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Study of a Reagentless Cyclic Ion Exchange Process for Natural-Water Treatment

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Abstract—A mathematical model has been developed and used to study a reagentless cyclic self-sustaining ion exchange process for preconditioning seawater and slightly saline solutions before their further freshening. The model is verified against experimental data. The effect of complexation on process efficiency is studied. The possibility of removing several selected cations from the aqueous solution before sending it to a freshener and of obtaining concentrated solutions of such cations is discussed. The selection of the best process scheme is considered. The case of slightly saline water with low sodium and high calcium is discussed. The process is shown to be stable.

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INTRODUCTION

A large number of processes are available for seawater freshening, each having its advantages and drawbacks. The largest difficulties with the two simplest freshening techniques, evaporation and membrane filtering, arise with poorly soluble calcium salts. They clog the membrane's pores and cause the accumulation of scale on the heating elements. Therefore, the water requires preconditioning before freshening in order to remove calcium from it. This procedure is referred to as water softening.

The development of the cyclic self-sustaining ion exchange process considered in this paper aims to create an efficient method for seawater softening. The advantage of this process is that it does not require any reagents except for those contained in the initial solution. The main idea [1, 2] proposed for the solution of this problem is based on electric selectivity [3, 4] implying that the sorbent is selective with respect to multivalent ions when the concentration of ions in the solution is low and to monovalent ions when this concentration is high. Thus, sorption is first used to remove calcium from seawater by ion exchange. After sorption, part of the water is sent for further freshening, while the remaining part, with much lesser volume and higher concentration, is used to regenerate the sorbent to the initial conditions.

A flow diagram of the cyclic self-sustaining process of the ion exchange softening–freshening of water is shown in Fig. 1. The ionite initially occurs in the Na-form. At the sorption stage, the initial solution is pumped through the sorbent at a constant rate until the concentration of a multivalent ion (e.g., Ca or Mg) in the freshening tank is equal to a specified share f of this ion's concentration in the initial solution (in our calculations, f was taken equal to 1/100). Next the softened water from the tank is divided into two parts: the Φ-fraction is clear water sent to users, while the $(1 - \Phi)$-fraction is returned via an accumulator to the sorbent regeneration process. This is the end of the cycle and the process is repeated.

Initially, attempts were made to experimentally solve the problem of seawater softening by this technology; however, the operation of the plants thus constructed was too expensive. Mathematical simulation, carried out later, showed that the parameters used in the experimental studies of this multiparameter problem were poorly chosen [5]. Further analysis of the problem showed this method became cost-effective with the proper choice of parameters, resulting in an efficiency index higher than the worldwide average for seawater softening processes.

The application of mathematical modeling revealed additional potentialities of the method [6, 7]; therefore, the properties of the cyclic self-sustaining ion-exchange processes should be studied in more detail.

The features examined in this study include:

- seawater softening with the aim of enhancing the life of the membrane or evaporator heating plate by reducing the Ca salt deposition;
- removal of Ca and other cations, such as Mg;
- the application of the process not only to seawater, but also to natural low-concentration solutions; and,

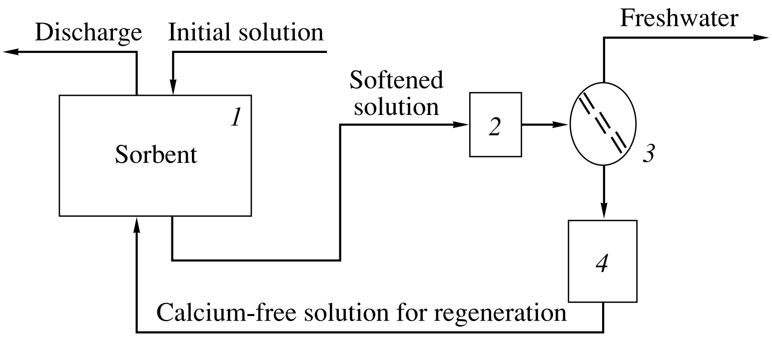

Fig. 1. Flow diagram of the self-sustaining softening–freshening process. (*1*) Cation exchange resin column, (*2*) freshening tank, (*3*) freshener (membrane or heating element), (*4*) brine accumulator.

- the production of separated concentrated solutions.

The availability of these features significantly extends the potentialities of the practical application of the process.

MATHEMATICAL MODEL

Studies with the aim of finding the model that best describes the cyclic ion exchange process were started in [5–10] and are continued in this paper. The objective of this work is to determine the functional form of the model, whose complexity in agreement with the accuracy of the available experimental data. The model is verified by comparing the numerical modeling results with the experimental data. The influence of various effects on the model's structure is examined, coefficients are evaluated, and the initial and boundary conditions are determined.

The obtained results allow us to conclude that the numerical model presented below adequately describes the ion exchange processes of the type considered.

The symbols used in this paper are listed in the Appendix.

The mathematical model of the cyclic self-sustaining process of ion exchange softening–freshening can be described by the following system of equations:

1. Mass balance equations

$$c_{\mathrm{Na}}^{\Sigma} = c_{\mathrm{Na^+}} + c_{\mathrm{NaSO_4^-}}, \quad c_{\mathrm{Ca}}^{\Sigma} = c_{\mathrm{Ca^{2+}}} + c_{\mathrm{CaSO_4}}, \quad c_{\mathrm{Mg}}^{\Sigma} = c_{\mathrm{Mg^{2+}}} + c_{\mathrm{MgSO_4}}, \tag{1}$$

$$c_{\mathrm{SO_4}}^{\Sigma} = c_{\mathrm{SO_4^{2-}}} + c_{\mathrm{NaSO_4^-}} + c_{\mathrm{CaSO_4}} + c_{\mathrm{MgSO_4}}, \quad c_{\mathrm{Cl}}^{\Sigma} = c_{\mathrm{Cl^-}}. \tag{2}$$

2. Equation for conversion from molar to molal concentration

$$m_{i,j} = c_{i,j}/(\rho - c_{i,j}M_{i,j} \times 10^{-3}), \quad i = \mathrm{Na^+, Ca^{2+}, Mg^{2+}}; \quad j = \mathrm{SO_4^{2-}, Cl^-}. \tag{3}$$

3. Equation for conversion from component concentrations to activities

$$a_i = m_i\gamma_i(I), \quad a_j = m_j\gamma_j(I), \quad a_{ij} = m_{ij}\gamma_{ij}(I). \tag{4}$$

The explicit form of the dependence of activity coefficients on the ionic strength of the solution is described below.

4. Transfer equation for cations and anions, respectively

$$\varepsilon\frac{\partial c_i^{\Sigma}}{\partial t} + v\frac{\partial c_i^{\Sigma}}{\partial x} + \frac{\partial \bar{c}_i}{\partial t} = 0, \tag{5}$$

$$\varepsilon\frac{\partial c_j^{\Sigma}}{\partial t} + v\frac{\partial c_j^{\Sigma}}{\partial x} = 0. \tag{6}$$

Equations (5) and (6) differ in that $\bar{c}_j = 0$, since the sorbent absorbs only cations.

