Optimization of the regeneration of the sodium-cation ion-exchange filter

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Abstract. A new methodology has been developed for determining the volumetric coefficients of internal mass transfer according to the results of an experimental study. The values of volumetric coefficients of internal mass transfer were calculated and their dependence on the technical characteristics of the regeneration process of the sodium-cation exchange filter under dynamic conditions was established. A computer model of the process of regeneration of the sodium-cation exchange filter in nonequilibrium and non-stationary conditions in the form of a computer software package ("Regeneration-1", "Regeneration-2"), recommended for scientific, design, commissioning and operating organizations, relevant industries. For the first time, the task of optimizing the ion-exchange nonequilibrium regeneration of the sodium-cation exchange filter as a separate stage of the filter cycle was posed and solved. The analytical dependence of optimizing the specific consumption of NaCl salt for nonequilibrium regeneration of the sodium-cation exchange filter as a separate stage of the filter cycle is obtained.

1. Introduction

Over the twentieth century, the world's population has increased almost four times. At the same time, the consumption of fresh water increased nine times, including for drinking and communal needs – 13 times. As a result, water resources in various regions of the world became catastrophically short of water [1–5]. In the next 20 years, taking into account current trends in population growth and the global economy, an increase in the demand for fresh water by at least 100 km$^3$ per year is expected. According to the UN [1, 2], more than 1.2 billion people live in conditions of constant shortage of fresh water, about 2 billion people suffer from it regularly (in the dry season, etc.).

The existing shortage of fresh water can be compensated for by the use of natural highly saline waters (water of the seas and oceans, salt lakes, groundwaters) using ion-exchange technologies.

Ion-exchange technology is widely used in industry [5–11]. Study their patterns is one of the main problems of modern science. The technological process of ion-exchange solution processing includes two main stages:

- removing from a solution passed through an ion-exchange material, the desired ion (or group of ions) of a certain type in exchange for the ion contained in the ion-exchange material. In this case, the solution is purified from ions of a certain type, and the ion-exchange material is saturated with these ions, the number of ions capable of such an exchange in it decreases and the ion-exchange material is “depleted”, the stage of sorption or absorption of ions of a given type;
- introducing into the “depleted” ion-exchange material ions capable of being exchanged for an
ion of a given type by passing through it a special solution containing an ion capable of being exchanged, usually in a higher concentration, the stage of regeneration or restoration of the ability of an ion-exchange material to absorb ions of a given type from processed solution.

Ion exchange softening of natural, waste and sea waters to produce suitable for feeding steam and hot water heat generators and heat desalination plants is one of the most relevant areas of application of ion exchange technologies. The process of ion-exchange water softening consists in replacing the Ca$^2+$ and Mg$^2+$ cations, which are the basis of poorly soluble scale-forming hardness salts (CaCO$_3$, CaSO$_4$, Mg (OH) 2), with a Na$^+$ ion, as a result of which only well-soluble sodium salts remain in the water. Regeneration of the ion-exchange material is carried out with a NaCl solution with a concentration of from 6 to 12 %. This process is called sodium-cation exchange water softening and is carried out using ion-exchange materials capable of exchanging cations (sulfonated coal, KU-2, KU-4, etc.).

The dynamics of ion-exchange sorption is the subject of numerous works by domestic and foreign scientists [6, 10, 11]. However, along with significant achievements in this area, the results obtained are not enough to solve some practical problems. The scientific and mathematical description of real sorption systems operating under dynamic conditions remains a very difficult issue, due to insufficient knowledge of many processes and phenomena that occur during ion-exchange.

