INVESTIGATION OF CYCLIC SELF-SUSTAINING ION EXCHANGE PROCESS FOR SOFTENING WATER SOLUTIONS ON THE BASIS OF MATHEMATICAL MODELING

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Abstract

New possibilities of using ion exchange pretreatment of saline waters to desalination, with a view to removal of scale forming components, such as calcium and magnesium, are considered in the paper. A cyclic self-sustaining process driven by electro-selectivity effect is discussed. In this process, no additional chemicals, except for brines formed during desalination, are required for regeneration of ion-exchanger in operation cycles. The paper deals with the development of a computer model for description and prediction of the performance of ion exchange columns. Theoretical description and modeling assumptions included the set of differential equations of mass balance, initial, boundary and operational conditions. The impact of the phenomenon of isothermal supersaturation of solutions in ion exchange bed was taken into consideration. Correlations between observations and calculations were tested. The mathematical model was verified by experiments carried out with seawater and a model solution of brackish water and with modified zeolite of A-type which was used as a softening cation-exchanger. Experimental break-through curves (concentration histories) were fitted by calculation data with a good accuracy. Issues related to the choice of optimal parameters were addressed. The stability of the process was analysed in case of a leakage of solutions. The results of investigation demonstrate the possibility of maintaining the cyclic self-sustaining process in a wide range of compositions of raw solutions.

Introduction

Ion exchange is widely applied in various industrial technologies, especially, in water preparing for power plants, as well as for waste water treatment. At the same time, deep demineralization or softening processes which can be efficiently performed with the use of

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ion-exchangers are advisable for surface and underground raw waters of low mineral content. It is mainly related to operation costs for regeneration of resins in work cycles. The higher is the concentration of dissolved salts in water, the more often resins need to be regenerated.

Different approaches were proposed to solve the regeneration problems, even to avoid the application of chemical reactants. An example is the Sirotherm process (CSP) in which sorption and desorption effects in operation cycles are realized with the use of special poly-ampholite sorbents with thermo-regulated properties. Cold work solution is demineralized at its passing through a sorption bed, regeneration of the sorbent is performed with the same solution in hot form. The CSP technology was developed by Brayen Bolto [1], it was successfully used for treatment of slightly saline and brackish waters.

Another approach connected with processing more saline waters was proposed by Klein G. and co-authors [2-3] for treatment of seawater prior to its further desalination, where deep decalcination would solve the problems of gypsum core formation on heating surfaces of distillers or membrane clogging in reverse osmosis devices. The main idea suggested for solving the problem and called as the "self-sustaining" coupled process (SS) of softening and desalination seemed to be evident and could be formulated as follows:

- to use an approciate cation-exchanger for strong decalcination of initial seawater;

- to carry out its regeneration by brine which appears after a desalination cycle and is returned to the head of the process.

A thermodynamic basis for the validity of such an idea is the effect called "electro-selectivity" [4] or the concentration-valency-effect [5]. In line with this effect, the efficiency of the regeneration process is provided by the decrease of sorbent selectivity toward bivalent Ca^{2+} versus mono-valent Na^+ in a more concentrated solution with the same equivalent ratio of these ions.

In practice, the efficient SS-process, in form of many recurring cycles of sorption-regeneration, turned out difficult for implementation. First experimental attempts were made to solve a seawater pretreatment problem with the use of strong acid cation-exchanger with sulfonic functional groups, however pilot tests showed its low efficiency [3]. D. Barba and co-authors [6] were the firsts who tried to predict theoretically special requirements to cationic resins which could ensure the feasibility of the cyclic SS-process. They used an equilibrium model of ion-exchange dynamics and showed the prospects of using sorption materials with extra-high selectivity toward Ca^{2+} over Mg^{2+}. Ion-exchange resins, namely, Activite and Taylor-made cationic exchangers, containing more than one sulfonic acid group per aromatic ring in their structure [6], as well as specially modified inorganic polymers like artificial zeolites of A-type [7] were proposed for this purpose. Further computation of

successive cycles of SS-process with the use of a general dynamic model at a different variety of parameters allowed clarification of the requirements to sorbent characteristics and operation conditions [7-9]. For example, it was shown that deep desalination of seawater with the production of highly concentrated brine leads to the formation of super-saturated solution of gypsum at a stage of regeneration, and it additionally shifts the equilibrium of the process to a desirable direction. The generalized results of theoretical and experimental studies of seawater decalcification using the electroselectivity and supersaturation effects to maintain the feasible SS-process are presented in book [10].

