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Extraction of Uranium from Mineralized Waters of the Shaazgay Nuur Lake (Mongolia)

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Abstract

Processes were studied concerning uranium extraction from the mineralized water of the Shaazgay Nuur Lake using the techniques of galvanochemistry and ion exchange on anionites. The application of galvanochemical method with the use of coal and steel wool as galvanic couple has been demonstrated to allow almost completely extracting the uranium from the mineralized water with the uranium content amounting to about 1 mg/L. A quantitative extraction of uranium from the mineralized water using anion exchangers AM-P, Purolite A-400 and Purolite A-560, has been shown to be possible, both in static and dynamic modes.

Key words: naturally occurring mineral water, uranium, galvanochemical treatment, sorption, anion

INTRODUCTION

The soda type lakes of the northwestern Mongolia, located in the territory of uranium-ore areas contain elevated concentrations of uranium (up to 1–3 mg/L) being of interest as a promising non-conventional uranium source [1]. However, the use of this type of uranium raw materials requires for the development of methods for the extraction of uranium from the lake waters. A number of methods of extracting uranium from naturally occurring and technological alkaline type solutions, such as sorption on iron hydroxo compounds [2] formed in the course of using the galvanochemical method, as well as adsorption on anion exchangers [3, 4].

The matter of the galvanochemical method consists in the fact that the contact between two different conductive materials in a conduc-

tive liquid medium results in appearing a galvanic cell (galvanic couple) due to the difference in the electrode potentials inherent in the materials in the medium. Using a steel-coke (charcoal, graphite) galvanic packing results in the formation of a plenty of iron-carbon galvanic couples. Iron is polarized anodically to pass into the solution, whereas oxygen is reduced at the cathode (carbon) to produce hydroxyl ions with no external power supply. Iron compounds formed in the course of interaction between iron cations and hydroxyl ions adsorb uranium from the solutions under treatment. The sorption on iron compounds is attractive due to a relatively low cost of the reagents and due to the possibility of using waste products (metal shavings, etc.).

Within an oxidative environment in carbonate solution, the uranium exists in the form of

sufficiently stable uranyl ion carbonate complexes $[\text{UO}_2(\text{CO}_3)_3]^{2-}$, that can be recovered from the solution with the use of anion exchange resins. Ion exchange process for extracting the uranium from liquids is sufficiently well developed from technological and instrumental point of view [5].

The purpose of this work consisted in investigating the possibility of using the two modifications of sorption method for the extraction of uranium from the lake water: sorption onto iron hydroxo compounds formed in the course galvanochemical process, and sorption on anion exchangers.

EXPERIMENTAL

In the experiments we used naturally occurring water taken from the Shaazgay Nuur Lake and modelling mineralized water (ordinary and concentrated solutions). Natural water from the lake had the following composition (mg/L): Li 0.87, Na 4170, Ca 8.0, Mg 14.6, Cl 4510, HCO_3^- 2190, CO_3^{2-} 570, SO_4^{2-} 630, Si 4.3, B 10, Br 12, U-238 0.8–0.9; the total salinity being equal to 12 g/L. The ordinary solution as prepared *via* dissolving a calculated amount of reagents in distilled water. The concentrated solution was obtained by means of a ten-fold evaporation of the source (ordinary) solution.

Uranium impurities were simulated by introducing a calculated amount of uranyl ammonium carbonate ($\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$). The uranium concentration was varied within the range of 1–30 mg/L.

For the experiments of galvanochemical treatment of naturally occurring mineralized water we used a laboratory-scale plant with a vertical vibrational galvanic coagulator [6]. In order to prevent the hydrolysis of uranium-containing solutions we performed preliminarily acidifying them. The processing of the solutions was carried out at a temperature of 18–20 °C in the field of galvanic couple Fe (St 3 grade steel)–C (coke), (particle size 5–10 mm, steel/coke mass ratio ~ (3–4) : 1).