Model solution characteristics. All concentrations are in mol/l

Experiment	Stage	Na	Ca	Mg	SO_4	Cl
no.	Sorption	0.45	0.01	0.06	0.06	0.47
(seawater)	Regeneration	0.675	0.015	0.09	0.09	0.705
no.	Sorption	0.9	0.00	0.12	0.12	0.9
(concentrated solution)	Regeneration	1.35	0.00	0.18	0.18	1.35

5. Equilibrium conditions for ion exchange between sorbent and solution phases (the law of mass action)

$$K_{\mathrm{Na}}\left(\frac{a_{\mathrm{Na}^+}}{\mu_{\mathrm{Na}}}\right) = K_{\mathrm{Ca}}\left(\frac{a_{\mathrm{Ca}^{2+}}}{\mu_{\mathrm{Ca}}}\right)^{1/2} = K_{\mathrm{Mg}}\left(\frac{a_{\mathrm{Mg}^{2+}}}{\mu_{\mathrm{Mg}}}\right)^{1/2}. \tag{7}$$

6. Ion exchange (interphase transport) kinetic equations:

$$\frac{\partial \bar{c}_i}{\partial t} = \beta_i(\mu_i - \bar{c}_i). \tag{8}$$

7. Electrical neutrality equation in the sorbent phase

$$\bar{c}_{\mathrm{Na}^+} + 2\bar{c}_{\mathrm{Mg}^{2+}} + 2\bar{c}_{\mathrm{Ca}^{2+}} = \bar{c}_{\Sigma}. \tag{9}$$

8. Complexation equilibrium conditions

$$k_{\mathrm{MgSO_4}} = \frac{a_{\mathrm{MgSO_4}}}{a_{\mathrm{Mg}^{2+}}a_{\mathrm{SO}_4^{2-}}}, \quad k_{\mathrm{CaSO_4}} = \frac{a_{\mathrm{CaSO_4}}}{a_{\mathrm{Ca}^{2+}}a_{\mathrm{SO}_4^{2-}}}. \tag{10}$$

9. The activities of components are evaluated by using the semiempirical Guggenheim formula

$$\ln(\gamma_{\pm})_{pq} = \ln(\gamma_{pq}) + \frac{z_p z_q}{z_p + z_q}\left(\sum_i \theta^*_{iq} m_i + \sum_j \theta^*_{pi} m_j\right). \tag{11}$$

The Debye–Huckel equation (12) was used to evaluate $\ln(\gamma_{pq})_{\mathrm{st}}$

$$\ln(\gamma_{pq})_{\mathrm{st}} = \frac{-z_p z_q I^{0.5}}{1 + I^{0.5}}, \tag{12}$$

$$\text{where } I = \frac{1}{2}\left(\sum_i m_i z_i^2 + \sum_j m_j z_j^2\right) \text{ is the ionic strength of the solution,} \tag{13}$$

$\theta^*_{iq}(I)$ is the pairwise interaction factor between the qth anion and the ith anion,

$\theta^*_{pj}(I)$ is the pairwise interaction factor between the pth anion and the jth anion.

The values of pairwise factors $\theta^*_{iq}(I)$ are derived from equations for clear electrolytes $\ln(\gamma_{\pm})_{pq} = \ln(\gamma_{pq})_{\mathrm{st}} + 2\frac{z_p z_q}{z_p + z_q}(\theta^*_{pq} m_p + \theta^*_{pq} m_q)$, since the value of $\ln(\gamma_{\pm})_{pq}$ for clear electrolytes is available from the tables. This allows $\theta^*_{iq}(I)$ to be evaluated and substituted into equation (11).

10. Equations relating the observed and calculated concentrations:

The model is complemented by an equation relating the observed concentrations with the concentrations at the outlet of the sorbent bed:

$$\frac{\partial C_i}{\partial t} = \frac{q}{V_P}(c_i^{\Sigma}|_{x = L} - C_i), \tag{14}$$

where V_p is the intermediate water volume in the measurement system and C_i is ith ion concentration measured in the experiment.

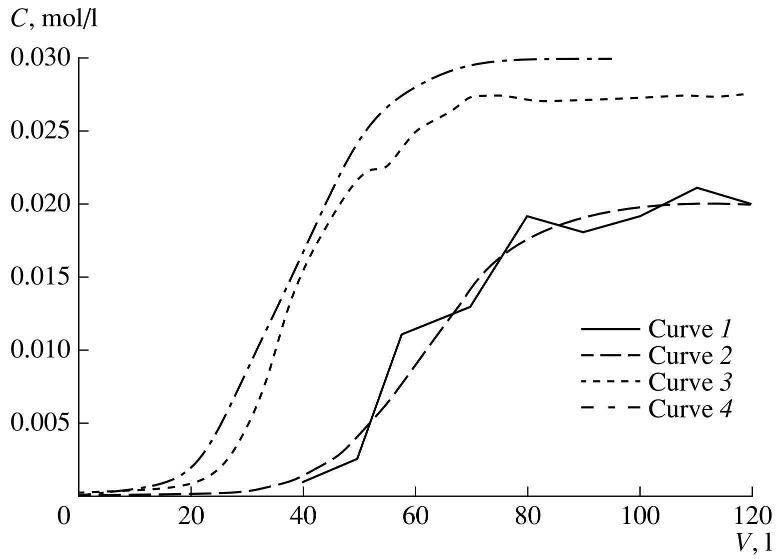

Fig. 2. Ca concentration [mol/l] at the outlet of the sorbent vs. the volume of solution [l] pumped during sorption.

Equation (14) is not used to describe the basic process. It is required to adequately compare the experimental and calculated results. The incorporation of (14) in the model is due to the procedure used to measure the ion concentration, where the concentration is measured not at the sorbent bed outlet but in a measurement device, i.e., there is an intermediate water volume between the outlet and the measurement point. The result is that the measured data characterize the concentration averaged over this water volume, rather than the instantaneous concentration.

11. The regeneration process is accompanied by the phenomenon of isothermal supersaturation by $CaSO_4$ [10]. If $CaSO_4$ concentration exceeds the solubility level, the current concentrations are to be recalculated to take into account the supersaturation effect. It is assumed in the model that only part of the Ca^{2+} and SO_4^{2-} ions is involved in the ion exchange, so that the resulting $CaSO_4$ concentration does not exceed the solubility level. The remaining Ca^{2+} and SO_4^{2-} ions merely move along with the solution.