Until recently, it seemed that the cyclic SS-processes can be realized only for the treatment of solutions like seawater which contain the exceeding concentrations of sodium compared with calcium ions. At the same time, desalination processes are important for a wide range of natural and waste waters. Often, they contain large quantities of calcium sulfate, close to gypsum saturation. Therefore, direct application of demineralization methods, including membrane technologies, is impossible due to precipitation of gypsum on membranes in concentrating sections. Today, any large metallurgical or hydrometallurgical plant in the World produces annually millions of cubic meters of such waste waters which should be treated. A typical example is the Russian metallurgical "Norilskiy Nickel" company which needs to treat about 3,000,000 m^3/year of waste waters, enriched with calcium sulfate [11]. A large variety of natural low saline waters which can be considered as the potential sources for fresh water, are characterized by the excesses of concentration of Ca^{2+} compared with Na^+.

This paper, on the basis of mathematical modeling technique, demonstrates that a cyclic SS ion exchange process can be also applied for treatment of solutions containing the exceeding concentrations of calcium. This is not obvious a priory because sodium is the main component for calcium elution during regeneration and it is not immediately clear how calcium can be eluted from the sorbent bed in cyclic processes.

Experimental Part

Materials and methods

Experiments were carried out with the use of modified zeolite-A [7, 9]. The total cation exchange capacity of the ion-exchanger was estimated to be $\overline{c}_\Sigma = 4.4 \, eq/l$. Sorption columns were loaded by the granules of 0.75±0.1 mm in diameter. Seawater and the model solution of reverse osmosis brine, as shown in Table 1, were used in experiments.

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Test equipment and experiments

A schematic diagram of the cyclic SS softening-desalination process is drawn in Figure 1. A bench-scale experimental equipment consisted of the columns 1 and 5 with a sorbent bed L=40 cm, S=100 cm^2 in each one, collecting tanks 2 and 4, and the quadruple effect distillation (MED) unit for 20 l/h of fresh water was used. Initially, the cation-exchanger in both columns was in Na-form. The solutions No 1 or No 2 passed through one of the sorbent beds, for example in column 1, with a fixed flow rate until the calcium average concentration of calcium c_f in the softening tank 2 reached a certain fixed level $f = c_f / c_{0,Ca}$ of the concentration in the initial solution (for example, **f** was assumed in calculations to be 0.01). After that, softened water from the tank 2 was processed in the distillation unit with the production of two portions: ϕ - as the fresh water and $(1-\phi)$-portion as the concentrated brine recycled for sorbent regeneration. Starting from this point, the columns 1 and 5 both were introduced into operation, alternately in sorption and regeneration modes. Since the sorbent was not completely decalcinated at the regeneration stage, the second cycle, compared with the first one, had less duration. Starting from the 3-rd cycle, a stationary-state regime took place, the according effluents from columns were analyzed for drawing concentration history curves.

Theoretical Description

Mathematical model

The processes studied were ion exchange reactions between calcium, magnesium and sodium ions:

$$2\underline{R^-Na^+} + Ca^{2+} = \underline{R_2^-Ca^{2+}} + 2Na^+$$
$$2\underline{R^-Na^+} + Mg^{2+} = \underline{R_2^-Mg^{2+}} + 2Na^+$$
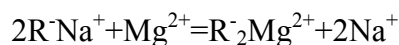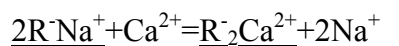
Underlined quantities refer to species in the resin phase

The ion exchange process discussed can be described within the bounds of the following mathematical model. This model generalizes results of studies described in [9, 12-14]. There has been shown that it is acceptable to use the model to fit the experimental data.

