# МЕЖДИСЦИПЛИНАРНЫЕ ИССЛЕДОВАНИЯ

# INTERDISCIPLINARY RESEARCH

# CALCULATION OF ION EXCHANGE COLUMN FOR PURIFYING OF LITHIUM HYDROXIDE SOLUTION FROM CHLORINE ANIONS

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*In the article possibility of water solution LiOH tertiary treatment from chlorine anions after electrolysis is viewed. Analyzing the existing purification methods, it is proposed to use the purification of lithium hydroxide in an ion exchange column. A mathematical model and a computational algorithm for ion exchange column having stationary and moving anionite layers AB-17-08 in OH-form are given. Relationships of the main parameters such as working cycle period, usage ratio of ionite exchange volume and specific ratio of solution being purified per 1 kg ionite for standard column have been received. The curves of the chlorine anions density in ionite depending on its layer height in the solution being purified in the middle and at the end of the working cycle period are given. In the article recommendations on prevention of ionite granules abrasion during the operation in ion exchange columns are given.*

***Keywords:*** *anionite in OH-form; lithium hydroxide solution; ion exchange; Langmuir equation; mass transfer; mass exchange; working cycle period*

# РАСЧЕТ ИОНООБМЕННОЙ КОЛОННЫ ДЛЯ ОЧИСТКИ РАСТВОРА ГИДРОКСИДА ЛИТИЯ ОТ АНИОНОВ ХЛОРА

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*Рассмотрена возможность доочистки водного раствора LiOH от анионов хлора после электролиза. При анализе существующих методов очистки предложено использовать очистку гидроксида лития в ионообменной колонне. Составлена математическая модель и алгоритм расчета ионообменной колонны с неподвижным и движущимся слоем анионита АВ-17-08 в ОН-форме. Получены зависимости основных параметров: времени рабочего цикла, степени использования обменной емкости ионита и удельного объема очищаемого раствора на 1кг ионита для стандартной колонны. Получены и проанализированы графики зависимости концентрации анионов хлора в ионите от высоты его слоя в очищаемом растворе в середине и в конце времени рабочего цикла. Даются рекомендации по предотвращению истирания гранул ионита во время эксплуатации ионообменных колонн.*

*Ключевые слова:* анионит в ОН-форме; раствор LiOH; ионообмен, уравнение Ленгмюра; массоотдача и массопередача, рабочее время цикла

**Introduction**

Being a polymerization catalyst, lithium hydroxide is used in the production of batteries and in pharmacology for the synthesis of various lithium salts, which are used to treat animals and humans. Lithium hydroxide is used as a carbon dioxide absorber. The results of direct measurements confirming the greenhouse effect increasing caused by the concentration of carbon dioxide rise in the atmosphere are known [16]. The largest sources of emissions of greenhouse gas are agriculture, various production, transportation, processing and consumption of fossil fuels, burning of biomass, etc. The absorption of carbon dioxide and its further use is necessary to preserve the natural balance [20].

A lot of works are devoted to the problems of lithium hydroxide purification and regeneration. Authors of a number of articles [15, 18, 19] consider the problem of LiOH production through electrodialysis from its natural brine. Energy consumption of electrodialyzer is rather high and current consumption in the purification process of lithium hydroxide solution requires special operation safety rules. Current provides water electrolysis. Oxygen is emitted on the anode and hydrogen is emitted on the cathode. The process is of special fire and explosion hazards. Danger of emergencies and accidents, explosions and fires is high, they can occur in case of a technological condition violation, in case of electrolytic gas leakages, especially hydrogen and oxygen being mixed in explosive proportions inside units of equipment.

Ion exchange membranes used in electrodialysis have high current resistance. Membrances, containing ionite powder heterogeneous with surface impurity, need cleaning. Moreover the membrane cleaning is rather complicated and expensive process. It needs additional expenditure. Homogenous membranes have low mechanical strength [8]. Membranes selectivity falls because of their sensitivity to abrasive materials. When ion exchange membrane is used, a concentrated polarization takes place near its active layer. It makes membrane selectivity lower too. Field of application of ion exchange membranes is limited and application of nanotechnologies is predicted to enforce the strength of the membranes [6]. To prevent pollution of membranes LiOH solution should be purified from weighted and colloidal particles. In this connection electrodialysis is used in low capacity industries.

