

Model and Software for Layer-By-Layer Calculation of the Regeneration Process for Cation Exchanger

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ABSTRACT

For layer-by-layer calculation of cation exchanger regeneration by limited volume method the value of the coefficient of mutual diffusion of sodium calcium ions for sulfonated coal and Ky-2 cation exchangers is determined. Determined is the height of a single calculated layer which makes it possible to eliminate the mass transfer equation from the description of the process and to restrict balance equation and the isotherm equation. Developed is a computer program for layer-by-layer calculation of the process of filter regeneration which allow it to get output curves corresponding to output curves for industrial cation exchangers. The obtained dependences can be used in layer-by-layer calculation of the regeneration process and with a complete simulation of the regeneration process of the sodium cation exchanger which allows to determine the optimal technological parameters of the filter for various initial conditions.

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Received: June 21, 2023; **Accepted:** June 26, 2023; **Published:** June 30, 2023

Keywords: Cation Exchanger, Regeneration, Layer-by-Layer Calculation, Modeling

Introduction

To obtain the required quality of water at the lowest economic cost, it is necessary to solve optimization problems by increasing the efficiency of existing installations and newly designed cation exchanger installations [1-6]. The regeneration of ion exchange filters accounts for the main costs of the water treatment process. Regeneration stage is one of the most difficult to describe from a mathematical point of view and is carried out by the method of layer-by-layer calculation [7-9]. However, the results obtained do not always coincide with the practice. Finding the parameters of the layer-by-layer calculation of the regeneration process for cation exchange filter giving calculated results that coincide with the practice are considered in this work.

For the fulfillment of the economic calculation of the regeneration process, it is necessary to find the dependency between reagent expenditure and cation working exchange capacity. To solve this kind of task under non-line isotherm is very difficult, that's why the calculation of the regeneration process today is carried out by layer-by-layer method using a computer [10,11]. This allows to exclude the mass transfer equation from the process description and to limit by balance and isotherm equations. Regeneration process of cation exchanger is limited by inter diffusion kinetics. But under simultaneous diffusion of two ions and because of their different mobility, the electric field could appear inside the granule. The action of these fields is taken into account by introduction of effective coefficient of the diffusion [12,13]. In technical literature there are only the coefficients of inter diffusion on the replacement of metal ions by hydrogen ions [10,14]. Therefore, the effective

coefficient of inter diffusion during the replacement substitution of sodium ion with calcium ion needs to be defined experimentally.

Exchange of ions in concentrated solutions i.e. regeneration solutions of sodium cation exchangers are not always described by Nikolski equation [15]. In this connection it is necessary to determine the apparent coefficient of ion exchange corresponding to the regeneration conditions and allowing one to describe the ion exchange according to isotherm equation. In a layer-by-layer method for the calculation of regeneration process under other equal conditions there are two physical quantities: an effective coefficient of inter diffusion and apparent coefficient of ion exchange the values of which influence the form of a diagram and correspondingly the exchange capacity of the cation exchanger. In the present work, we adopt an approach in which the apparent coefficient of ion exchange is calculated so as to satisfy the conditions for coincidence of an experimentally determined work. The effective coefficient of inter diffusion is found experimentally. It determines the length of a single layer which corresponds to onset of balance of ion exchange.

Materials and Methods

Research purpose

1. To determine effective coefficient of inter diffusion of sodium ion and calcium for finding the height of the calculated layer.
2. To determine the apparent coefficients of ion exchange allowing to get the results closely coincide with the experiments by using a layer-by-layer method of calculating the regeneration process

Layer-by-Layer Calculation of Regeneration Process of Sodium Cation Exchanger

The calculation of regeneration stages today is possible only by layer-by-layer method. The regeneration process is limited by

inter diffusion kinetics. One of the basic matters of layer-by-layer calculation is the consideration of kinetics process which is in its turn is considered by the length of a calculated single layer. The physical sense of this layer is that it presents the length of the column under which the balanced enrichment of the ion exchanger in K times is established according to much sorbitized ion [10]. The height of the layer is determined from relation:

$$h_c = \frac{V}{\beta_k} \quad (1)$$

where, V - the speed of the liquid flow through the layer, β_k - kinetics coefficient;

$$\beta_k = \frac{\pi^2 D_{ef}}{r^2}$$

D_{ef} - effective coefficient of the internal diffusion; r - radius of the ion exchanger grain.