When developing the mathematical model the following factors were taken into account:

- ion exchange kinetics between the solution and sorbent (interphase transfer);
- longitudinal mass transfer (ions Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^- and their compounds);
- ion exchange equilibrium between the sorbent and solution;

- formation of sulfate compounds by Ca^{2+} и Mg^{2+} ions in the solution;

- phenomenon of isothermal supersaturation investigated in [12-14].

The system of equations describes the process dynamics in the column and balance correlation between component concentrations in the system.

Conditions of mass balance:

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

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

Differential mass balance in the column for cations and anions, correspondingly:

$$\varepsilon \frac{\partial c_i^{\Sigma}}{\partial t} + v \frac{\partial c_i^{\Sigma}}{\partial x} + \frac{\partial \overline{c}_i}{\partial t} = 0 \tag{3}$$

$$\varepsilon \frac{\partial c_j^{\Sigma}}{\partial t} + v \frac{\partial c_j^{\Sigma}}{\partial x} = 0 \tag{4}$$

Equations (3) and (4) differ from each other due to $\overline{c}_j = 0$, because the sorbent absorbs cations only.

Equations of ion exchange kinetics (interphase transfer):

Kinetics of the process is described by the linear-driving-force approach.

$$\frac{\partial \overline{c}_i}{\partial t} = \beta_i \left(\mu_i - \overline{c}_i \right) = \beta_i^{film} \left(a_i - \eta_i \right) \tag{5}$$

Mass transfer coefficient β_i^{film} in the ion exchange column can be found by the following equation [15, 16]:

$$\beta_i^{film} = 0.01 \frac{v^{0.47}}{d^{1.53}} \text{ [cm/sec]} \tag{6}$$

Preliminary calculations with the use of Helfferich diffusion criterion for non-linear isotherms [4] showed a minor influence of the film diffusion stage.

Conditions for ion exchange equilibrium between the sorbent and solution phases (active mass law):

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

Electroneutrality condition in the sorbent phase:

$$\overline{c}_{Na^+} + 2\overline{c}_{Mg^{2+}} + 2\overline{c}_{Ca^{2+}} = \overline{c}_{\Sigma} \tag{8}$$

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Conditions for complexation equilibrium:

$$k_{MgSO_4} = \frac{a_{MgSO_4}}{a_{Mg^{2+}} \cdot a_{SO_4^{2-}}}, \quad k_{CaSO_4} = \frac{a_{CaSO_4}}{a_{Ca^{2+}} \cdot a_{SO_4^{2-}}} \tag{9}$$

Complexation of sodium ions with sulfate was assumed to be negligible. A value of the calcium sulfate stability constant was taken from standard data and was assumed to be as follows $k_{CaSO_4} = 204; \ k_{MgSO_4} = 230$.

Equations for conversion of concentrations into activities of components:

$$a_i = c_i \gamma_i (I), \quad a_j = c_j \gamma_j (I), \quad a_{ij} = c_{ij} \tag{10}$$

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

The activities coefficients of solution components in a molecular form are assumed to be equal to unity.

Initial, boundary and operational conditions define <u>conditions for flow rates</u> in different stages of the cyclic ion exchange process and accounts for starting and boundary conditions:

$$\nu = \begin{cases} \nu_0, & for \quad 0 \le t \le T/2 \\ -\nu_0 (1-\phi), & for \quad T/2 \le t \le T \end{cases} \tag{11}$$

$1/(1-\phi)$ is the extent of a brine concentration after desalting.

The first half of the cycle is sorption and the second one is regeneration. The durations of the sorption and regeneration processes were assumed to be the same in Equation (11), in order to model permanent operation with two columns working in counter-phase, as illustrated in Figure 1.

<u>Boundary conditions</u> for a sorbent bed of length **L** were defined in the following way. During the sorption stage (for **x**=0, 0<**t**<**T**/2) boundary concentrations correspond to a composition of a low saline water solution:

$$c_i^\Sigma = c_i^\Sigma \big|_{water\ solution}, \ c_j^\Sigma = c_j^\Sigma \big|_{water\ solution}, \text{ for } \boldsymbol{i} = Na^+, \ Ca^{2+}, \ Mg^{2+} \text{ and } \boldsymbol{j} = SO_4^{2-}, \ Cl^- \tag{12}$$

The regeneration stage (for **x**=**L**, **T/2** < **t** < **T**) is carried out by brine, which is created after the sorption stage and further separation of softening water in desalter 3 (see Figure 1).