Scientists are seeking new technologies for lithium extraction from brines [17]. In our opinion it is necessary to pay more attention to the purification of the LiOH solution in ion exchange columns. Ion exchange columns have high productivity. LiOH purification in ion exchange columns doesn't need additional expenditure for previous clearing of solution and current.

According to the organizational and technical structure, ion exchange columns of continuous and periodic action are used in industry. The calculation methods of the columns are anologous to the calculation methods of other mass transfer devices [11-14].

An industrial method for obtaining an aqueous solution of sodium hydroxide by electrolysis of a solution of table salt is widely used and it becomes necessary to refine the obtained hydroxides from chlorine anions [9, 10].

Producing lithium hydroxide from LiCl solution by means of electrolytic method results in obtaining substance which contains up to *2,5 kg/m³* of chlorine anions. The chlorine anions concentration is to be reduced to *0,078 kg/m³*

that is 32 times less in accordance with regulations. In this case level of tertiary treatment is to be around 97%.

## Purpose

Aim of this work is modeling and calculation for ion exchange column both periodic and uninterrupted actions intended for purification lithium hydroxide water solution from chlorine anions.

## Calculation methods for ion exchange column

It is appropriate to use anionite granules AB-17-08 in OH – form for the both ion exchange columns of the uninterrupted and periodic action. In this case exchange reaction takes place [7, 8]

$$ROH^+ + Cl^- \rightarrow RCl^+ + OH^-,$$
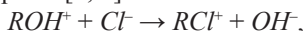
and ions of chlorine are removed from the solution. Then they are substituted with ions OH‑produced through electrolysis. Thus ions of chlorine are not just removed from the solution but ions of OH are inserted instead of them. It slightly contributes to the electrolysis substance LiOH in desired solution.

In the article algorithm for calculation of ion exchange column with stationary anionite layer is used, which we've described for cation and anion columns in a number of works [3, 5, 6]. The physical picture of the change in its concentration is given on the Fig. 1.
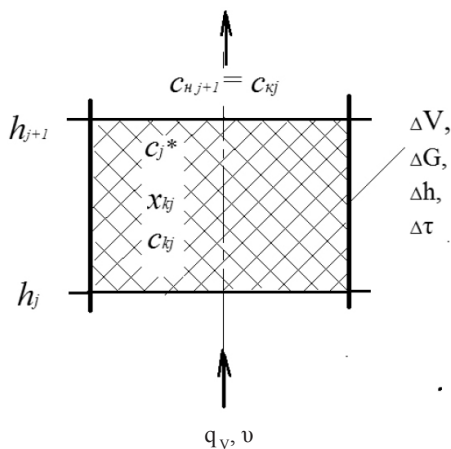


**Fig. 1.** Diagram of changes in ions of chlorine concentration at the moment $\tau_i$ in $j$-m ionite layer at height $\Delta h$ and time $\Delta\tau$, for which solution passes through the ionite layer in the column of periodic action.

Algorithm for calculating an ion exchange column with a stationary anion-ite layer.

1. Equation of equilibration line (signs for parameters and their size are given in Table 1 [7]:

$$x^* = \frac{ac}{1 + bc},\tag{1}$$

under the conditions $a = \dfrac{\kappa_p x_0}{c_{_н}}$, $b = \dfrac{\kappa_p - 1}{c_{_н}}$ и $x_0 = x_{_н}^*$.