12. The model is completed by initial and boundary conditions [6, 7].

VERIFICATION OF THE MATHEMATICAL MODEL

The model described above is based on the results of experimental data treatment [11]. Additionally, the model was verified by comparing the calculated and experimental data in a wider range of concentrations than before. For this purpose, several experiments were carried out in the Vernadsky Institute of Geochemistry, Moscow. The experiments followed the scheme shown in Fig. 1 and involved the sorption and regeneration of the sorption column by solutions simulating seawater (experiment 1) and by concentrated solutions (experiment 2). The concentrations of elements in the solutions are given in the table.

The verification criterion was the similarity of the following calculated and experimental variables:

(1) breakthrough calcium concentration curve for sorption process;

(2) calcium concentration curves at the exit from the regeneration process; and,

(3) the amount of $CaSO_4$ precipitate accumulated during regeneration.

Calcium was used as a representative element in the experimental verification of the mathematical model. This choice can be justified by the following circumstances: first, the major objective of the water softening process is the removal of calcium as the most hazardous element, which reduces the life of engineering equipment; second, calcium sulfate is poorly soluble, hence the gypsum precipitation can serve as a criterion; and third, the similarity of ion exchange properties allows the experimental results to be extended to the sorption and regeneration models of magnesium and other bivalent elements.

Figures 2 and 3 exemplify experimental and calculated breakthrough curves for sorption and regeneration, respectively.

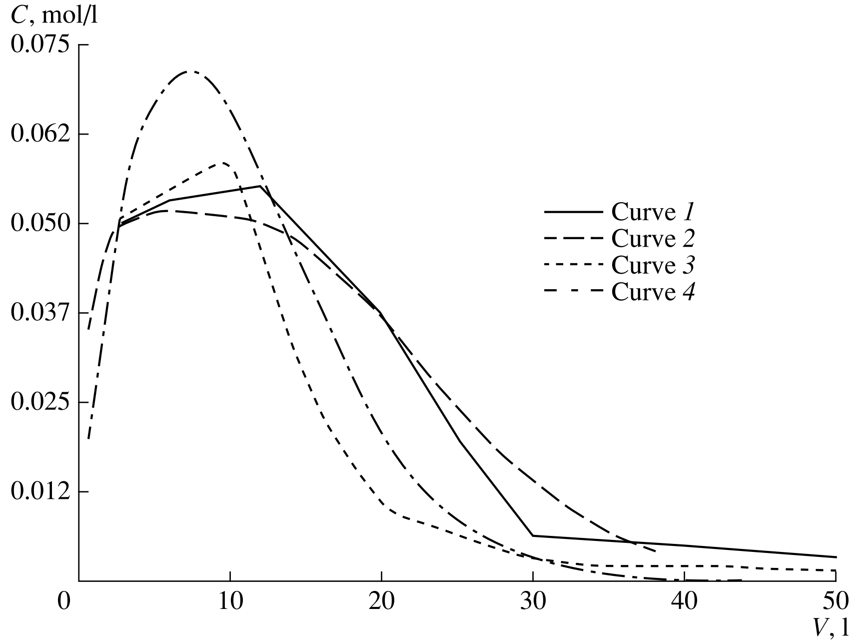

Fig. 3. Ca concentration [mol/l] at the outlet of the sorbent vs. the volume of solution [l] pumped during regeneration.

Curve *1* represents data obtained from experiment no. 1.

Curve *2* is obtained by numerical modeling of experiment no. 1.

Curve *3* represents data obtained from experiment no. 2.

Curve *4* is the result of the numerical modeling of experiment no. 2.

The results of the experimental verification of the model are as follows:

1. The model correctly predicts gypsum precipitation. No precipitation was recorded either in experiment no. 1 or in the appropriate calculation, while both experiment no. 2 and its numerical simulation featured such precipitation. The amount of precipitation in experiment no. 2 accounted for 4% of the total Ca amount, whereas the numerical model predicted it to be 3.5%. Such agreement can be regarded as satisfactory, considering the measurement errors in the experiment.

2. The shapes of the model and experimental curves in the sorption (Fig. 2) and regeneration (Fig. 3) processes have some common features, which confirm the adequacy of the major relationships underlying the model.

3. The model and experimental breakthrough concentration curves for a concentrated solution coincide (within the accuracy of the experiment) all over the regeneration process (curves *3* and *4* in Fig. 3). The maximum discrepancy between the experimental and calculated breakthrough concentrations for experiment no. 1 with seawater does not exceed 15% (curves *1* and *2* in Fig. 3). The respective discrepancy in the case of sorption (Fig. 2) also does not exceed 15%.

Thus, numerical modeling presents a good description at both the qualitative and quantitative (with allowance made for experimental accuracy) level and, hence, the mathematical model can be used to forecast the course of ion exchange process.

PROBLEM FORMULATION

The problems formulated and solved in this study are as follows:

1. It is shown that the cyclic process develops even in the absence of complexation, i.e., owing to the electric selectivity effect alone. However, the contribution of complexation can enhance the efficiency of the process.

2. Studies are carried out to examine the possibility of using the cyclic self-sustaining ion exchange process to remove not only Ca but also other selected cations, such as Mg, from the aquatic solution fed to the freshener.

3. The possibility to separate several selected cations in the regeneration process is examined. The best process scheme is chosen. An example is considered with three fractions of the solution being obtained from an initial solution containing two bivalent ions A and B: one fraction that is purified from these cations (output from the freshener) and the other two fractions consisting of concentrated solutions of each component alone. The concentrated solution is understood to be a solution with a higher relative concentration of the component. For definiteness, hereafter, we assume that cations A and B correspond to Ca and Mg.

4. The problem of softening slightly saline water with low sodium and high calcium is considered. The stability of the process is examined.

SOFTWARE IMPLEMENTATION

To solve this problem, a Cbased program was developed for the numerical solution of the system of equations presented above. The program was tested to ensure the absence of software errors and assess the errors of the method used to solve the system of equations. For this purpose, the calculation's results were compared with the results obtained by using analogous programs developed earlier for a narrower class of problems [6, 7]. The comparison of particular model results, obtained by different programs, shows them to be in good agreement. Some particular cases were verified analytically. These measures reduce the likelihood of software errors and increase the agreement between the experimental and numerical results.

THE RESULTS OF NUMERICAL MODELING

Problem no. 1. Studying the Effect of Complexation on the Attainment of a Steady-State Cyclic Regime

The examination of the cyclic process in the absence of complexation involved the simulation of a single-column process (Fig. 1) with the following sorbents: industrial KB4 and KU2; modified A ceolite [11] or a test sorbent. The test sorbent was a sorbent, whose properties could be varied in the course of the numerical modeling with the aim of reaching the desired result.

The chemical contents of the input solution, simulating seawater, was specified as follows:

1. ($C_{Na} = 0.4$; $C_{Ca} = 0.0095$; $C_{Mg} = 0.055$; $C_{SO_4} = 0$; $C_{Cl} = 0.529$);

2. ($C_{Na} = 0.4$; $C_{Ca} = 0.0095$; $C_{Mg} = 0.055$; $C_{SO_4} = 0.025$; $C_{Cl} = 0.497$).