<u>Starting conditions</u> for the first cycle (for **t**=0) are as follows:

$$\begin{cases} c_{Na} = c_{Na}^{init}, & c_{Ca} = c_{Mg} = c_{SO_4} = 0 \\ \bar{c}_{Na} = \bar{c}_\Sigma, & \bar{c}_{Ca} = 0 \end{cases} \tag{13}$$

The model should be accompanied by an equation, which links the calculated concentration and the concentration measured in an experiment at the outlet of the sorbent column.

$$\frac{\partial C_i}{\partial t} = \frac{v \cdot S}{V_P} \left(c_i^{\Sigma} \big|_{x=L} - C_i \right) \tag{14}$$

Equation (14) is not used for the description of the main process. Equation (14) is to model the technique used for measurement of ions' concentrations in order to compare experimental and calculation results. The concentration is not measured strictly at the outlet point, but in the measuring device so that there is some liquid volume between the outlet and measuring points. This is the reason, why experimental data are volume-averaged concentrations rather than the instantaneous ones.

Modeling assumptions

Activity coefficients:

The model describes experiments properly for low concentrated solutions with component activities close to concentrations ($\gamma \sim 1$). The problem is more difficult for highly concentrated multi-component solutions. In our case, activities of components are calculated using the Guggenheim formula:

$$\ln(\gamma_{\pm})_{pq} = \ln(\gamma_{pq})_{st} + 2\frac{z_p z_q}{z_p + z_q} \left(\sum_i \theta_{iq} \cdot c_i + \sum_j \theta_{pi} \cdot c_j \right) \tag{15}$$

Value of $\ln(\gamma_{pq})_{st}$ is derived from the equation of Debay-Hukkel:

$$\ln(\gamma_{pq})_{st} = \frac{-z_p z_q I^{0,5}}{1 + I^{0,5}} \tag{16}$$

where $I = \frac{1}{2}\left(\sum_i c_i \cdot z_i^2 + \sum_j c_j \cdot z_j^2 \right)$ is the ionic strength of the solution, $\qquad$ (17)

$\theta_{iq}(I)$ is a coefficient of mutual interaction between anion **q** and cation **i**, and

$\theta_{pj}(I)$ is a coefficient of mutual interaction between cation **p** and anion **j**.

Values of mutual interaction coefficients $\theta_{iq}(I)$ are derived from the following equation for pure electrolytes $\ln(\gamma_{\pm})_{pq} = \ln(\gamma_{pq})_{st} + 2\frac{z_p z_q}{z_p + z_q}\left(\theta_{pq} \cdot c_p + \theta_{pq} \cdot c_q\right)$ because

$\ln(\gamma_{\pm})_{pq}$ value is known from tables for pure electrolytes. This allows to calculate $\theta_{iq}(I)$ values and then to use the defined values in Equation (15) for the multicomponent solutions.

It also should be taken into account how the average coefficient of ion activity is related with activity coefficients of separate ions [13]:

$$\left(\gamma_{\pm}\right)_{ij}^{\left(z_i + z_j\right)} = \gamma_i^{z_i} \cdot \gamma_j^{z_j} \tag{18}$$

where z_i and z_j are charge quantities of ions i and j.

Equation (18) allows calculating certain combinations of activity coefficients of separate ions that appear in Equations (1)-(10), for example:

$$\frac{\gamma_{Mg}}{\left(\gamma_{Na}\right)^2} = \frac{\left(\gamma_{\pm,MgSO_4}\right)^2}{\left(\gamma_{\pm,NaSO_4}\right)^3} \tag{19}$$

Dependences of $\dfrac{\gamma_{Ca}}{\left(\gamma_{Na}\right)^2}$ and $\dfrac{\gamma_{Mg}}{\left(\gamma_{Na}\right)^2}$ on the ionic strength and components concentrations presented in such a way allow to make calculations for any saturated or unsaturated solutions, which appear in the cyclic ion exchange process during the sorption and regeneration stages. In addition, for $CaSO_4$ supersaturated solutions it is necessary to consider generation of $CaSO_4$ surplus mentioned below.