The uranium concentration was determined by means of photometric analysis technique using arsenazo III [7]. Control assays were performed using a HACH DR/2010 spectropho-

tometer (the USA). The level of uranium extraction (α) was calculated according to the formula $\alpha = [(C_0 - C_{\text{fin}})/C_0] \cdot 100 \%$ where C_0 is the initial uranium concentration in mg/L; C_{fin} is the concentration of uranium after removal, mg/L.

The composition of galvanic slime precipitate formed in the course of uranium extraction from natural mineralized water was investigated using a Bruker D8 Advance diffractometer within the angular range $2\theta = 5\text{--}70^\circ$ with a copper anode, CuK_α radiation.

In order to perform the experiments concerning the sorption of uranium in a static mode onto ion exchangers AM-P, Purolite A-400, Purolite A-560 we used an AVU-6C shaker. A portion of previously prepared sorbent was placed into a flask with the solution under investigation with a certain S/L ratio. The solution was stirred for 12 h, then the solid and the liquid phases were separated from each other. The liquid phase was analyzed for uranium. For determining the static exchange capacity (SEC) using the solutions based on naturally occurring mineral water additionally introduced with uranium in the form of $\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$.

According to the analysis we calculated the uranium distribution coefficient K_d (in cm^3/g) and the SEC value (in mg/g) using the formulas

$$K_d = \frac{(C_0 - C_t)V}{C_t m}$$

$$\text{SEC} = (C_0 - C_t)V/m$$

where C_t is the concentration of uranium at the moment of t , mg/L; V is the volume of solution, cm^3 ; m is the mass of sorbent, g.

The results of uranium sorption under static conditions were analyzed using a logarithmic Freundlich equation [8]:

$$\log a_e = \log K + (1/n)\log C_e$$

where a_e is the uranyl ion equilibrium adsorption level on the ion exchanger, mol/g; C_e is the equilibrium concentration of the uranyl ions, mol/L; $1/n$ and K are the Freundlich constants.

Experiments concerning the uranium desorption were carried out under stirring a 1 M NaOH or NaCl solution with a weighed sample portion of the sorbent with a known initial weight of uranium, during 24 h at room temperature. Then the solid and the liquid phases were separated from each other to determine the concentration of uranium in the desorbate.

The experiments concerning the kinetics of uranium sorption in a static mode were performed with the use of uranium-containing naturally occurring mineralized water and AM-P, Purolite A-400 and Purolite A-560 anion exchangers at a room temperature ($T = 20\text{ }^{\circ}\text{C}$). A portion of the previously prepared air-dry anionite (1.0 g) was placed into a flask with 500 mL of the solution. Then, at regular time intervals, we performed sampling and analyzing the solutions. The exchange level was calculated according to formula

$$F = (C_0 - C_t)/(C_0 - C_{\infty})$$

where C_{∞} is the mass fraction of uranium in the equilibrium solution, mg/L.

The experiments on the dynamic sorption of uranium were performed using a Purolite A-560 anionite. The investigations were carried out with the use of a glass column with an internal cross-section area equal to 1.15 cm^2 , the packing layer height being of 3.3 cm; the volume of the ion exchanger packing amounting to 3 mL (2.2 g). The anion exchange resin was pretreated with 200 mL of 1 M NaCl solution, to be washed then with 100 mL of distilled water at a linear flow velocity of 3–4 m/h. Ion exchange was studied by means of a dynamic method with monitoring the uranium concentration at the outlet of the ion exchanger. The flow rate of natural mineralized water through the column was equal to 0.5 L/h, the linear velocity of the solution being of 4.3 m/h, pH 9.68, temperature $20\text{ }^{\circ}\text{C}$. Sampling for uranium was performed for every 0.5 L flow through the column.