Having the value D_{ef} and knowing the height of the load H_0 , the number of the layers of sodium cation exchanger can be defined and the kinetics process can be considered.

$$M = \frac{H_0}{h_c} \quad (2)$$

Diffusion equation in spherical coordinates is written as [1];

$$D_{ef} \left(\frac{\partial^2 a}{\partial^2 R} + \frac{2\partial a}{R\partial R} \right) = \frac{\partial a}{\partial t} \quad (3)$$

where, R - distance from the center of the grain;
 a - the concentration of ion in grain.

The solution of the diffusion problem is obtained as a sum of the terms of the convergent series and for diffusion from the sphere ,the concentration on the surface of which is constant (this corresponds to the regeneration process) , the equation is given [16]:

$$F = 1 - \frac{a}{a_0} = 1 - \sum_{n=1}^{\infty} \frac{6}{n^2 \pi^2} \cdot e^{-n^2 \pi^2 F_0} \quad (4)$$

where, $F_0 = \frac{D_{ef} t}{r^2}$;

a_0 – the maximum content of ion in grain;
 F_0 – the dimensionless time, or criterion of Fourier homochronism.

In the literature, it is described two methods of measurement of the effective coefficient of internal diffusion, one of which is based on the use of limited volume of the solution [10]. In comparison with other method “method of a thin layer” the method of limited volume doesn’t require a special device and is simple in using. For the determination of the effective coefficient of inter diffusion the method of limited volume was used. The weights from the ion exchanger with the volume of 1ml were put into vessel containing 200 ml of 4% sodium sulfatum solution prepared on distilled water. Before, the ion exchanger was completely transferred into Ca -form. Solutions were carefully mixed and in a definite period of time the calcium ion content in the solution was determined.

Having defined the share increment according to nomogram of dependence F from F_0 (fig. 1) the dimensionless time was determined. Knowing the value of F_0 , the dependence of the effective coefficient of internal diffusion was calculated from the dependency (4), (table.1).

Table 1: The Averaged Values of D_{ef} for the Replacement of Ions $Na^+ - Ca^{2+}$.

| Ion exchange | D_{ef} , sm ² /sec |
|-----------------|---------------------------------|
| Sulfonated coal | $3.15 \cdot 10^{-6}$ |
| Ky - 2 | $2.9 \cdot 10^{-7}$ |

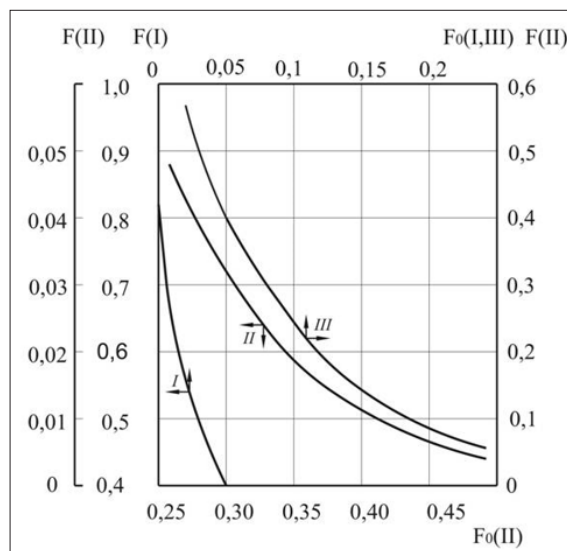


Figure 1: Nomogram of the dependence of the increment part in sorbed ions on the grain of ion exchanger F from the criterion by Fourier homochronism F_0 for sphere ([16])

Eliminating from the description of the process of regeneration the equation of mass transfer and considering the balance equation and isotherm equation, the following system will be obtained [10]:

$$\left. \begin{aligned} -V \frac{\Delta C_i}{\Delta x} &= \frac{\Delta a_i}{\Delta t} \\ K &= \frac{a(x,t)[A - C(x,t)]^2}{[E_n - a(x,t)]^2 C(x,t)} \end{aligned} \right\} \quad (5)$$