2. Sherwood number of the outer mass transfer for the solution is viewed as a function of defining Reynolds and Schmidt criteria:

$$Sh = 2 + 1{,}5(Sc)^{\frac{1}{3}}\sqrt{(1 - \varepsilon_0)}\,\mathrm{Re}.\tag{2}$$

3. Surface coefficient of outer mass transfer

$$\beta_c = \frac{Sh \cdot D_c}{d_э},\tag{3}$$

and volume coefficient of mass exchange

$$k_V = \frac{6\beta_c(1 - \varepsilon_0)}{d_э}.\tag{4}$$

4. Dividing the whole ionite layer $n$-equal in height parts $\Delta h$ (Fig. 1) in accordance with mass exchange equation for the ions being extracted in layer having thickness $\Delta h$ at a height $h_j(j,n)$

$$q_V \cdot c_{нj} \cdot \Delta\tau = q_V \cdot c_{kj} \Delta\tau + k_V \Delta V(c_{нj} - c_j^*)\Delta h/v,\tag{5}$$

you ought to find out the concentration $c_{кj}$ for the calculated moment of each layer $\Delta h$.

5. Final concentration of the extracted ions of chlorine in ionite for the layer $h_j$ at the moment $\tau_i$ can be determined in accordance with material balance

$$x_{кj} = x_{нj} + \frac{q_V}{3600\Delta G}(c_{нj} - c_{кj}).\tag{6}$$

6. Using equation of equilibration line (1) we find equilibrium concentration

$$c_j^* = \frac{x_{нj}}{a - b \cdot x_{нj}},\tag{7}$$

under the conditions $c_j^* \geq c_{нj}$ at the moment $\tau_i$ and the ionite layer(s) $j$ looses its ability to exchange ions and after that it functions as a filter.

7. The calculations are finished under the condition $c_{к j=n} \geq c_к$.

Algorithm for calculation of the ion exchange column of the uninterrupted action

1. Concentration of chlorine ions in ionite at the exit

$$x_к = 0{,}99\, x_{_н}^*.\tag{8}$$

2 Ionite consumption

$$G = q_V \frac{c_{_H} - c_{_K}}{x_{_K} - x_{_H}}. \tag{9}$$

3. Calculation of transference units number (*TUN*)

$$TUN = \sum_{i=1}^{m} \frac{\Delta c}{c - c^*}. \tag{10}$$

4. Height of the moving ionite layer

$$H = (\upsilon \cdot TUN) / k_V. \tag{11}$$

5. Volume of the moving ionite layer

$$V = \frac{\pi D^2 H}{4}. \tag{12}$$

6. Average time of ionite existence in the column

$$\tau = \frac{V \rho_{_H}}{G}. \tag{13}$$

7. Speed of the ionite movement from top to bottom of the column

$$U = \frac{H}{3600 \cdot \tau}. \tag{14}$$

8. Specific consumption of ionite for *1 m3* of solution being purified

$$y = {q_V} / {G}. \tag{15}$$

9. Calculation of chlorine ions profiles (on height) for the solution being purified and in ionite

*a)* $\Delta h = H/m$,

*b)* $c_1 = c_{_H}$, $x_1 = x_{_H}$,

*c)* $c_{p1} = x_1/(a_2 - b_2 x_1)$,

*d)* $c_2 = c_1(1 - k_V \cdot \Delta h / \upsilon) + (k_V \cdot \Delta h / \upsilon) c_1^*$,

*e)* $x_2 = x_{_K} - (q_V / G_V)(c_{_H} - c_2)$;

*f)* readdressing: $x_1 = x_2$, $c_1 = c_2$ and repeating «*m*» - times of items (b-*f*) and corresponding concentrations accordingly;

*g)* calculations are over after «*m*» - times repetitions.