Phenomenon of isothermal supersaturation:

The regeneration process is accompanied by the phenomenon of $CaSO_4$ isothermal supersaturation [13]. If the concentration of compound $CaSO_4$ exceeds the solubility concentration, then it is necessary to recalculate the current ion concentrations in order to take into account the supersaturation effect. It is assumed for modeling that only part of ions Ca^{2+} and SO_4^{2-} would be involved in ion exchange in order that the resulting concentration of compound $CaSO_4$ would not exceed the concentration of solubility. It is assumed in the model that the remaining part of ions Ca^{2+} and SO_4^{2-} ($CaSO_4$ surplus) is simply transferred together with the solution as "ballast", without involvement in ion exchange.

Results and Discussions

Typical concentrations of cations in brines produced experimentally in distillation unit (tank 4) in steady-state regime of the SS-process are given in Table 2. In further experimental and theoretical study of ion exchange dynamics, the compositions of solutions presented in Tables 1, 2 were used. In the experiment 1, for example, initial solution No 1 was used at sorption stages and No 3 - at the regeneration stages of cyclic process.

The experimental and calculated concentration-volume histories are presented in Figure 2 (sorption stages) and Figure 3 (regeneration stages).

Modeling has shown that CaSO₄ precipitations in Experiment 2 occurred following the regeneration stage and its amount was equal to 3.5% from the total amount of calcium. The

amount of $CaSO_4$ precipitation in Experiment 2 was about 4%. There was $CaSO_4$ precipitation in Experiment 1 neither in calculation nor in practice.

The following equilibrium and kinetic parameters of the model were clarified in previous article [9] and used here:

ε =0.35; K_{Na}=1, K_{Ca}=0.93, K_{Mg}=0.22; β=7-10 1/hr.

Results given in Fig. 2 and 3, demonstrate good qualitative and quantitative assessment that corresponds to experimental accuracy.

It is very interesting to clarify the limitations of the SS-process from a view of composition of solutions to be processed. The point in question is, will the process be valid with solutions, containing exceeding concentrations of Ca^{2+} compared to Na^+? Numerical experiments can give us the answer and predict the potentials of the SS-process for different types of natural and waste waters. An example of composition of typical waste water to be treated is shown in Table 3. At a sacrifice of high concentration of calcium sulfate, it is very difficult to find the efficient method of processing such a solution.

In conducting numerical experiments the cyclic SS-process was defined as the following. For each cycle, the sorption stage is carried out until a calcium concentration in the tank for softened water reaches a level f for calcium concentration. For any value of f, it is very important to find the duration of sorption stages for stable steady-state SS-process (t_S) compared to that of Ca^{2+} sorption on a pure Na-form of ion-exchanger (t_0). It was assumed in numerical experiments that either $k = t_0/t_s$ =1.33 or k=1.18 and f =0.01. The process is supposed to be cyclic if the total amount of calcium in the column after the sorption stage keeps unchanged starting with a certain cycle.

The stable cyclic SS-process was defined to be such a process, wherein given a single transient fault the total amount of calcium in the column returns to the pre-accident calcium amount within several cycles after such a fault.

Before having results of numerical calculations the process was expected to be cyclic only if the input sodium concentration exceeds considerably the input calcium one because sodium is the basic component for calcium elution from the column. However, while modeling it was found that the process also proceeds even if the calcium concentration in the initial solution is higher than the input concentration of sodium. This can be explained by the effective reuse of sodium accumulated in the sorbent from the very beginning. Although only a small amount of sodium enters to the system, process cycling is maintained because the same amount of sodium leaves the system during the regeneration stage.

Figures 4 and 5 present the result of parameter studies. Figure 4 depicts the case of the fixed solution flow rate v. Figure 5 depicts the case of the fixed coefficients β.