It is important to take into account that most of the works on the calculation of dynamic ion-exchange systems consider dilute solutions whose concentration does not exceed 0.1 H, where the external diffusion kinetics is the limiting stage of ion exchange. Nevertheless, the use of alternative sources of natural and industrial wastewater involves waters with high salinity up to 0.5 H. Since real ion-exchange processes are accompanied by a mass of additional external and internal factors that influence the course and quality of the ion exchange process itself under dynamic conditions, there are empirical dependencies cannot fully claim scientific validity. However, one must not underestimate the accumulated practical experience in operating ion-exchange systems at various enterprises – it needs to be studied and generalized with efforts to develop a mathematical apparatus that describes ion-exchange processes.

Currently, the characteristics of the process of softening fresh water of drinking quality (total salinity up to 2000 mg / l) have been most fully studied. The characteristics of the cation exchanger regeneration process (salt content of the regenerating NaCl solution from 50 g / l to 120 g / l) have not been completely studied.

The regeneration process was studied mainly experimentally. Attempts to quantify the process are few in number and have been undertaken mainly to demonstrate computational methods for the simplified kinetic scheme, while modeling the regeneration process of the sodium-cation exchange filter requires a detailed consideration.

Therefore, the search for a new method for calculating the non-stationary and nonequilibrium dynamic regeneration process, as well as the development of a computer model of the cation exchanger regeneration process for its quantitative description and optimization, is undoubtedly relevant, which was the main objective of this work.

2. Methods and materials

Experimental studies were conducted on the basis of the laboratory of the Department of Heat and Gas Supply and Real Estate Expertise of the North Caucasus Federal University. For the experiment was designed and installed special setup (Fig. 1).

The experimental setup consists of two ion-exchange columns, which are connected in a special way for the supply and removal of solutions through a hose system. In the system there are tanks for the initial and regeneration solution, pumps for supplying the initial and regeneration solution to the ion-exchange columns. While the regeneration process is taking place in one column, the other column undergoes depletion in order to save time. Before the regeneration process, it is necessary to loosen the cation exchanger, and after the regeneration process it is necessary to wash the cation exchanger, for this purpose a separate pump is provided (Fig. 2).
Figure 1. Photo of the experimental setup

Figure 2. Schematic diagram of the experimental setup

Ion-exchange columns with a diameter of 32 mm and a height of 1060 mm are made of quartz glass. The columns are filled with swollen cation exchanger KY-2×8 with a layer height of 600 mm. The remaining volume of the column above the cation exchange resin is filled with an appropriate...
solution, depending on the process. Bottom layer of cation exchanger in the ion exchange column is limited by a special drainage device, which is covered with nylon fabric, the cell diameter of which is about 0.2 mm, which prevents cation exchanger from flowing.

In this study, the analysis of the samples was carried out according to the titrimetric method, as the most accessible and simple method for determining the quantitative content of ions $Ca^{2+}$, $Mg^{2+}$ и $Cl^-$. This method provides sufficient measurement accuracy.

The titrimetric method of stiffness analysis is based on the use of reactions of complexing metal ions with complexones, accompanied by the formation of stable, slightly dissociated, water-soluble intramuscular salts.

The experimental research plan is designed to determine the numerical values of the volumetric coefficients of the external and internal mass transfer ($\gamma_i$ и $\gamma_i$, $\beta_i$ и $\beta_i$) when comparing the experimental output curves of changes in the total concentration and concentration of the absorbed ion with the calculated ones according to the developed programs “Regeneration-1” and “Regeneration-2”.

The “Regeneration-1” program is designed to solve the system of equations for the dynamics of regeneration of the sodium-cation exchange filter by changing the total concentration of the regeneration solution using the finite difference method, and the “Regeneration-2” program is used to solve the system of equations of the regeneration dynamics of the sodium-cation exchange filter according to the change in the concentration of the displaced ion in the regeneration solution by the finite difference method.

38 experiments were conducted to study the regeneration process in pair exchange $Na^+–Ca^{2+}$ and 31 experiments in pair exchange $Na^+–Mg^{2+}$.