Moreover, for the test sorbent, the process was also verified for a solution with a higher Ca concentration and the following composition:

3. ($C_{Na} = 0.4$; $C_{Ca} = 0.1$; $C_{Mg} = 0.055$; $C_{SO_4} = 0.115$; $C_{Cl} = 0.48$);

Hereafter, all concentrations are expressed in terms of [mol/l].

Clearly, no complexation takes place in the first case ($C_{SO_4} = 0$). Therefore, the process works only owing to the electric selectivity effect. The results of numerical modeling show that, under the given conditions, the cyclic process is fulfilled for all sorbents considered. With complex-forming SO_4 ions added to the solution (the second model solution), the stationary cyclic regime will be attained in a shorter time (in a smaller number of cycles), and the speed of attaining the steady-state regime will be maximum when the amount of SO_4 is sufficient to make the solution supersaturated during regeneration.

The test sorbent was chosen to illustrate the case when the electric-selectivity effect alone is not enough to induce cyclic regime. Alternative calculations were used to select the characteristics of a sorbent whose coefficients K used in the mass action law (7) are $K_{Na} = 1$, $K_{Ca} = 4$, and $K_{Mg} = 1.2$, whereas the characteristic exchange time between the solution and the sorbent was assumed to be (about) several minutes. It was found that the process would not develop (given such characteristics of the test sorbent) if there were no SO_4 ions in solution, i.e., no complexation. However, the presence of complexation supports the process and allows it to reach a steady-state regime after 7 cycles with supersaturation taken into account (i.e., when calcium sulfate solubility is low enough to allow precipitation) and after 10 cycles without supersaturation. In the latter case, the solubility of calcium sulfate is sufficiently high to prevent precipitation.

Thus, the studies showed that the cyclic process for seawater occurs for both of the industrial sorbents, as well as for the modified ceolite A, even when the model takes into account only ionic exchanges based on the effect of electric selectivity (i.e., when complexation factors k in (10) are zero). However, equations (10) are indispensable, since complexation enhances the efficiency of the process and, taking it into account in the model, allows the operation of an ion exchange plant to be evaluated more adequately [6].

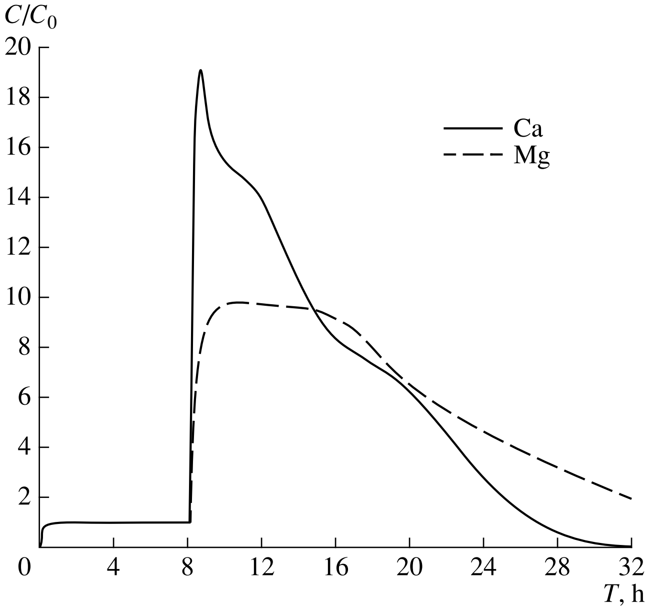

Fig. 4. Breakthrough concentration curve in regeneration process vs. time. Each concentration is divided by the input concentration of the appropriate component in the input solution.

Additionally, it was found that there exist sorbent characteristic values with which the effect of electric selectivity alone is not enough to support the formation of a self-sustaining process. Therefore, in some cases, the inclusion of complexation in the model may radically change the estimate of the possible occurence of such a process.

Problem no. 2. Modeling an Ion Exchange Process in Two Sorption Columns

A multicolumn variant of the process was used to examine the problems of water purification from several cations and their separation in concentrated forms. The multication purification was implemented by replacing a single sorbent (see the flow diagram in Fig. 1) by several successive columns with sorbents, each sorbing one of the cations to be removed from the solution before feeding to the freshener. To illustrate the procedure, the results obtained for the case of two sorbents, used to remove Ca and Mg cations from the solution, are presented. Alternative calculations carried out for these cations showed the most efficient pair among the sorbents listed above to be modified ceolite A and the industrial sorbent KB4, respectively. Seawater ($C_{Na} = 0.4$; $C_{Ca} = 0.01$; $C_{Mg} = 0.06$; $C_{SO_4} = 0.025$; $C_{Cl} = 0.48$) was used as the initial solution. The concentration of Ca and Mg in the solution that forms in the desalination tank after sorption does not exceed the *f*th portion of the input solution concentration (in this case, $f = 1\%$ for Ca and Mg). As can be seen from Fig. 4, with the evaporation coefficient of $\Phi = 5$, the resulting concentrated output mixture of Ca and Mg (“Discharge” arrow in Fig. 1) will feature the concentrations of Mg and Ca that are 9.8 and 19 times higher (respectively) than those in the input solution.

Thus, to obtain, in the desalination tank, an aquatic solution purified of several selected cations, it is sufficient to use the system shown in Fig. 1, where a single sorbent column is replaced by several successive columns with different sorbents, each removing a certain cation.

Problem no. 3. Modeling Cation Separation

For studying the possibility of separating several selected cations in a concentrated form, the flow diagram of the process was somewhat modified (Fig. 5). As noted above, if each sorbent is selective to a specific cation, these sorbents will be mostly saturated by these very cations. Now, if part of the regeneration flow after the second sorbent is removed from the process, rather than sent to the regeneration of the first sorbent, we will obtain a concentrated solution of the given cation at the outlet from the second sorbent (point E_6 and path 6 in Fig. 5).

