



APPLICATION OF THE ADSORPTION PROCESS FOR GEOTHERMAL WATER PROCESSING

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Abstract. The article considers methods of lithium extraction from geothermal water. The authors present a technological scheme for obtaining lithium products from highly mineralized brines and calculate the quantities of the products obtained. The authors have developed a new design of an adsorber for the absorption of lithium ions by aluminium hydroxide. Also we have calculated the necessary flow rate of geothermal water passing through the adsorber.

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Introduction

The specific physical and chemical properties of lithium have led to its wide application in the automotive industry for the production of batteries, ferrous and non-ferrous metallurgy for deoxidizing and changing the physical and chemical properties of alloys, and nuclear and nuclear power generation for the production of tritium, etc. According to expert forecasts, the global consumption of lithium will increase to 200000 t/year by 2025 [1].

The main sources of lithium extraction are the complex rare-metal granite pegmatite deposits and the surface and inter-grain rupa of salt deposits and lakes. Today, lithium is usually extracted from the ground by the process requiring large quantities of water or from salt water dried in large salt evaporation pools [2].

There is a need to develop methods for extracting lithium from hydromineral raw materials due to the rapid growth of the lithium economy and the current lack of extraction of lithium compounds in the Russian Federation.



Main body

The production of lithium from geothermal waters is highly promising nowadays. Meanwhile, 78% of natural lithium reserves are concentrated in geothermal waters [1]. These reserves, due to their characteristic physical and chemical properties, are widely used in various industries in Russia and abroad, including the strategic ones.

ZAO "ECOSTAR NAUTECH", Novosibirsk, Russia has developed technology and equipment allow ones to receive lithium after desorption it from sorbent a solution of lithium chloride with impurities Mg, Ca, and perform processing on demanded compounds of lithium: chloride, hydroxide, carbonate, bromide, fluoride, etc. It essentially reduces cost price of commodity products due to complex use of the specified raw materials with extraction of bromine, magnesium, calcium, and other valuable components [3].

Geothermal waters mined on the territory of Yaroslavl region have a low thermal energy potential and are currently used as an anti-icing agent. The analysis of Mediaginskaya well composition shows the presence of valuable chemical elements and compounds and, as a result, the task of thermal waters complex processing is relevant one. Based on the mass fraction and well capacity, promising chemical compounds with respect to possible industrial processing are sodium, calcium, magnesium, potassium chlorides, potassium bromide, potassium iodide, reactive bromine, and iodine.

The most valuable compound in the geothermal waters of the Medjaginskaya well is lithium chloride.

Adsorption using alumina-containing materials (including active aluminium hydroxide) as sorbents is an effective way to extract lithium from aqueous solutions. The phenomenon of adsorption is related to the existence of attraction forces between the molecules of the adsorbent and the molecules of the absorbed substance. A complex consideration of the equilibrium regularities makes it possible to identify the optimum conditions for the process.

Adsorption in a fixed adsorbent layer is a continuous process, and the concentration of the absorbed substance varies in time and space. We assume that a liquid of quantity G passing through a layer of height dH changes its concentration by dY (Fig. 1).

The liquid releases the absorbed component (a.c.) over the time: $d\tau$: $-Gd\bar{Y}d\tau$.

Over time $d\tau$ the concentration in the extracted element will increase by: $d\bar{X}$: $S_{an}dH\rho_Hd\bar{X}$.

The combined solution of these equations gives the material balance equation for the periodic adsorption process: $-Gd\bar{Y}d\tau = S_{an}dH\rho_Hd\bar{X}$.

The latter equation is used to determine the change in the relative mass concentration of the absorbed component in the liquid phase $d\bar{Y}$.

Depending on the speed of the liquid mixture, the shape of the adsorption isotherm, the size, shape and packing of the adsorbent grains, the adsorbent concentration as well as other

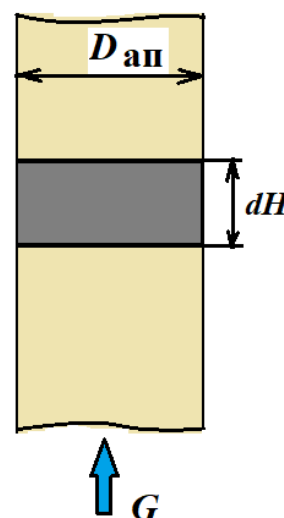


Fig. 1. On deriving a material balance equation for a periodic adsorption process



conditions of the process in the fixed adsorbent bed, the external mass transfer rate (characterized by the value β_{yV}) or the internal mass transfer rate β_{xV} may have a decisive influence on the overall adsorption rate. The influence of the external and internal diffusion resistances on the K_{yV} value is very often comparable, with their relative influence varying along the length of the mass transfer zone.