RESULTS AND DISCUSSION

Extraction of uranium using a galvanochemical method

In the course of experiments on the galvanochemical purification we maintained the following parameters. For ordinary solution: the acidity of the initial solution was adjusted to pH 3.0, water flow rate $Q_{\text{sln}} = 2.0\text{--}3.0\text{ L/h}$, airflow rate $Q_{\text{air}} = 2.0\text{ L/min}$. For concentrated solution: the acidity of the initial solution was adjusted to pH 3.3, $Q_{\text{sln}} = 2.0\text{--}3.0\text{ L/h}$, $Q_{\text{air}} = 2.0\text{ L/min}$. The vibration frequency of the galvanic packing was equal to 40 Hz. In the course of the galvanochemical treatment of the

TABLE 1

Galvanochemical processing of model solutions

Ordinary solution				Concentrated solution			
pH	C_0	C_{fin}	$\alpha, \%$	pH	C_0	C_{fin}	$\alpha, \%$
7.2	1.25	1.17	6.4	7.34	11.0	1.00	90.9
8.2	1.25	1.125	10.0	8.2	11.0	1.00	90.9
9.0	1.25	0.625	50.0	9.1	11.0	0.50	95.5
9.6	1.25	0.485	61.2	9.5	11.0	0.01	99.9
10.4	1.25	0.37	70.4	10.0	11.0	0	100.0
11.0	1.25	0	100.0	11.0	11.0	0	100.0

ordinary processing solution changed the acidity changed from pH 3.0 to pH 6.79, whereas the acidity of the concentrated solution changed from pH 3.3 to pH 7.34. The resulting solutions were basified by means of adding $\text{Ca}(\text{OH})_2$ to obtain pH value ranging within 7.3–11.0, in order to separate galvanic slime precipitate. The results of processing the solutions are presented in Table 1.

It can be seen that increasing the pH level of the solution results in increasing the level of uranium extraction from the solution. At high solution pH values, the uranium can be recovered almost completely.

In the course of the experiments on the galvanochemical processing of real natural mineralized water, the process parameters were as it follows: $\text{pH}_{\text{ini}} = 3.71$, $Q_{\text{sln}} = 2.0\text{--}3.0\text{ L/h}$, $Q_{\text{air}} = 2.0\text{ L/min}$, the galvanic packing vibration frequency being equal to 30 Hz. In the course of galvanochemical processing the real naturally occurring mineralized water, the pH value changed within the range from pH 3.71 to 6.16. The resulting solutions were alkalified via the addition of $\text{Ca}(\text{OH})_2$ to obtain pH value ranging within 9.0–11.0. It was found out that at pH value ranging within 6.16–11.04 and $C_0 = 0.83\text{ mg/L}$ the uranium extraction level amounted to 100 %. Thus, under comparable experimental conditions, the processing of real natural mineralized water exhibits a higher level of uranium extraction as compared to the model solutions. In order to explain the differences between the real natural water and model solutions one needs further investigation.

The resulting precipitate of galvanic slime, according to XRD, represents a multiphase

TABLE 2

Uranium sorption from natural mineralized water on anion exchangers with adjusted uranium content

Parameters	Initial uranium content C_0 , mg/L				
	5.0	10.0	18.0	23.0	30.0
	<i>AM-P</i>				
C_{fin} , mg/L	0.375	1.25	3.5	4.5	7.0
K_d , cm ³ /g	6166	3500	2071	2055	1642
SEC, mg/g	2.31	4.375	7.25	9.25	11.5
	<i>Purolite A-400</i>				
C_{fin} , mg/L	0.62	1.25	3.0	4.37	6.5
K_d , cm ³ /g	3532	3500	2500	2131	1807
SEC, mg/g	2.19	4.375	7.5	9.315	11.75
	<i>Purolite A-560</i>				
C_{fin} , mg/L	0.375	1.37	2.25	3.25	4.5
K_d , cm ³ /g	6166	3149	3500	3041	2833
SEC, mg/g	2.31	4.315	7.875	9.875	12.75

substance that includes lepidocrocite (γ -FeOOH), goethite (α -FeOOH) and magnetite (Fe_3O_4). The precipitate contains 30–50 g/t uranium thus, it could be sent for processing in order to extract the uranium. An efficient reagent for the leaching of uranium from galvanic slime is presented by a saturated solution of ammonium carbonate that provides the level of uranium leaching up to 98 % at an insignificant content of iron impurities in the solution [9].