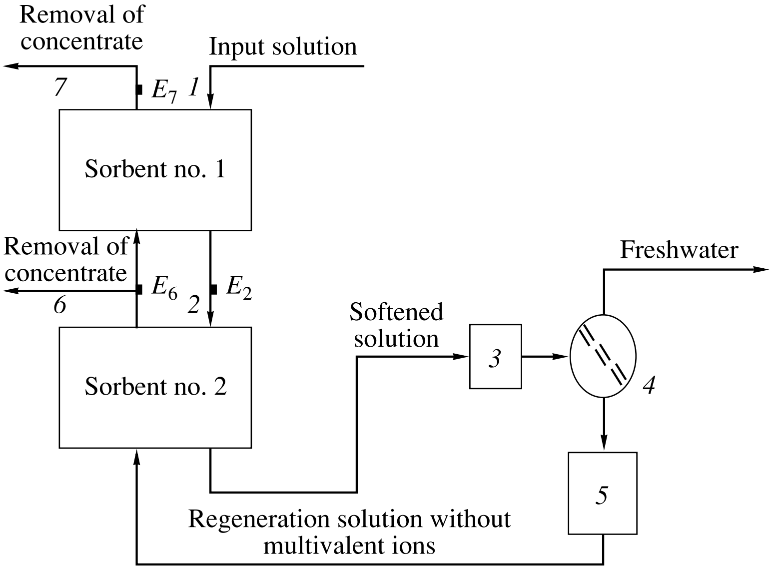

Fig. 5. Flow diagram of a multicolumn cyclic self-sustaining ion exchange process for the softening–freshening of aquatic solutions with separation of components. (1, 2) Columns with cation-exchange resin, (3) freshening tank, (4) freshener, and (5) brine retention tank.

It is worth mentioning that the regeneration quality of sorbent no. 1 (Fig. 5) deteriorates in the process of the separation of these elements (Fig. 5), since the solution volume involved in the process decreases relative to the previous problem because of the removal of part of solution via path 6. Thus, if the task is merely to remove several polyvalent elements from the solution without their separation, one should use the basic scheme of the cyclic process (Fig. 1), where the sorption column consists of a number of series-arranged sorbents, each being selective to one of the elements.

The major problem in the separation of elements (problem no. 3) is to evaluate the volume of the solution that will be left after the partial withdrawal and that will be used to regenerate the other sorbents. Clearly, such a process can proceed only within a limited range of parameter values. The optimal volume of the solution, corresponding to the number of available sorption columns, and the concentrations of components in the solution coming from the columns were estimated by using alternative calculations on mathematical models.

This paper presents the results of modeling a cyclic process with 2 sorbents. Sorbent no. 1 was modified ceolite, and sorbent no. 2 was the industrial sorbent KB4.

The evaporation coefficient for the solution in the tank between the sorption and regeneration stages was taken to be $\Phi = 5$.

The output solution of the second column (arrow 6 in Fig. 5) contains 70% of the Mg contained in the initial solution, while the mean Mg concentration in the output solution is 8 times as high as that in the initial solution (Fig. 6). Introducing a factor of the relative increase in the concentration between the two elements as $R_B^A = (c_A/c_B)^{\text{regeneration}}/(c_A/c_B)^{\text{initial solution}}$, where c denotes the mean concentration in a portion of the solution, we obtain the first portion of the solution (passing via path 6) having $R_{\text{Ca}}^{\text{Mg}} \geq 500$.

As shown in Fig. 7, the output solution from the first sorbent (arrow 7 in Fig. 5) has a mean annual Ca concentration 15.4 times as large as its concentration in the input (initial) solution (with no allowance made for the dead volume, i.e., the volume of solution remaining in the sorbent at the moment when the sorption is stopped). The coefficient of the relative increase in the Mg concentration relative to Ca in the second portion will be $R_{\text{Ca}}^{\text{Mg}} = 4$ (again with no allowance made for the dead volume).

It can be easily seen that between 4 and 18 hours from the beginning of the regeneration process, the solution from the tank (after the passage of sorbent no. 2) was discharged from the system and did not take part in the process any further, since it left the system via path 6 (Fig. 5).

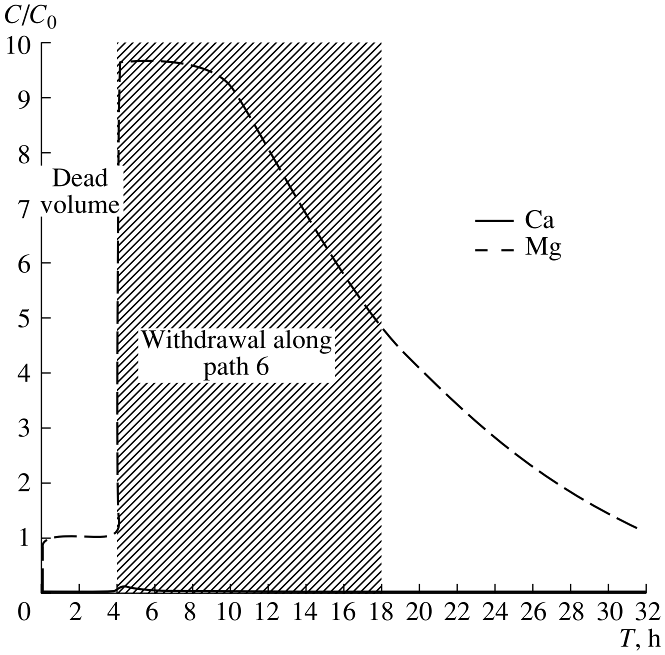

Fig. 6. Time dependence of the component concentrations in the solution approaching the end of the 2nd sorbent (nearest to the tank) in the regeneration process (point E_6 in Fig. 5). Each concentration is divided by the input concentration of the appropriate component in the sorption process (i.e., by the component concentration in the input solution).

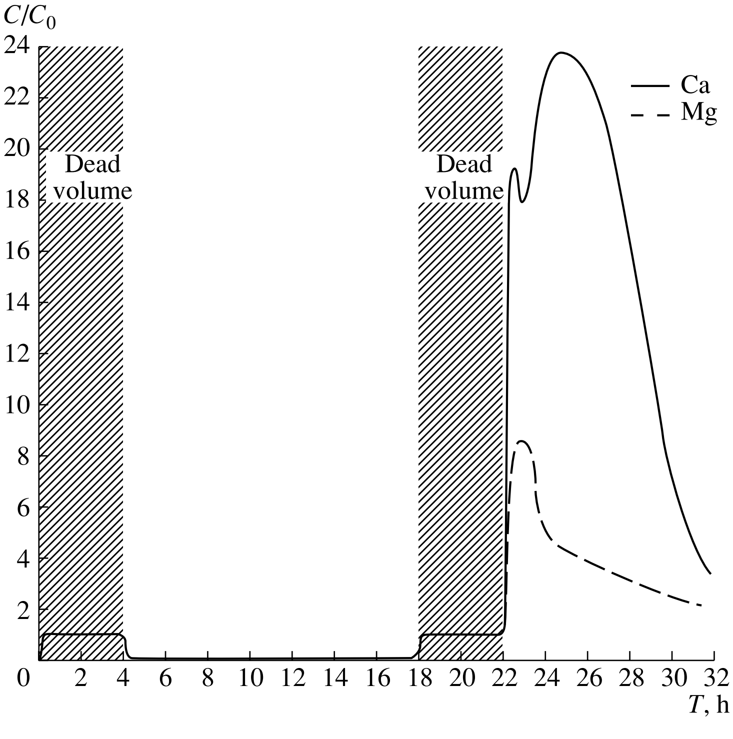

Fig. 7. Time dependence of component concentrations in the solution coming from the 1st sorbent in the regeneration process (point E7 in Fig. 5). Each concentration is divided by the input concentration of the appropriate component in the sorption process (i.e., by the concentration of the component in the input solution).