In experiments on the study of the regeneration process in pair exchange $Na^+–Mg^{2+}$ the following values of the main initial characteristics in different combinations were taken:

- $C_{CI} =$ 1680 ÷ 1920 milligram-equivalent/l;
- $W_P =$ 0.338 ÷ 5.72 m / h;
- $C_{rr} =$ 100 ÷ 515 milligram-equivalent/l;
- $C_{in} =$ 40 ÷ 99.5 milligram-equivalent/l;

where $C_{CI}$ – concentration of regeneration solution supplied to the upper section of the ion exchanger layer in the filter, milligram-equivalent/ l; $C_{rr}$ – total concentration of softening solution in the process of sodium-cation exchange softening prior to the regeneration process, milligram-equivalent / l; $C_{in}$ – initial concentration of ion absorbed by softening ($Ca^{2+}$ or $Mg^{2+}$) in softened solution preceding the regeneration process, milligram-equivalent/l; $W_P$ – transmission rate of the regeneration solution through the ion exchange column, m / h.

In experiments on the study of the regeneration process during the pair exchange of $Na^+–Ca^{2+}$ the following values of the main initial characteristics were taken:

- $C_{CI} =$ 1675 ÷ 1920 milligram-equivalent/l;
- $W_P =$ 0.49 ÷ 1.49 m / h;
- $C_{rr} =$ 15 ÷ 507 milligram-equivalent/l;
- $C_{in} =$ 10 ÷ 122 milligram-equivalent/l.

In all experiments, the height of the cation exchanger layer was maintained at 60 cm and the concentration of hardness ions in the initial regeneration solution, $C_{1PP}$, fed to the upper section of the cation exchanger layer in the filter is not higher then 0.267 milligram-equivalent/l.

Particular numerical values of volumetric coefficients of internal mass transfer with a change in the total concentration of the regeneration solution, as well as $\beta_i^2$ when the concentration of the ion displaced from the cation exchanger changes ($Ca^{2+}$ or $Mg^{2+}$) are determined by comparing the
Experimental output regeneration curves at the output of the sodium-cation exchange filter and the calculated output regeneration curves determined using the “Regeneration-1” and “Regeneration-2” programs for each experiment. Moreover, the volumetric coefficients of external mass transfer $\gamma_i$ with a change in the total concentration of the regeneration solution and $\beta_i$ with a change in the concentration of the ion ($Ca^{2+}$ or $Mg^{2+}$) displaced from the cation exchanger are not determinative, because during the regeneration of the sodium-cation exchange filter on KU-2 × 8 cation exchanger, which occurs at large concentrations (more than 0.5 H), the intradiffusion region is limited. The values $\gamma_i, \beta_i, c^{-1}$, were set:

- for pair exchange $Na^+–Ca^{2+}$ $\gamma_i = 0.05 \, c^{-1}, \beta_i = 0.038 \, c^{-1}$;
- for pair exchange $Na^+–Mg^{2+}$ $\gamma_i = 0.05 \, c^{-1}, \beta_i = 0.031 \, c^{-1}$.

Moreover, the values of the coefficients $\gamma_i$ and $\beta_i$ were selected in such a way that the calculated output curve of the regeneration of the sodium-cation exchange filter coincided as much as possible with the experimental experimental data. In accordance with the theory of mathematical statistics, the smallest sum of the squared deviations of the points of the experimental and calculated output curves is taken as a selection criterion (Fig. 3).

Having obtained the values of the effective volumetric mass transfer coefficients and for all the experiments carried out, a correlation analysis was carried out, which was performed on a computer in Microsoft Excel. The tightness of the relationship between the obtained dependences was estimated by the correlation relation $R$.

![Figure 3. Comparison of calculated and experimental points of output curves.](image)

Analysis of the correlation coefficients allows us to identify significant dependences by internal diffusion characteristics $\beta_i = f (C_{pr}, C_{rx}, C_{in})$ and $\gamma_i = f (C_{pr})$.

