ratio of Li/Na by 80 times in comparison with the initial solution occurs already in the sorption phase.

When using the lithium form of the cation exchanger, it is possible to obtain solutions in which the molar ratio of Li/Na equals 10.4.

During the regeneration of the cation exchanger, an increase in the concentration of sodium chloride is at least three times higher than the initial one, which is partially used to displace residual lithium from the sorption column. For the regeneration of the cation exchanger from the hydrogen form to lithium, a part of the obtained concentrate is used in the form of lithium chloride.

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The paper was received on 11 July, 2019.
The paper was accepted for publication on 9 December, 2019.