Calculation results that demonstrate the possibility of maintaining a cyclic SS- process in a wide range of concentrations are presented in Figure 4. The results were got at the following assumptions:

- Rate of solution flow through the sorbent having a volume of 1 l is 10 l/hr.
- Duration of the second cycle is reduced by a quarter in comparison with the duration of the first one: k=1.33.

It should be noted that allowed values of coefficients K_{Ca} for the processes of such a type vary depending on values of mass transfer coefficients β (see Figure 4). For instance, if values of mass transfer coefficients β are equal to 10 1/hr and column volume is equal to 1 l, then a cyclic process can be realized for a solution flow rate of $v=10$ l/hr through the sorbent provided that a value of coefficient K_{Ca} varies between 0.38 and 0.70.

The results of process investigation for some fixed values of calcium and sodium concentrations in the initial solution are shown in Figure 5. They make it possible to define the maximum solution flow rate through the sorbent with volume of 1 l, when a cyclic process could be performed, depending on K_{Ca}. The duration of the second cycle was assumed to be decreased in k=1.18 times in comparison with the duration of the first one.

Figure 5 presents data enough to determine a range of ion exchange equilibrium coefficients for different initial calcium and sodium concentrations and for a fixed solution flow rate, when a cyclic process could be performed. For example, such a process can be realized for a flow rate equal to 4 l/hr and a value of coefficient K_{Ca} lying between 0.34 and 0.54 even if the calcium concentration exceeds 50 times the sodium concentration.

A value of coefficient K_{Ca} can also be derived from Figure 5 for the conditions of the maximum solution flow rate through the sorbent. Thus, it is necessary to use different sorbents for different initial solutions if one poses a problem to realize a process with the greatest possible flow rate. When increasing the calcium concentration in relation to the sodium concentration the peaks of the curves drift to the left, i.e. a value of coefficient K_{Ca} tends to the limit being equal to 0.4.

Based on the explanation above the following question arises: what will happen if some amount of sodium leaves the system due to some cause?

To resolve the issue the stability of the process was analyzed. Disturbance was caused in the system by one-time reducing of regeneration time by 15 percent. The remaining 15 percent of solution designated for regeneration were discarded in the modeling process, i.e. this remaining part of solution was not involved in regeneration. This is equivalent to a

sodium leak from the system. After that, the stages of both sorption and regeneration were modeled in the same way as before the leakage.

Dependences of the total amount of calcium on a cycle number for two processes (the unperturbed process and the process with a modeled leakage during the 50th cycle) are plotted in Figure 6. One can see from the plot that after the leakage the process returns to an unperturbed state and transient fault consequences became negligible after several following cycles. This allows concluding that the intake solution compensates the modeled sodium leakage. It should be noted that the process stability is important for real industrial ion exchange systems, operation of which may be accompanied with moderate losses of useful reagents.

Application of such a type of processes to hard sewage, where the concentration of calcium is close to the concentration of solubility, gains an extra advantage. While extracting pure water, the concentration of calcium sulfate in the solution that left the system as brine increases considerably in comparison with its concentration in the solution entered to the system. As a result, the solution becomes supersaturated during the regeneration stage. By force of phenomenon of isothermal supersaturation the calcium sulfate precipitates into a solid form just after leaving the column, not inside the column [14]. Thus there is a considerable amount of $CaSO_4$ in a solid form (as sediment) at the end of each cycle. Therefore it is not necessary to perform any additional actions for its extraction.

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List of Symbols

a_i	activity of positive charged ion i in the solution	mol/l
a_j	activity of negative charged ion j	mol/l
a_{ij}	activity of solution component in a molecular form	mol/l
b	dimensionless coefficient	-
c_i	concentration of cation i ($i - Na^+, Ca^{2+}, Mg^{2+}$)	mol/l
c_j	concentration of anion j ($j - SO_4^{2-}, Cl^-$)	mol/l
$\bar{c}_i$	concentration of cation i in a sorbent	mol/l
C_i	concentration of i–th ion measured in the experiment.	mol/l