The obtained empirical coefficients are averaged between all the experiments carried out and as a result the following dependences are obtained:

- for pair exchange $Na^+–Ca^{2+}$
  
  $\gamma_i = 0.0048 \cdot C_{pr} + 1.05 \cdot 10^{-4} \cdot C_{pr}^2, \, c^{-1}$,
  
  $\beta_i = 0.00345 \cdot C_{pr} + 0.00562 \cdot \alpha_{pr}, \, c^{-1}$;

- for pair exchange $Na^+–Mg^{2+}$
  
  $\gamma_i = 0.0073 \cdot C_{pr} + 7.9 \cdot 10^{-7} \cdot C_{pr}^2, \, c^{-1}$,
  
  $\beta_i = 0.00747 \cdot C_{pr} + 0.0067 \cdot \alpha_{pr}, \, c^{-1}$.
where \( C_{\text{pr}} \) – concentration of regeneration solution, milligram-equivalent/ml; \( \alpha_{\text{pr}} \) – relative concentration of regeneration solution.

3. Results
Using the experimental values of the volumetric coefficients of the external and internal mass transfer (\( \gamma_1, \beta_1, \gamma_2, \beta_2 \)) and the programs “Regeneration-1” and “Regeneration-2”, it is possible to calculate the output curves of changes in the concentration of the regeneration solution and changes in the concentration of the displaced ion (\( \text{Ca}^{2+} \) или \( \text{Mg}^{2+} \)) for given initial characteristics of the process of regeneration of sodium-cation exchange filter (\( C_{\text{pr}}, W_{\text{pr}}, C_{\text{inf}}, \alpha_{\text{pr}} \) etc.) within the range of experimental research data.

Examples of output curves of field experiments and constructed using a computer model are presented in Fig. 4.

![Figure 4](image)

**Figure 4.** The output curves of the regeneration process of the sodium-cation exchange filter with the \( \text{Na}^{+}-\text{Ca}^{2+} \) pair exchange according to the conditions of private experience: round dots — experimental data, thick line — calculated curve for individually selected mass transfer coefficients; thin line with rhombic dots – calculated curve according to the derived equations of mass transfer coefficients

The developed numerical model of the regeneration process can be used to assess the effectiveness of this process and its optimization.

The effectiveness of any process is determined by the ratio of the value of the beneficial effect from it to the costs of its implementation in comparable units.

The costs of the regeneration process are determined mainly by the specific consumption of the regenerating agent (for the sodium-cation exchange filter, the \( \text{Na}^{+} \) ion in the form of \( \text{NaCl} \) salt). The remaining costs: depreciation of equipment, energy costs for pumping solutions, costs for maintenance personnel, etc. are almost constant for various modes of the regeneration process and may not be taken into account when optimizing the process.

The reagent consumption (\( \text{NaCl} \)) for regeneration of the sodium-cation exchange filter is taken into account by the following indicators, the formulas of which are developed for the numerical model:

- specific current consumption of \( \text{NaCl} \) salt for regeneration, \( d_{\text{pr}} \), milligram-equivalent \( \text{NaCl} / \text{ml} \),
- degree of regeneration \( n_{\text{pr}} \),
- current relative specific consumption of \( \text{NaCl} \) salt for regeneration \( g_{\text{pr}} \), milligram-equivalent / milligram-equivalent.

Fig. 5 shows dependency graphs \( n_{\text{pr}} = f \left( d_{\text{pr}} \right) \), \( g_{\text{pr}} = f \left( d_{\text{pr}} \right) \) for a special case: regenerated cation exchanger KU-2x8 is initially in equilibrium with the source softened water; relative concentration of
absorbed cation in the initial state \( \alpha_{\text{abs}} = \frac{C_{\text{in}}}{C_r} = \frac{70.7}{326} = 0.22 \); layer height of KU-2x8 cation exchanger in the sodium-cation exchanger \( H_s = 200 \) cm; total concentration of the regeneration solution entering the upper layer of cation exchanger in the sodium-cation exchanger \( C_{\text{re}} = 1800 \) milligram-equivalent/l; the rate of passage of the regeneration solution through the cation exchanger layer in the sodium-cation exchanger \( W_r = 1 \) m/h.