Having expressed Δx and Δt through the values determined from experiments Δm (m - volume of swollen ion exchanger) and $\Delta \phi$ (ϕ - solution volume), with the account that $H_0 = \Delta x \cdot M$, and , the $\Phi = n \cdot \Delta \phi$ equation system can be written in the following way:

$$\left. \begin{aligned} (a_{m,n-1} - a_{m,n}) \Delta m &= (C_{m,n} - C_{m-1,n}) \Delta \phi \\ K &= \frac{a_{m,n} (A - C_{m,n})^2}{(E_n - a_{m,n})^2 C_{m,n}} \end{aligned} \right\} \quad (6)$$

n - The number of solution portions;
 A - the cation exchanger concentration in the solution;
 E_c - the complete exchange volume of the cation exchanger;

$$\Delta m = f \cdot \Delta x$$

$$\Delta \phi = f \cdot \Delta x \cdot \rho$$

f - a cross- sectional area of the exchanger;
 ρ - porosity loading

Having denoted $x = a_{m,n}; y = C_{m,n}; a = a_{m,n-1}; b = C_{m-1,n}$, after some conversions, the system of equations (6) is reduced to one unknown number

$$y^3 + By^2 + Qy - A^2D = 0 \quad (7)$$

where $D = \frac{D^*}{\rho(K\rho + 1)}$; $D^* = (a + \rho b)$

$$B = \frac{2\rho(KE_c - A) - D^*(2K\rho + 1)}{\rho(K\rho + 1)}; \quad Q = \frac{A(\rho A + 2D^*) + K(E_c - D^*)^2}{\rho(K\rho + 1)}$$

After the introduction of a new variable [9], $Y = Z - \frac{B}{3}$

the equation takes the form:

$$Z^3 + pZ + q = 0 \quad (8)$$

where, $p = Q - \frac{B^2}{3}$; $q = \frac{2B^3}{27} - \frac{BQ}{3} - A^2D$.

The cubic equation received is solved according to Cardano formula [17]. The calculation of regeneration process by layer-by-layer method is considered for steady state of the Na- cation exchanger work which softens water of a definite content. Then on the filter load before each process of regeneration will be the same amount of sorbitized ions of hardness. The amount of sorbitized ions of hardness, taking into account the averaging, can be calculated from the previously discussed technique. This avoids consideration of the first cycllies of softening and regeneration starting from completely regenerated cations.

Results and Discussion

Layer-by-layer Calculation Program

For calculating the regeneration process by layer-by-layer method and for finding the apparent coefficient of ion exchanger the program was written on programming language C++.. The enlarged block diagram is given in Figure 2.

In block 1, the initial data is input and in the block 2 the number of layers and the number of portions of the solution are calculated. In blocks 3 and 10, a process calculation cycle is formed on the layers and in blocks 4 and 8 by portions of the passed solution. In block 5, the concentration of the regeneration solution is calculated supplying to the load depending on the number of portions. In block 6, the cubic equation is solved (7). In block 7, the calculated data of the given layer and the given portion are calculated. The checking of quantity of passed portions is carried out in block 9 and the checking of quantity of layers is carried out in block 11. In block 12, the working exchange capacity of the charge is calculated, in block 13, the calculated and the experimental exchange capacity is compared. If the exchange capacities coincide with the accuracy , the calculated data is displayed on the screen with the help of block 15. Otherwise, in block 14, a new apparent coefficient of ion exchange is searched and the calculation of the regeneration process is continued till the conditions in block 15 are carried out.