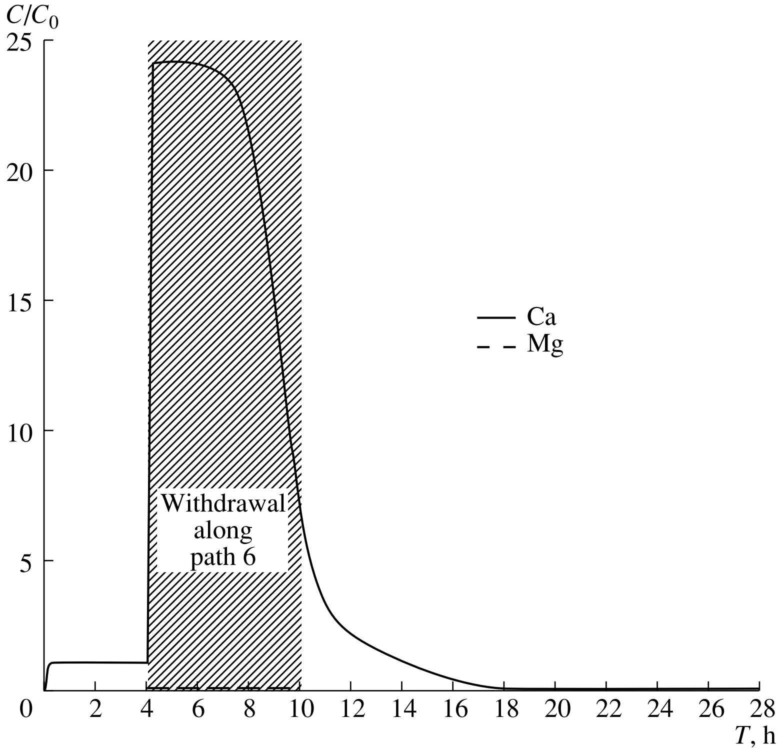

Fig. 8. Time dependence of component concentrations in the solution near the end of the 2nd (near the tank) sorbent during regeneration (point E_6 in Fig. 5). All concentrations are normalized by dividing by the input concentrations for the sorption process (initial solution concentrations).

Note that Na occurs in all portions of the water. This is quite natural, as the cyclic ion exchange process is based on the electric selectivity effect [3], that is, Na is a working substance of the process and all ionic processes in the sorbent (replacements) of multivalent cations take place on account of Na.

Thus, the use of the sorbents mentioned above for seawater makes it possible to implement a scheme for the separation of two cations on two sorbents (modified ceolite A and industrial sorbent KB4).

Studying the best scheme for implementing the process revealed the following regularity, associated with the arrangement order of the sorbents. Sorbent no. 2 should be chosen to be selective with respect to Ca, if it is completely purified during regeneration. However, when the solution in the system after regeneration is supersaturated with Ca, sorbent no. 2 should be selected to be selective to Mg.

The second example, considered below, refers to the case where sorbent no. 2, selective to Mg (modified ceolite A), is used as the second sorbent. The first sorbent is taken to be a test sorbent, selective to Mg and nonselective to Ca and having K coefficients in formula (7) $K_{Na} = 1$, $K_{Ca} = 0.2$, and $K_{Mg} = 2$. In order to enhance the purification efficiency, ceolite A was located closer to the tank (sorbent no. 2), since it is completely purified during the regeneration.

The solution coming from ceolite A (arrow 6 in Fig. 5) contains 86% of the Ca entering the sorption stage (in the initial solution), and the mean Ca concentration in the output solution is 20 times as high as that in the input solution (Fig. 8), while almost no Mg reaches this sorbent.

As it is shown in Fig. 9, the solution coming from the test sorbent (arrow 7 in Fig. 5) has a mean Mg concentration that is 9 times higher than that in the input (initial) solution (with no allowance made for the dead volume). The coefficient of the relative increase in the Mg concentration relative to Ca in the second portion is $R_{Ca}^{Mg} = 11$ (with no allowance made for the dead volume).

As is evident from the foregoing, the overall characteristics in the second case are somewhat better.

Thus, it is clear that a simple modification of the process flow diagram (see Fig. 5) allows one to obtain, in addition to purified water, concentrated solutions of separated cations.

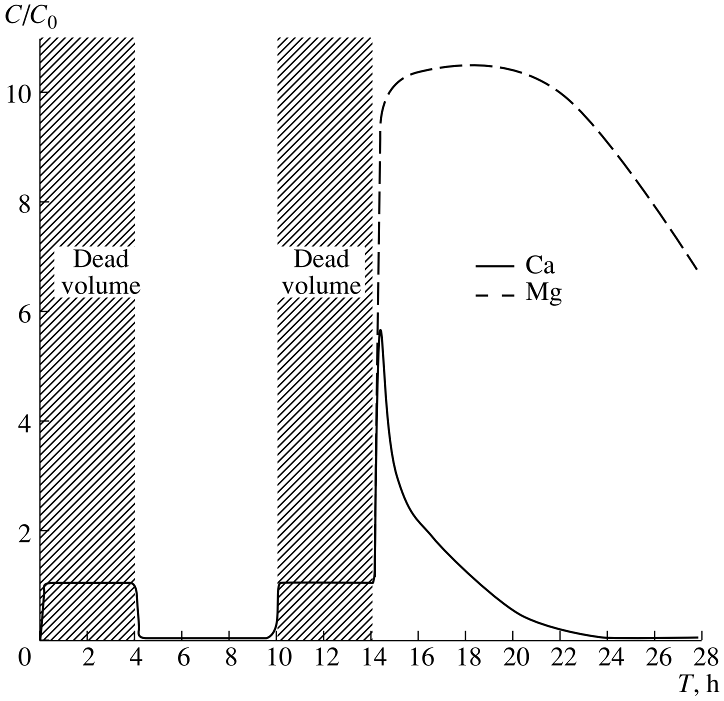

Fig. 9. Time dependence of component concentrations in the solution coming out from the 2nd sorbent during regeneration (point E_7 in Fig. 5). Between 4 and 10 hours from the beginning, the solution from the tank (after the passage of the 2nd sorbent) was discharged from the system, thus being withdrawn from the process (line 6 in Fig. 5). All concentrations are normalized by dividing the initial solution by the input concentrations for the sorption process.