Figure 5. Dependency graphs \( n_r = f(d_r) \) и \( g_r = f(d_r) \) for a special case.

Analyzing the graphic dependencies of the main characteristics of the regeneration process \( n_r = f(d_r) \) and \( g_r = f(d_r) \) we can conclude that there are inflection points and extreme points (Fig. 5), i.e. about the possibility of optimizing the nonequilibrium regeneration of the sodium-cation exchange filter as a separate stage of the filter cycle.

Considering the regeneration process as a separate stage of the filter cycle of the sodium-cation exchange filter, it is advisable to take the specific relative consumption of salt as an optimization criterion \( g_r \).

Due to the fact that analytical dependencies are more accessible to engineers and technicians than computer models, the goal of further work is to obtain a regression multivariate dependence of the optimality of reagent consumption based on planning and conducting computational experiments, as well as adding an optimization method to the software package.

The purpose of conducting computational experiments with a computer model of an isolated regeneration process is to obtain a regression multivariate dependence \( d_r = f(C_{\text{re}}, W_r, C_{\text{in}}, C_{\text{in}}) \) at extreme points of relative specific consumption \( g_r \) (Fig. 5). In other words, using a computer model, the problem of optimizing an isolated process of nonequilibrium regeneration is solved and the regression dependence of the specific consumption of NaCl salt at extreme points of the relative specific consumption \( g_r \) on four factors is determined: the total concentration of the softened solution in the process of sodium-cation exchange softening preceding the regeneration process \( C_{\text{re}} \), the initial concentration of absorbed when softening an ion (\( Ca^{2+} \) or \( Mg^{2+} \)) in a softened solution \( C_{\text{in}} \), the input rate of the regeneration solution \( W_r \) and the concentration of the regeneration solution \( C_{\text{re}} \).
So, for a multifactor computational experiment, a first-order plan for PFE 24 at two levels has been adopted. In order to facilitate practical use for describing the objective function, the regression equation in the form of a linear polynomial with terms of interactions is adopted.

Thus, the obtained equation for determining the optimal specific consumption of NaCl salt for the regeneration of the sodium-cation exchange filter, depending on significant factors, is presented below.

\[
\begin{align*}
    d_r^- &= 0.66 + 0.64 \cdot C_p - 0.012 \cdot W_p + 5.61 \cdot C_{pu} - \\
    &- 6.77 \cdot C_{pu} - 0.33 \cdot C_{pu} \cdot W_p - 0.39 \cdot C_{pu} \cdot C_{pu} + \\
    &+ 3.3 \cdot C_{pu} \cdot C_{pu} - 0.34 \cdot W_p \cdot C_{pu} + 1.14 \cdot W_p \cdot C_{pu} - \\
    &- 25 \cdot C_{pu} \cdot C_{pu},
\end{align*}
\]

(1)

where \( C_p, C_{pu}, C_{pu} \) – concentrations in milligram-equivalent /ml, \( W_p \) – in m/h, \( d_r^- \) – milligram-equivalent NaCl/ml.

4. Conclusion

Thus, the search for the optimal specific salt consumption can be carried out using both the developed computer numerical model and the analytical optimization equation (1). The equation for optimizing the specific consumption of salt (1) is more acceptable than a computer model, and also accessible and recommended for engineers designing and operating sodium-cation exchange filters.

Application of the above formula makes it possible to develop practical recommendations for improving the process of regeneration of KU-2x8 cation exchanger while softening highly mineralized waters. Maintaining an optimal specific salt flow rate will reduce the operating costs of sodium-cation exchange filters.

The developed numerical model can be used to simulate the technological processes of water treatment of thermal power plants in order to predict and optimize their operation, as well as to quantify and optimize other ion-exchange processes.

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