Uranium extraction using anion exchangers

Uranium sorption-desorption in static mode. Results concerning the sorption of ura-

TABLE 3

Parameters of uranium sorption from natural mineralized water on anion exchangers (according to the Freundlich equation)

Ionites	K	$1/n$
AM-P	0.0195	0.547
Purolite A-400	0.10	0.699
Purolite A-560	0.125	0.699

nium from the solutions with different uranium content those were prepared from naturally occurring mineral water with the use of AM-P, Purolite A-400 and Purolite A-560 anion exchangers at 20 °C and pH 9.68 ($S/L = 1 : 500$) under static conditions, as well as the results of K_d and SEC calculation are presented in Table 2. The experimental data are satisfactorily described by the Freundlich isotherm model; the values of Freundlich constants (K and $1/n$) are presented in Table 3. The samples of anion exchangers saturated with uranium obtained in the course of the sorption experiments were used in order to determine the possibility of uranium desorption under static conditions. The conditions uranium desorption and the results obtained are presented in Table 4. It can be seen that the two-stage regeneration from AM-P, Purolite A-400 and Purolite A-560 anion exchangers provides the uranium desorption level ranging within 70–86 %. Uranium concentration values obtained at the first stage of desorption equal to 42–60 mg/L are comparable with those obtained *via* the extraction by means of underground leaching method.

TABLE 4

Desorption of uranium from anion exchange resins under static conditions. Resin mass 1.0 g, regenerating solution volume 100 mL

Anionites	Trapped, mg	Residue, mg*	Regenerating solution	C_{fin} , mg/L**	Desorbed uranium, mg	Desorption level, %	
						Stage	Total
<i>Stage I</i>							
AM-P	6.2675	–	1 M NaOH	42.25	4.225	67.4	–
Purolite A-400	7.026	–	1 M NaCl	60.0	6.0	85.4	–
Purolite A-560	7.4255	–	1 M NaCl	52.0	5.2	70.0	–
<i>Stage II</i>							
AM-P	–	2.0425	1 M NaOH	1.37	0.137	6.7	69.6
Purolite A-400	–	1.026	1 M NaCl	0.75	0.075	7.3	86.5
Purolite A-560	–	2.2255	1 M NaCl	1.0	0.1	4.5	71.4

* After stage I of sorption.

** C_{fin} is the concentration of uranium in desorbate.

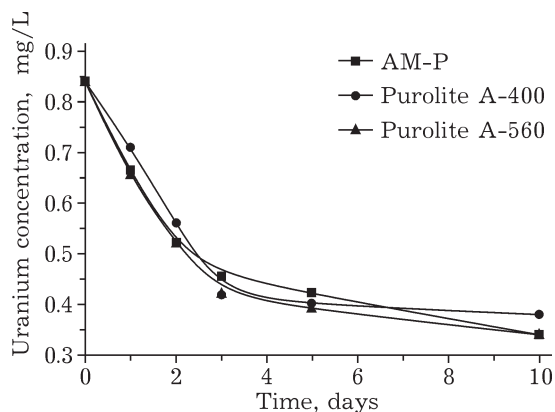


Fig. 1. Kinetics of uranium sorption from uranium-containing natural mineral water on anion exchangers.

Kinetics of uranium sorption in a static mode. The results of experiments concerning the kinetics of uranium sorption onto anion exchangers in a static mode and the calculation of the uranium exchange level depending on time are presented in Figs. 1 and 2. Basing on the data obtained one could conclude that the exchange half-time periods ($\tau_{1/2}$) for different anion-exchange resins are comparable to be equal to 36 h for AM-P, 40 h for Purolite A-400, 35 h for Purolite A-560. Thus, the minimum exchange half time is observed for Purolite A-560 anion exchanger which we further used for the experiments on the sorption of uranium in a dynamic mode.