**Results of calculations and discussion of the results**

Shown in Fig. 2 profiles of chlorine ions concentrations in the solution (a) and in ionite (b) according to ionite layer height in the middle (τ = *4* hours) and at the end of the working cycle period (τ = *8* hours) for the column with 1m diameter with stationary ionite layer (curves 1 and 2) and with moving ionite layer (curves 3) are given.
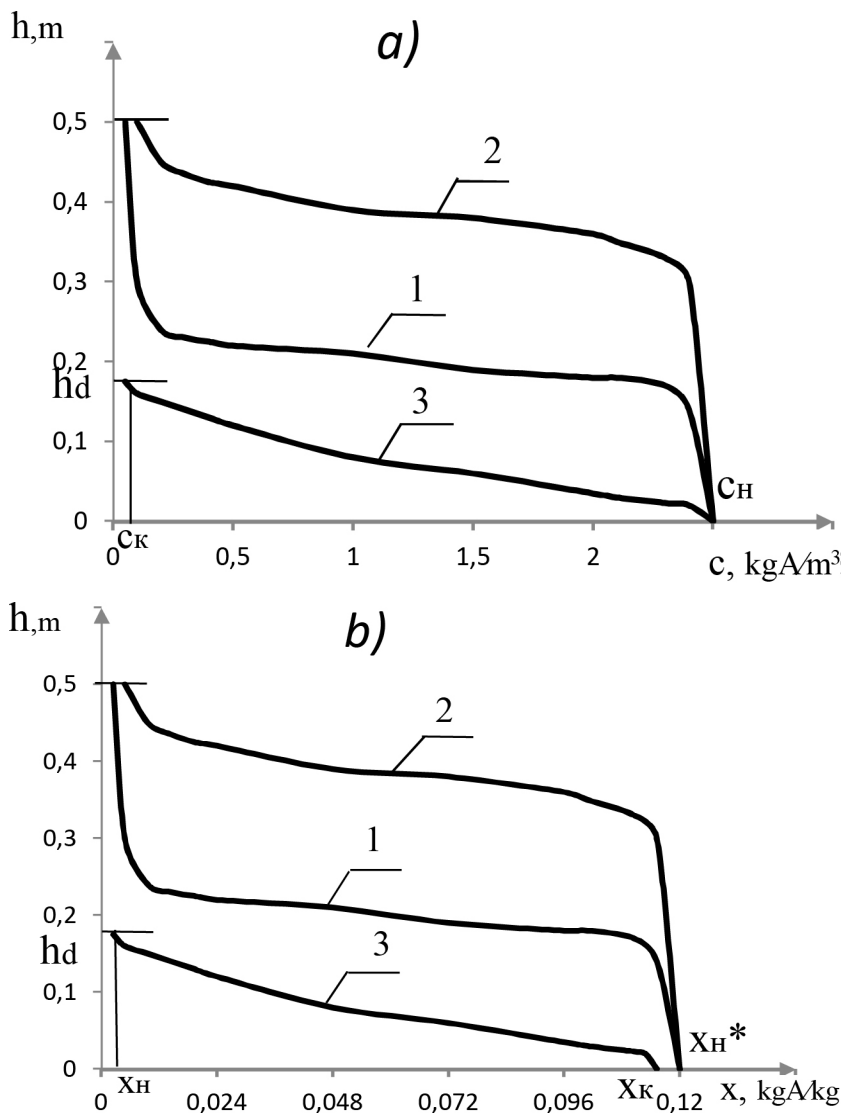
**Fig. 2.** Drawings of chlorine ions concentrations in the solution (a) and in a layer of grains (b) at the height of ionite: 1 – in four hours after the working cycle beginning; 2 – in eight hours at the end of the working cycle; 3 – in the antiflow ion exchange column of uninterrupted action.