The adsorption of lithium by active aluminium hydroxide has been studied for a long time. Indeed, the researches results do not coincide and in some cases they contradict each other.

The concentration of LiCl in the geothermal water extracted from the Medjaginskaya well is 0.059 kg/m^3 . The capacity of this well is $5 \text{ m}^3/\text{h}$ of water. For more efficient extraction of lithium ions from geothermal water it is necessary to increase the concentration of LiCl by 7-10 times. After preliminary removal of part of the solvent (water) in the evaporator we increase the concentration to 0.5 g/l [4-6]. This requires evaporation of $4.41 \text{ m}^3/\text{h}$ of water. The flow rate of concentrated geothermal water through the adsorber will then be $0.59 \text{ m}^3/\text{h}$.

The following stages were identified in the development of the technology for processing geothermal water extracted in the Yaroslavl region: obtaining the concentrate by evaporating part of the solvent, adsorption of lithium ions by active aluminium hydroxide, obtaining other valuable products using the spinning, roasting and drying processes.

Figure 2 shows a technological scheme for obtaining different types of products from geothermal water [2].

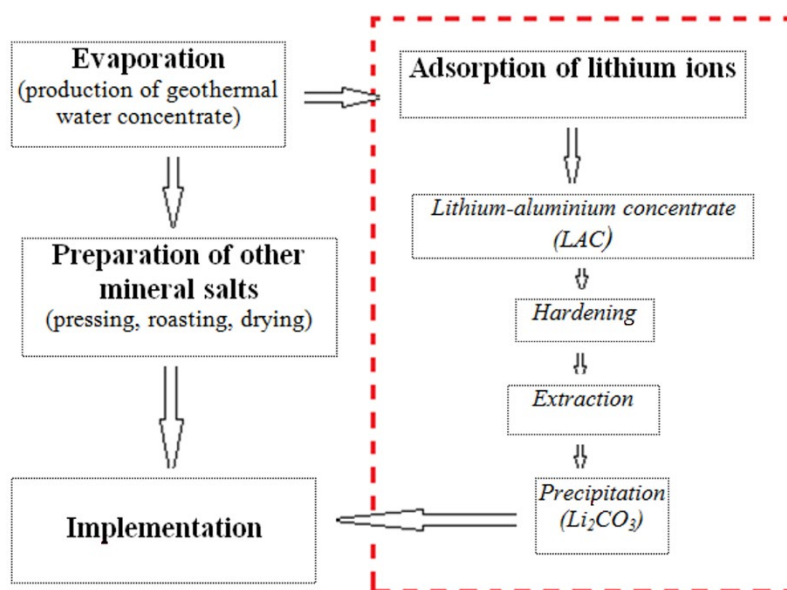


Fig. 2. Technological scheme for geothermal water processing

To increase the efficiency of adsorption process, a new design of adsorber for extraction of lithium ions from geothermal water was developed at the Department of Chemical Technology of Organic Substances at Yaroslavl State Technical University, Yaroslavl, Russia (Fig. 3) [7]. The apparatus of the proposed design can be used for capturing valuable and harmful substances or ions from liquid homogeneous systems in petrochemical, chemical, machine building, paint, varnish, and other industries.



Adsorption takes place on a fixed layer of granular adsorbent with active aluminium hydroxide, which is located as a "stationary" layer inside the apparatus. Due to the large surface area per unit volume of the adsorbent, this method of lithium ion extraction is effective.