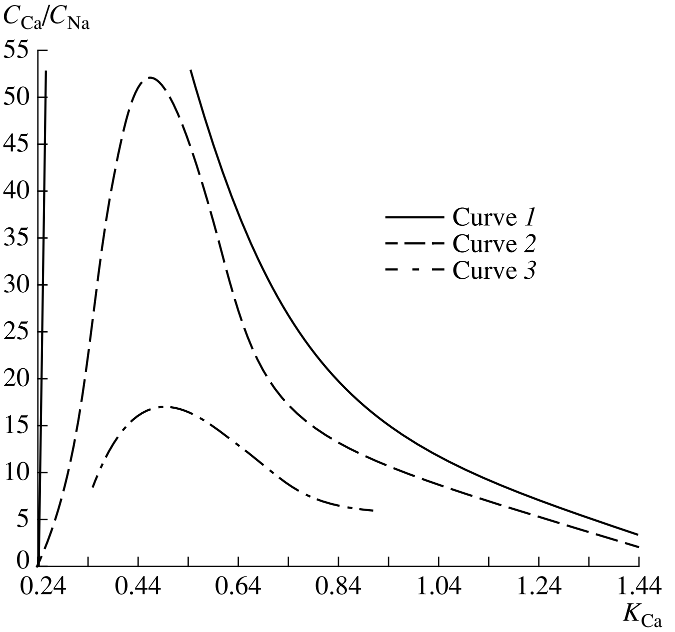

Fig. 10. The maximum value of C_{Ca}/C_{Na} in the initial solution vs. the values of K_{Ca} at different kinetic factors. The model parameters at which the cyclic softening process is still feasible are simulated. The rate of solution feed to the sorbent (1 l in volume) was 10 l/h. The duration of the second cycle was one quarter less than that of the first one ($k = 4/3$). Curve *1*: $\beta = 30$ 1/h; curve *2*: $\beta = 20$ 1/h; curve *3*: $\beta = 10$ 1/h.

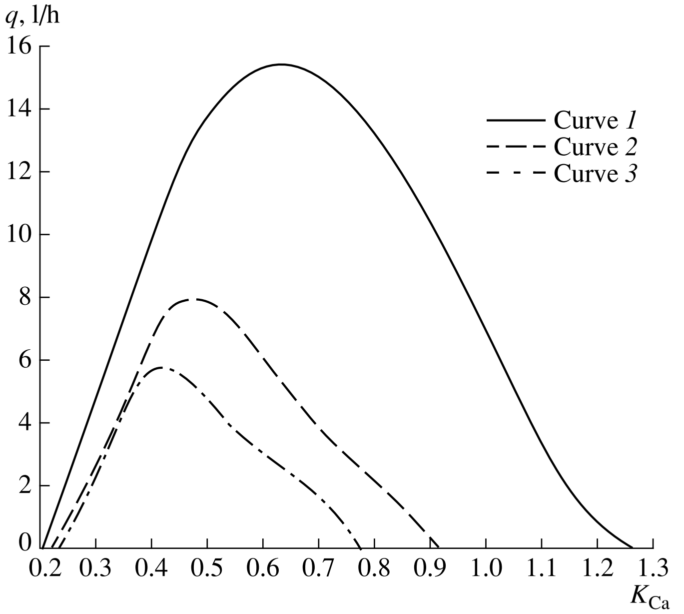

Fig. 11. The maximum volumetric solution flow rate at which the cyclic softening process is still feasible as a function of K_{Ca} at different input concentrations. The duration of the second cycle is reduced by k = 20/17 times relative to that of the first cycle. Sorbent volume is 1 l.

Curve *1*: C_{Na} = 0.01 mol/l, C_{Ca} = 0.048 mol/l; curve *2*: C_{Na} = 0.002 mol/l, C_{Ca} = 0.052 mol/l; curve *3*: C_{Na} = 0.001 mol/l, C_{Ca} = 0.0525 mol/l.

Problem no. 4. Studying the Preconditioning Process of Slightly Saline Waters

The so-called difficult-to-treat, i.e., calcium-rich, waters are often met in practice; therefore, it makes sense to find the threshold concentrations of elements in the initial solution at which the cyclic process can still be implemented. As it will be shown below, the process proceeds even when the Na concentration is appreciably smaller than the Ca concentration, though at first glance, one has nothing to regenerate the sorbent with. This situation will also be elucidated.

Figure 12 gives the results of calculations showing that the cyclic self-sustaining process can be implemented within a wide range of concentrations (at least for the calcium-to-sodium input concentration ratio of up to 52).

It is worth mentioning that the range of admissible values of K_{Ca} coefficients significantly depends on the kinetic coefficients β (Fig. 10) for these types of processes. For example, with the kinetic coefficients β = 10 1/h and the sorption column volume of 1 l, the cyclic process can be implemented at the solution flow rate in the sorbent of *q* = 10 l/h with K_{Ca} varying from 0.38 to 0.70.

Figure 10 gives the results of studying the process at several fixed concentrations of sodium and calcium in the initial solution. These results allow one to determine the maximum possible rate of solution flow through the sorbent of volume 1 l at which the cyclic process is still feasible as a function of K_{Ca}.

Figure 11 allows one to determine the variation range of ion exchange equilibrium coefficients at which the cyclic process is feasible for different input concentrations of sodium and calcium and a fixed solution flow rate through the sorbent. For example, with the calcium-to-sodium concentration ratio of 52, the cyclic process is feasible with the coefficient K_{Ca} varying from 0.34 to 0.54, if the flow rate through the sorbent *q* = 4 l/h.

The value of K_{Ca} at which the maximum possible rate of sorbent flow through the sorbent can be attained can also be found from Fig. 11. Thus, if the goal is formulated as the implementation of the process at the maximum possible speed, different solutions will require different sorbents. When the calcium concentration increases relative to the sodium concentration, the peaks of the curves shift to the right, i.e., K_{Ca} tends to 0.4.

Note that Fig. 10 was constructed at a fixed rate of solution flow *q* through the sorbent, while Fig. 11 was constructed at a fixed β.

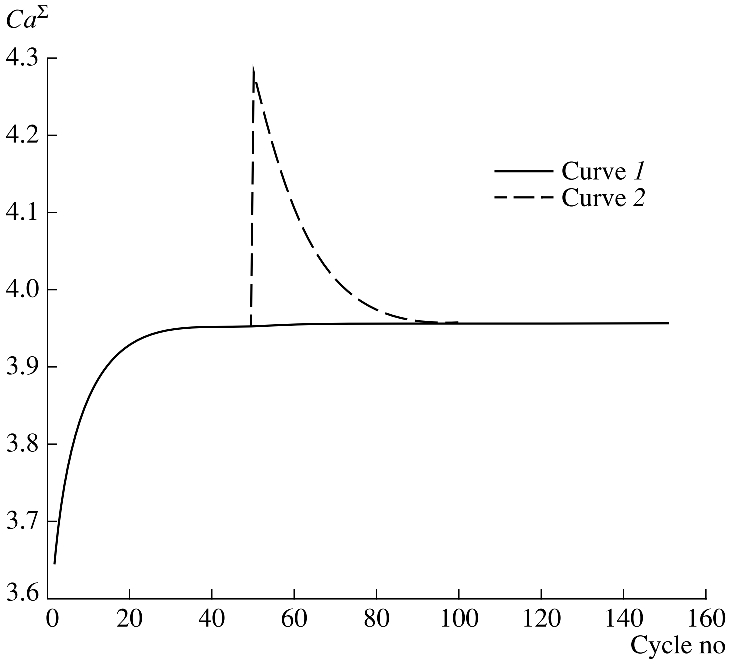

Fig. 12. The total amount of calcium in the sorption column as a function of the number of cycles after the sorption process: Curve *1*: undisturbed cyclic process; curve *2*: cyclic process with a perturbation at the 50th cycle.