*Table 1.*

**Initial and reference data, calculation parameters**

| № | Parameter | Value |
|---|---|---|
| | Initial data | |
| 1 | Productivity on the solution being purified, $q_V$, m³/h | 1 |
| 2 | Initial concentration of chlorine anions in the solution, $c_u$, kg/ m³ | 2,5 |
| 3 | Final acceptable concentration of chlorine anions in the solution, $c_к$, kg/ m³ | $7,8 \cdot 10^{-2}$ |
| 4 | Pressure, $P$, atm. | 1,033 |
| 5 | Temperature, $t$, ˚C | 30 |
| 6 | Solution density, $\rho_W$, kg/ m³ | 1280 |
| 7 | Solution viscosity, $\mu$, P/sec | 0,055 |
| 8 | Coefficient of chlorine anions diffusion in the solid, $D_c$ m²/sec. | $1,6 \cdot 10^{-9}$ |
| 9 | Constant of anionite equilibrium at 30˚C, $k_p$ | 1,2 |
| 10 | Equivalent diameter of anionite particles, $d_э$ m | $6 \cdot 10^{-4}$ |
| 11 | Full anionite exchange tank AB-17-8, $x_0$*, kgA/ kg | 1,725 |
| 12 | Ion mass $Cl^-$, $M$, kg/ kmole | 35,5 |
| 13 | Specific volume of dry anionite, $\upsilon_0$, m³/kg | $3 \cdot 10^{-3}$ |
| 14 | The particles density filling, $\rho_0$, kg/ m³ | 340 |
| 15 | Coefficient of chlorine anions diffusion in the ionite particles, $D_u$, m²/sec | $2,9 \cdot 10^{-10}$ |
| 16 | Particle layer porousness, $\varepsilon_0$ | 0,4 |
| 17 | Height of the layer $H$, m | 0,7 |
| 18 | Column diameter $D$, m | 1 |
| | Calculation parameters for the column of periodic action | |
| 1 | Fictitious solution speed $\upsilon$, m/sec | $3,54 \cdot 10^{-4}$ |
| 2 | Reynold's number, $Re$ | $4,94 \cdot 10^{-3}$ |
| 3 | Schmidt number, $Sc$ | 26855 |
| 4 | Sherwood number, $Sh$ | 4,44 |
| 5 | Coefficient of outer surface mass transference, $\beta_c$, m/sec | $1,18 \cdot 10^{-5}$ |
| 6 | Volume coefficient of mass exchange, $k_V$, 1/sec | $7,1 \cdot 10^{-2}$ |
| 7 | Constant of equilibration line (1) $a$ and $b$ correspondingly, m³/kg | $5,76 \cdot 10^{-2}$ $8 \cdot 10^{-2}$ |
| 8 | Equilibrium concentration in ionite corresponding to the initial concentration of ions of chlorine in the solution, $x_u$*, kgA/ kg | 0,12 |
| 9 | Equilibrium concentration in ionite corresponding to the finite concentration of ions of chlorine in the solution, $x_u$*, kgA/ kg | $4,465 \cdot 10^{-3}$ |
| 10 | The initial concentration of ions of chlorine in ionite after regeneration, $x_u$, kgA/ kg | $3,795 \cdot 10^{-3}$ |

*Continuation of the table*

| 11 | Volume of ionite layer, $V_c$, m³ | 0,3925 |
|---|---|---|
| 12 | Mass of ionite layer, $M_c$, kg | 218,06 |
| 13 | Maximum ionite particles absorption of chlorine ions, $M_y$. kgA | 25,34 |
| 14 | Maximum working cycle period, $\tau_m$, hour | 10,46 |
| 15 | Working cycle period, $\tau$, hour | 7,99 |
| 16 | Specific consumption of ionite for 1 m³ of solution being purified, $y_n$, m³/kg | 0,0367 |
|  | Calculation parameters for the column of the uninterrupted action |  |
| 1 | Concentration of chlorine ions in ionite at the exit from the column, $x_k$, kgA/ kg | $1,188 \cdot 10^{-1}$ |
| 2 | Ionite consumption, $G$, kgA/ hour | 21,06 |
| 3 | Transference units number, TUN | 33,95 |
| 4 | Ionite volume in the column, $V$, m³ | 0,133 |
| 5 | Height of the moving ionite layer, $h$, m | 0,169 |
| 6 | Initial concentration of chlorine ions in ionite after regeneration, $x_н$, kgA/ kg | $3,795 \cdot 10^{-3}$ |
| 7 | Time of ionite movement in the column, $\tau_n$, hour | 2,144 |
| 8 | Speed of ionite movement in the column, $U$, m/sec | $2,19 \cdot 10^{-5}$ |
| 9 | Specific consumption of ionite for 1 m³ of the solution being purified , $y$, m³/kg | 0,0475 |

According to the graphs of the drawing the height of the moving layer of ionite in the column of the periodic action (curves 1 and 2) doesn't go over ½ of its whole layer height. The rest part of its height is either saturated fully (i.e. it is in a dynamical equilibrium relative to the initial concentration of chlorine ions being trapped in the solution) or it doesn't participate in the ion exchange process. It is evident that the curves 1a and 1b correspond to the concentration of ions of chlorine in the middle of the working cycle period ($\tau$=4 hours). *100 mm* ionite layer has been used at the entrance. Ionite at height *100÷300mm* participates in ion exchange process and the upper *200 mm* of the ionite layer aren't involved in the process. At the end of the working cycle period ($\tau$=8 hours) the upper layer of ionite with height 200 mm participates in ion exchange. The lowest part of the layer (300 mm) is saturated with ions of chlorine so it doesn't participate in the ion exchange process.