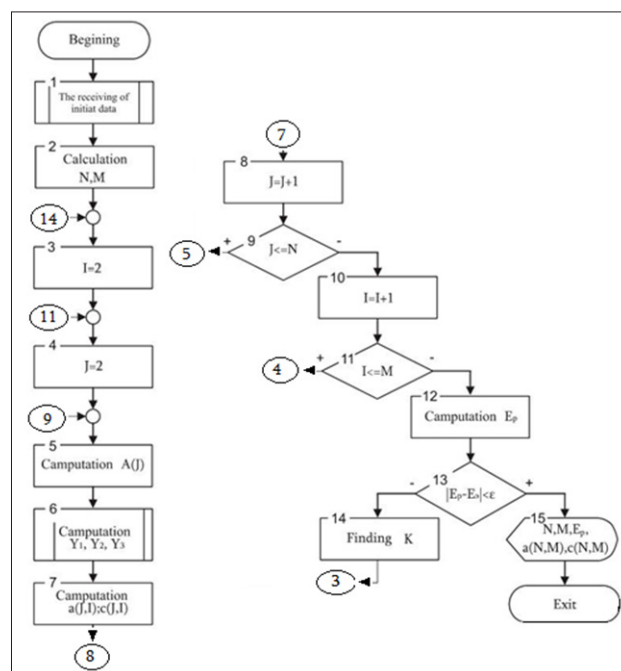


Figure 2: Enlarged Block-Diagram of Each Layer Calculation of Sodium-Cation Exchanger Regeneration Process

Regeneration Output Curves

The calculation of sulfonated coal regeneration by sodium sulfate solution and sodium salt was made by layer method. The received theoretical diagrams with quite accurate for practice agrees with the experimental data got on industrial Na-cation exchangers with a diameter of 3.0 m and the height of the charge of 2.0 m (figure 3, 4). The change of the curvature on the descending branches of diagrams corresponds to the beginning of exchanger washing. Having received on the base of theoretical calculations the graphical dependence for apparent coefficient of ion exchange on the concentration of the regeneration solution (figure 5) we determined by interpolation the coefficients of ion exchange for 1.0; 1.5; 2.0; 3.0; 4.0 % of regenerating solution of sodium sulfate. Having changed a little the calculation program for the regeneration process with the account found seemed coefficients of ion exchange, for the given concentration defined was the dependency of exchange capacity of the cation exchanger from the specific discharge of a reagent, which can be used for the optimization of Na-cation installations work.

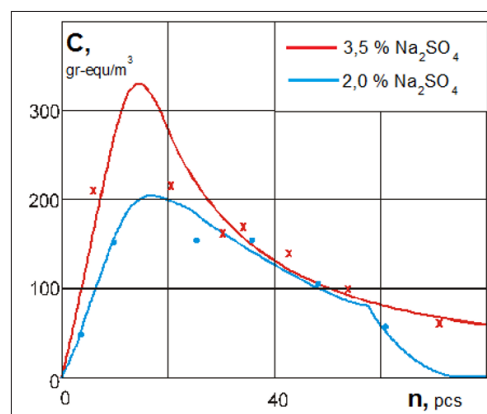


Figure 3: The Calculated Diagrams and Experimental Periods during the Regeneration of Sulfo Coal by Sodium Sulfate Solution

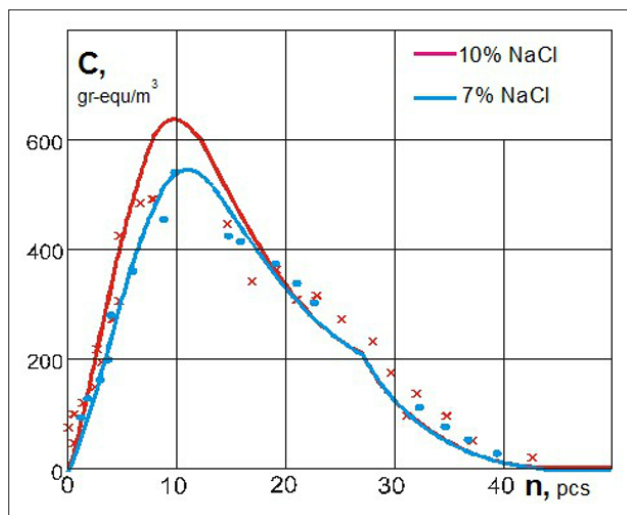


Figure 4: The Calculated Diagrams and Experimental Periods during the Regeneration of Sulpho Coal by Table Salt.

Apparent Ion Exchange Rate

The graphical dependence between the apparent coefficient of ion exchange and the concentration of the regeneration solution can be approximated by the equation [17].

$$K = aC^b + K_{del} \quad (9)$$

where, K - apparent coefficient of ion exchange;
 C - the concentration of regenerating solution;
 K_{del} - the coefficient of ion exchange for dilute solutions.