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c_{ij}	molar concentration of composition ij (ij - $NaSO_4^-$, $MgSO_4$, $CaSO_4$) in a solution	mol/l
$c_{i,j}^{\Sigma}$	total molar concentration of substance in a solution	mol/l
$\bar{c}_{\Sigma}$	total sorbent capacity	eq/l
d	dimensionless coefficient	-
K_i	ion exchange equilibrium coefficient	-
k_{ij}	thermodynamics stability constant of compound (complex) ij	l/mol
L	length of sorption column	dm
M_i	molecular weight of component	kg/mol
m_i	molal concentration of ions in solution	mol/ kg H_2O
m_{ij}	molal concentrations of salts in non-dissociated (molecular) form in the solution	mol/ kg H_2O
R	dimensionless coefficient	-
S	cross-section of the column,	dm^2
t	time	sec
T	duration of the whole cycle,	sec
V_p	volume of liquid between the outlet point and the point of measurements,	dm^3
x	longitudinal coordinate along the ion-exchange column	dm
$z_i, z_p,$ 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^0	mass transfer coefficient of ion i, when ions SO_4^{2-} are absent	1/sec
β_i	mass transfer coefficient of ion i in the ionite	1/sec
β_i^{film}	mass transfer coefficient of ion i in the thin film around a granule of ionite	1/sec
γ_i	activity coefficients	-
$\left(\gamma_{pq}\right)_{st}$	"stable part" of average ion activity coefficient of component pq	-
$\left(\gamma_{\pm}\right)_{pq}$	average ion activity coefficient of component pq	-
ε	porosity of sorbent bed	-
μ_i	equilibrium concentration of ion i in a sorbent	mol/l

η_i	activity of positive charged ion i at the granule surface	mol/l
ν	linear rate of solution	m/sec
ρ	solution density	kg/l
$\theta_{iq}(I)$	"weight" coefficients in Huggenheim equation	-
Φ	extent of extraction of demineralized water from the initial solution	-

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Table 1. Concentrations of elements in the solutions treated. All the data are given in [mol/l].

Experiment	Solution	Stage	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-
1	No1 (seawater)	Sorption	0.45	0.01	0.06	0.06	0.47
2	No 2 (brine)	Sorption	0.9	0.02	0.12	0.12	0.9

Table 2. Composition of distillation brines in experiments.

Experiment	Solution	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-
1	No 3	0.675	0.00015	0.09	0.09	0.705
2	No 4	1.35	0.00020	0.18	0.18	1.35

Table 3. Composition of process water (mg/l)

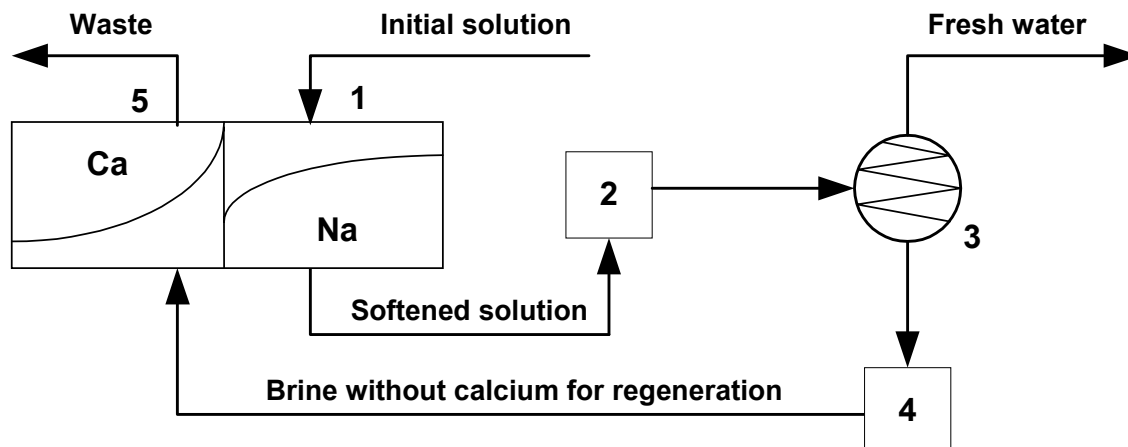| Total	Na^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Cl^-
2,777.0	107.6	426.0	124.6	1,616.0	91.8
A total contribution of other components such as Fe, Cu, Ni, Zn, Co was less than 10 mg/l.					