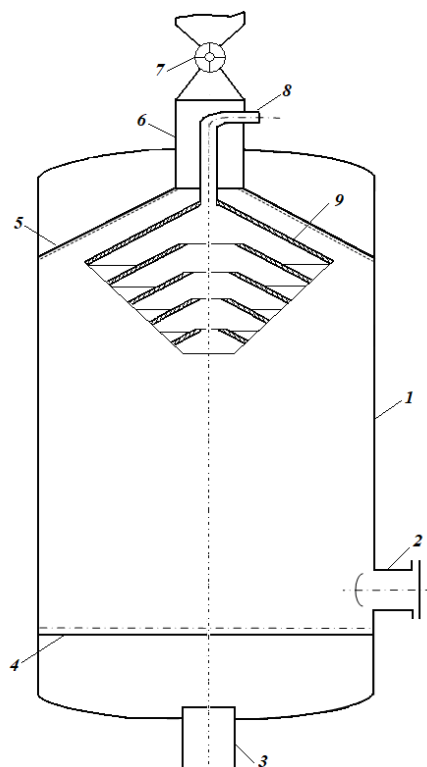


Fig. 3. High efficiency adsorber with cascade shock-jet nozzle: 1 - housing; 2 - door for saturated adsorbent discharge; 3 - outlet pipe for liquid discharge; 4 - bottom lattice; 5 - top lattice made as a truncated cone; 6 - top pipe; 7 - hermetic shutter 8 - geothermal water inlet pipe; 9 - cascade shock-jet nozzle

The homogeneous liquid flows through nozzle 8 into the cascade jet spray nozzle 9, which has a large number of holes for the liquid to escape. By passing through these nozzles, the liquid separates into droplets to form a polydisperse plume and is evenly distributed throughout the volume of the adsorbent. The extracted component is absorbed by the adsorbent and the processed liquid flows through the bottom grid 4. Then it flows out through the outlet nozzle 3. To prevent the processed liquid from escaping through nozzle 6, a sealed shutter 7 is installed on it. Once the adsorbent is saturated with the extracted (target) component, it is discharged through door 2 and enters for further processing (desorption).

The technical result of the proposed design is to solve the challenges associated with increasing the degree of the target component absorption by reducing stagnant zones in the apparatus. This is achieved by installing a cascade shock-jet nozzle in the adsorber at the top of the liquid spraying device.

Based on theoretical and experimental data from the previous researches, we calculated the developed adsorption apparatus [5]. Adsorber dimensions are: height $H_0 = 200$ mm, $D = 150$ mm. The adsorbent is aluminium hydroxide.

An adsorption isotherm for the system Li^+ - water - $\text{Al}(\text{OH})_3$, the equilibrium concentration dependence of the extracted component on the adsorbed substance concentration in the mixture at constant temperature was constructed according to the researches [9] and is shown in Fig. 3.

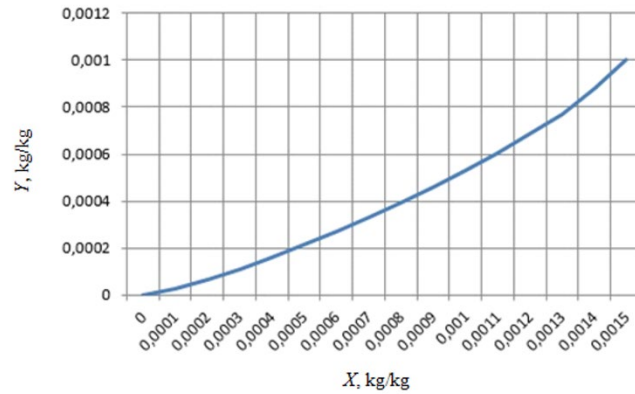


Fig. 3. The equilibrium concentration dependence of the extracted component on the adsorbed substance concentration in the mixture at constant temperature (adsorption isotherm for the system Li^+ - water - $\text{Al}(\text{OH})_3$)

The concentration of the substance to be adsorbed in the mixture depends on pressure and temperature. It is decreasing as the temperature increases and increasing as the pressure increases. The main characteristic of an adsorbent activity, which is measured by the weight of the substance absorbed as a percentage of the adsorbent weight or volume.

We calculated the adsorption time for the developed vertical adsorber.

Mass flow rate of water is: $G_{\text{H}_2\text{O}} = \rho \cdot V_{\text{H}_2\text{O}}$,

According to the adsorption isotherm (see Fig. 1) at $Y_1 = 0.0005 \text{ kg/kg}$ the equilibrium concentration of LiCl in aluminium hydroxide is $X^* = 0.00096 \text{ kg (LiCl)/kg (adsorbent)}$. We take the saturation concentration in the initial cross section of the layer as $X_n = 0.98 \cdot X^* = 0.00094 \text{ kg (LiCl)/kg (adsorbent)}$.