When C tends to zero (non-concentrated solutions) the resulting graph tends to cacique and crosses it. And that means that the apparent coefficient of the ion exchange takes the value 2.8 that is the value of the real ion exchange coefficient [17].

To determine the values of the coefficients a and b , the equation (9) is presented in the form :

$$y = lga + bx \quad (10)$$

where, $y = lg(K - K_{del})$; $x = lgC$.

For the corresponding values of the apparent coefficient of the ion exchange and for the concentration of ion exchange we get series of leaner equations and using the method of least squares (table 2) we find the values a and b .

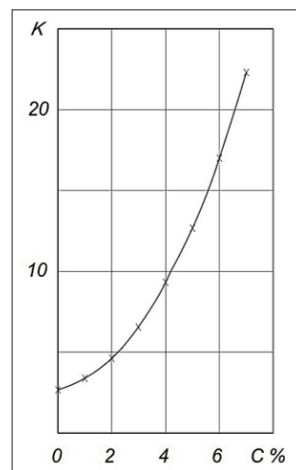


Figure 5: The Dependence of the Apparent Ion Exchange Coefficient on the Concentration of the Regeneration Solution

Table 2: Determination of a and b Values by Least Squares

| Initial data | | $K - K_{del}$ | $y = lg(K - K_{del})$ | $x = lgC$ | x^2 | xy | K as a calculated |
|--------------|------|---------------|-----------------------|-----------|-------|-------|---------------------|
| C | K | | | | | | |
| 1 | 3.6 | 0.8 | -0.097 | 0.00 | 0.00 | 0.00 | 3.503 |
| 2 | 4.8 | 2.0 | 0.301 | 0.301 | 0.091 | 0.091 | 5.009 |
| 3 | 6.6 | 3.8 | 0.580 | 0.477 | 0.228 | 0.277 | 7.117 |
| 4 | 9.3 | 6.5 | 0.813 | 0.602 | 0.362 | 0.489 | 9.747 |
| 5 | 13.0 | 10.2 | 1.009 | 0.699 | 0.489 | 0.705 | 12.801 |
| 6 | 17.0 | 14.2 | 1.152 | 0.778 | 0.605 | 0.196 | 16.366 |
| 7 | 22.2 | 19.4 | 1.288 | 0.845 | 0.714 | 0.088 | 20.301 |
| Amount | | | 5.046 | 3.702 | 2.489 | 3.546 | |

The total equations take the following form:

$$\left. \begin{aligned} 5,046 &= 7lga + 3,702b \\ 3,546 &= 3,702lga + 2,489b \end{aligned} \right\} \quad (11)$$

From here after transformation and substitution we find $a = 0,703$; $b = 1,652$ and equation (9) will finally take the following form:

$$K = 0,703C^{1,652} + 2,8 \quad (12)$$

The maximum discrepancy between the values obtained by the equation 12 and from the program for calculating the apparent total exchange does not exceed 7,8 % (table 2).

The obtained equation (12) makes it possible to calculate the apparent ion exchange coefficient at different values of the regeneration solution without using the computer program for calculating.

Conclusion

To calculate the height of the calculated layer by layer-by-layer calculation of the regeneration process of sodium cation exchanger experimentally by the limited-volume method the values of coefficients of interaction of ion sodium - calcium for sulfonated coal and $K_y - 2$ were determined.

A computer program was developed for layered calculation for the process of cation exchanger regeneration that allows to obtain output curves that coincide with the real output curves of the corresponding industrial filters. The program also makes it possible to establish the relationship between the apparent coefficient of ion exchange and the concentration of the regeneration solution.

The obtained dependences can be used in the full simulation of the cation exchanger regeneration process and the establishment of a relationship between the reagent consumption and cation exchange capacity that allows to determine the optimal parameters of the filter operation mode for various initial technological parameters.

Acknowledgements

The paper is based on the research conducted in the framework of the ISTC project G-725-“Regeneration of Na- Cation exchangers by Sulfate – Natrium Solution and recycling of spent regenerating solution”.

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