In the moving layer of ionite column of uninterrupted action in the ion exchange process participates only active layer having height $H_x$=*170mm* (Fig.2, curves 3a and 3b). Its height is less than height of the active layer of ionite with stationary layer (200 mm). The hydraulic resistance of stationary layer of ionite

(H=*300 mm)* is almost 3 times increase than the height of the layer of ionite in the ion exchange column of the periodic activity. 2/3 of its height doesn't participate in ion exchange and the solution is not filtered through it. Moreover, efficiency of ion exchange column of uninterrupted action is 30% superior to efficiency of the column working periodically (the last lines of Table 1). It is derived from the fact that usage of the exchange capacity of the lower ionite layers in column of periodic action equals 100%, that is $x_к = x_н^* = 0,12$ and in column of uninterrupted action it equals $x_к = 0,1188$ (Fig. 2b).
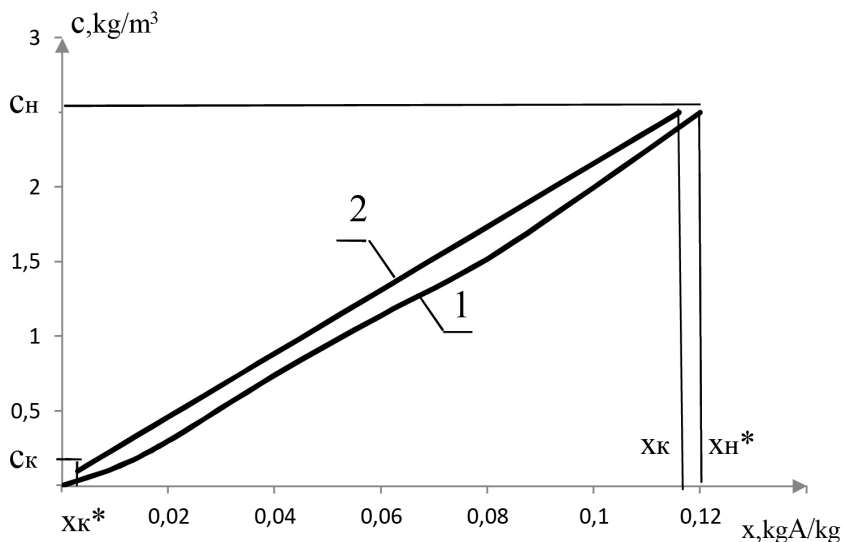


**Fig. 3.** Equilibrium (1) and working (2) lines of the ion exchange process in the column of uninterrupted action (calculation results, Table 1).

Significant disadvantage of the moving ionite layer is that the process is to be implemented in a unit of equipment with boiling layer [2, 4]. The disadvantage of globules and grains attrition can be avoided. The globules and grains should be coated with textile material. In this case attrition resistance will be twice higher (in accordance with experimental data).

**Conclusion**

Analysis of existing methods of LiOH water solution tertiary treatment from chlorine anions has been made. It is suggested to purify LiOH in ion exchange column. Calculations of ion exchange columns of periodic action and of un-

interrupted action showed the advantages of the latter one. It is explained to a greater degree with the usage of the exchange capacity of the ionite. In the process the hydraulic resistance of the moving ionite layer is 3 times less than that of the stationary layer. It proportionally leads to energy savings. Graphs of the dependence of the chlorine anion concentration in ionite at height of its layer are given. It is recommended to prevent attrition of ionite granules in ion exchange columns during the operation with coating of each globule with thinned textile or knitted material. It reduces the attrition of the globules and increases their operation by more than an order.

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