Before the results of the numerical calculations became available, the authors expected the process to attain the cyclic regime only if sodium concentration is much higher than that of calcium, since sodium is the major component for washing calcium from the sorption column. However, simulation has shown that the process also proceeds when the initial solution contains much more calcium than sodium. Let us elucidate this effect.

In the beginning of each cycle, the sorbent mostly contains sodium. During sorption, calcium ions accumulate in the sorbent, replacing sodium ions. The replaced sodium accumulates in the retention tank 2 (Fig. 1). Therefore, the brine used to regenerate the sorption column contains considerable amounts of sodium even though its concentration in the initial solution is low. This is the sodium that has entered the system in the initial solution plus the sodium contained in the column at the beginning of the cycle. All this sodium, which is quite abundant, takes part in the regeneration process, and only a small part of it is spent for the exchange with external installations. The cyclic character of the process is ensured by the fact that the amount of the sodium that enters the system during sorption and the amount coming out from the system during regeneration are equal.

In the context of the above explanation, the question arises as to what will happen if part of the sodium leaves the system for some reason.

A study of the process's stability was carried out to answer this question. For this purpose, a perturbation was introduced into the system by a one-time 15% reduction of the regeneration time. The remaining 15% of the solution intended for regeneration was removed in the simulated process, i.e., did not participate in the regeneration process. This is equivalent to a loss of sodium from the system. After that, the sorption and regeneration processes were simulated in completely the same manner as before the leakage.

Figure 12 gives the dependence of the total amount of calcium as a function of the cycle number for two processes: an undisturbed cyclic process and a process with a leakage simulated at the 50th cycle. As can be seen from the plot, the process has returned to the undisturbed state and the consequence of the perturbation disappeared within several subsequent cycles. This allows us to conclude that the simulated loss of sodium is compensated for at the expense of the initial solution. Note that the stability of the process can be of considerable practical importance for real industrial ion exchange systems, whose operation is commonly accompanied by small losses of useful reagents.

The application of such a process to "difficult" waters, i.e., waters with a calcium sulfate concentration close to saturation, has one more advantage. For such waters, the concentration product of Ca^{2+} and SO_4^{2-} ions in the sorption process accounts for a considerable portion of such a product in a saturated solution.

When the clear water is withdrawn, the solution volume decreases by a factor of p, while the amounts of Ca^{2+} and SO_4^{2-} do not change. Therefore, the calcium sulfate concentration in the solution coming out from the system increases by about p times relative to the input solution. This suggests that the solution becomes supersaturated during regeneration. Because of isothermal supersaturation, calcium sulfate precipitates in the form of solid residue after the solution has left the sorption column rather then in the column itself [10]. Thus, after each cycle we have a considerable amount of $CaSO_4$ in the form of solid residue, which can be extracted without any additional processing procedures.

CONCLUSIONS

In this study, a mathematical model and computer software were developed to enable the simulation of a cyclic self-sustaining process of ion exchange softening of natural waters.

The model was verified against the results of experimental studies and tested by a series of parallel calculations also using analogous programs written in other programming languages, as well as by comparison with analytical solutions for some particular cases.

The results of numerical modeling in this study are as follows:

1. The effect of complexation on the attainment of a cyclic regime was assessed, and the formation of a cyclic process was proved to be feasible for seawater with real industrial sorbents in the absence of complexation at the expense of electric selectivity alone.
2. The best operation regime was found for a purification plant including two sorption columns. The proposed scheme of natural-water purification from a set of bivalent elements was studied, and its operability at the specified parameters was demonstrated.
3. It was shown that portions of concentrated solutions of individual bivalent cations could be separated. The efficiency of the process was studied as a function of the distribution of solution flows sent for the removal (withdrawal of a concentrated solution of a cation after sorption) and regeneration of subsequent sorbents.
4. The feasibility of softening slightly saline water with low sodium and high calcium was proved. The stability of the process was examined.

APPENDIX

List of symbols

a_i activity of the ith positive ion

a_j activity of the jth negative ion

a_{ij} activity of solution component in molecular form

c_i concentration of the ith cation (i = Na^+, Ca^{2+}, Mg^{2+})

c_j concentration of the jth anion (j = SO_4^{2-}, Cl^-)

$\bar{c}_i$ concentration of the ith cation in the sorbent [g-ion/l]

c_{ij} molar concentration of ij compounds (ij = $NaSO_4^-$, $MgSO_4$, $CaSO_4$) in the solution, measured in mol/l

$c_{i,j}^{\Sigma}$ total molar concentration of substance in solution

$\bar{c}_{\Sigma}$ sorbent capacity [g-equiv/l]

K_i ion exchange equilibrium coefficient

k_{ij} thermodynamic stability constant of the ijth compound (complex)

L sorption column length

M_i molecular mass of component (g-mol (g-ion))

m_i molal concentration of ions in solution (g-ion (mol)/kg H_2O)

m_{ij} molal concentrations of salts in solution in undissociated (molecular) form

R dimensionless coefficient

R_B^A relative concentration amplification factor between cations A and B: $R_B^A = (c_A/c_B)^{\text{Regeneration}}/(c_A/c_B)^{\text{Sorption}}$. Here c is the mean concentration in the water portion

t time

V_p is the effective intermediate water volume at the outlet from the sorption column

x coordinate along the column

z_i, z_p, z_j, z_q charges of ions i and p (i, p = Na^+, Ca^{2+}, Mg^{2+}) and j and q (j, q = SO_4^{2-}, Cl^-)

β_i kinetic mass transfer factor for the ith ion

γ_i activity coefficients

$(\gamma_{pq})_{st}$ “stable part” of the mean ionic activity coefficient of component pq

$(\gamma_\pm)_{pq}$ mean ionic activity coefficient of component pq

ε sorbent bed porosity

μ_i equilibrium concentration of the ith ion in the sorbent [g-ion/l]

v linear speed of solution

ρ solution density (kg/l)

$\theta_{iq}(I)$ weight coefficients in Guggenheim equation

Φ solution evaporation factor

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