The duration of saturation of a 1 m high adsorbent layer is calculated according to the equation:

$$k = \frac{S \cdot \rho_H \cdot X_H}{G_{\text{H}_2\text{O}} \cdot Y_1}$$

The saturation time of the initial cross-section of the layer (s) is:

$$\tau_0 = \frac{\rho_H}{\beta_{ob} \cdot f} \int_0^{X_H} \frac{dX}{Y_1 - Y_1^*}$$

where β_{vol} is a volumetric mass transfer coefficient of lithium ions in water, $\frac{\text{kg}}{\text{m}^2} \cdot \text{s} \cdot \frac{\text{kg}}{\text{kg}}$.

To determine the mass transfer coefficient of lithium ions in water, the molecular diffusion coefficient of the adsorbent in the liquid at the process temperature (lithium ions in water) is calculated using the equation [9]:

$$D_\Gamma = \frac{1 \cdot 10^{-6}}{A \cdot B \cdot \sqrt{\mu} \cdot (V_A^{1/3} + V_B^{1/3})^2} \cdot \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

where A and B are correction factors: for water $B=4.7$; for lithium $A=1$;

V_A, V_B – specific molar volumes of components, cm^3/mol

$M_A; M_B$ are the molar masses for water and for lithium respectively.

The molecular diffusion coefficient is used to characterize the transport of lithium ions in water.

The direct calculation of the mass transfer coefficient for lithium ions in water is conducted in accordance with the criterion equation (for turbulent mode of motion - $\text{Re} > 10000$):

$$\text{Nu}_r = 0.53 \cdot \text{Re}^{0.54} \cdot \text{Pr}^{0.2}$$

where Pr is the Prantle (diffusion) criterion: $\text{Pr} = \frac{\nu}{D_\Gamma}$;



Re is the Reynolds criterion: $Re = \frac{W \cdot d_{ekv}}{\mu_{sm}}$,

W is the mass flow rate: determined by the ratio of the mass flow rate of the medium to the porosity of the adsorbent layer $W = \frac{Q \cdot \rho_{sm}}{\varepsilon}$,

d_{ekv} is the equivalent diameter (characteristic linear dimension): $d_{ekv} = \frac{4 \cdot \varepsilon}{f}$, f is the specific surface area of the adsorbent, m^2/m^3 .

The mass transfer coefficient is determined using equation [9,10] $\beta_{o6} = \frac{Nu_r \cdot D_r}{d_{ekv}}$.

The height of the absorber layer equivalent to one unit of transfer is: $h = \frac{G_{H_2O}}{\beta \cdot f \cdot S}$.

We calculate the height H of the adsorbent layer: $H = n \cdot h$, n is the number of transfer units (determined graphically using the equilibrium line (Fig. 1) and the working concentration line). The concentration difference determines the driving force of the process.

The duration of the adsorption process is: $\tau = \tau_0 + k \cdot (H - H_0)$.

The adsorption process is stopped when the concentration of lithium ions at the apparatus outlet reaches a predetermined overshoot value.

Using the initial data for the calculation, we get the following results:

$k = 121,5405 \text{ s/m}$; $\beta_{vol.} = 0,00149$; $\tau_0 = 1805 \text{ s}$; $H = 47,3385 \text{ m}$; $\tau = 7534 \text{ s} \approx 2 \text{ h}$.

The adsorption process produces a lithium-aluminium concentrate (LAC), which is the raw material for the production of pure lithium or lithium products.

Conclusions

Hence, we constructed an adsorption isotherm for the system Li^+ - water - $Al(OH)_3$ in the absence of equilibrium data using the affinity coefficient. This coefficient was defined as the ratio of adsorption potentials at equal values of adsorption volume for two different adsorbates on the adsorbent - aluminium hydroxide. Also we developed new design of high-efficiency adsorber, determined the equilibrium concentration, calculated the main indicator of the process - adsorption time, as well as the main design dimensions - diameter and height of the unit. The calculation was made on the basis of capacity and composition of Medyaginskaya well, Yaroslavl region, Russia.

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