Uranium sorption-desorption dynamics on Purolite A-560 anion exchanger. The output curve for uranium concentration depending on the amount of the solution flow through the

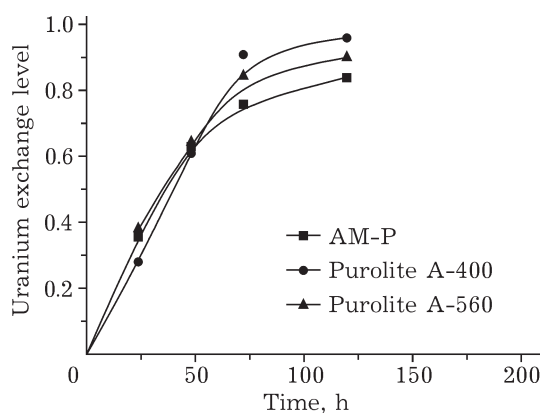


Fig. 2. Uranium exchange level depending on time in the course of sorption from natural mineralized water.

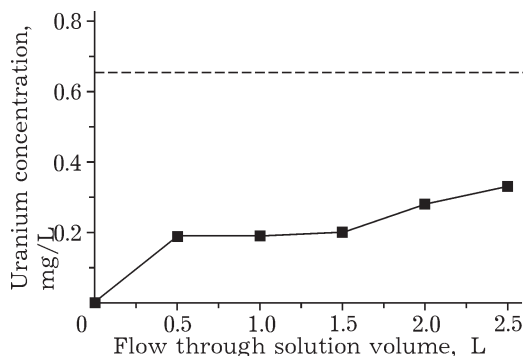


Fig. 3. Output curve for the sorption of uranium from natural mineralized water onto Purolite A-560 anion exchanger. The uranium content in the source water being equal to 0.65 mg/L.

sorbent is demonstrated in Fig. 3. Basing on the data obtained we calculated the dynamic exchange capacity (DEC) values those characterize the maximum mass of the ions retained within 1 g of the ion exchanger in the flow through mode for natural mineral water inherent in the Purolite A-560 anion exchanger. In the case of pH 9.68 and the initial uranium content equal to 1.625 mg, the content of uranium in the purified solution amounted to 0.625 mg. Thus, the anion exchanger has captured 1 mg of uranium (61.5%), the DEC value reached before a breakthrough amounting to 0.148 mg/g of the anion exchanger.

After feeding the column with 2.5 L (833.5 column volumes) of uranium-containing naturally occurring mineralized water we performed the desorption (regeneration) of uranium from the column packed with a Purolite A-560 anion exchange resin 3 mL in volume *via* the following procedure:

- washing with 100 mL of distilled water;
- desorbing the uranium with 50 mL of 1 M NaCl solution;
- finish washing with 100 mL of distilled water.

The regeneration solutions obtained were mixed to analyze for uranium. The concentration of uranium in the solution was equal to 3 mg/L.

Thus, in the course of the experiment there was 1.0 mg of uranium sorbed, whereas the amount of desorbed uranium was equal to 0.75 mg, so the desorption level $\alpha = 75.0\%$. Repeatedly washing the column with 50 mL of 1 M NaCl solution allowed us to increase the desorption level of up to 93 %.

CONCLUSION

The study performed indicates the application galvanochemical method to be promising for the extraction of uranium from solutions those simulate naturally occurring uranium containing lake water and naturally occurring uranium-containing waters. The influence of the main process parameters upon the parameters of galvanochemical purification (galvanic couple Fe (Steel 3)/C (graphite)) was investigated for model and real natural mineral waters. It has been found that at $Q_{\text{air}} = 2.0\text{--}3.0$ L/min, $T = 18\text{--}20$ °C, the acidity of the initial solution corresponding to pH 3.0–3.3, the vibration frequency of electrode unit equal to 30–40 Hz and alkalizing the solution up to pH 9.0–9.5 the efficiency of galvanochemical purification from uranium impurities reaches almost 100 %. The precipitate formed in the course of the galvanochemical extraction of uranium represents a multiphase substance and consists of iron oxide-hydroxides. The desorption of uranium can be carried out using ammonium carbonate.

The experiments performed indicate the possibility of using the sorption on anion exchangers AM-P, Purolite A-400, Purolite A-560 in

the static and dynamic modes for the quantitative extraction of uranium from the lake waters. In order to reveal the optimum conditions for extraction of uranium using anion exchangers it is required to carry out additional investigations.

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