Figure 1. Diagram of self-sustaining desalination process. 1,5 – columns with cation-exchanger, 2 – tank for softened water, 3 - destillation unit, 4- brine collector.
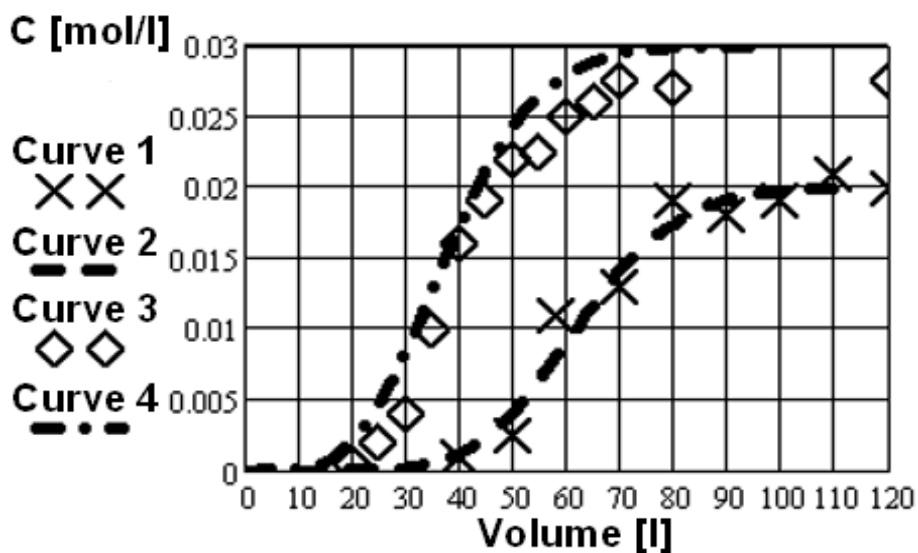
Figure 2. Experimental (points) and theoretical (lines) concentration-volume histories of Ca^{2+} at sorption stages for experiment 1 (curves 1, 2) and 2 (curves 3, 4).
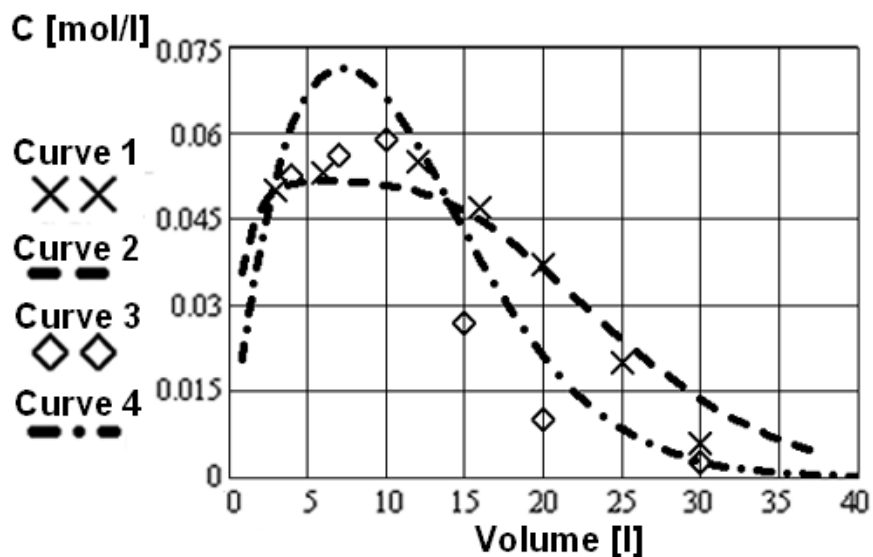

Figure 3. Experimental (points) and theoretical (lines) concentration-volume histories of Ca^{2+} at desorption stages for experiment 1 (curves 1, 2) and 2 (curves 3, 4).
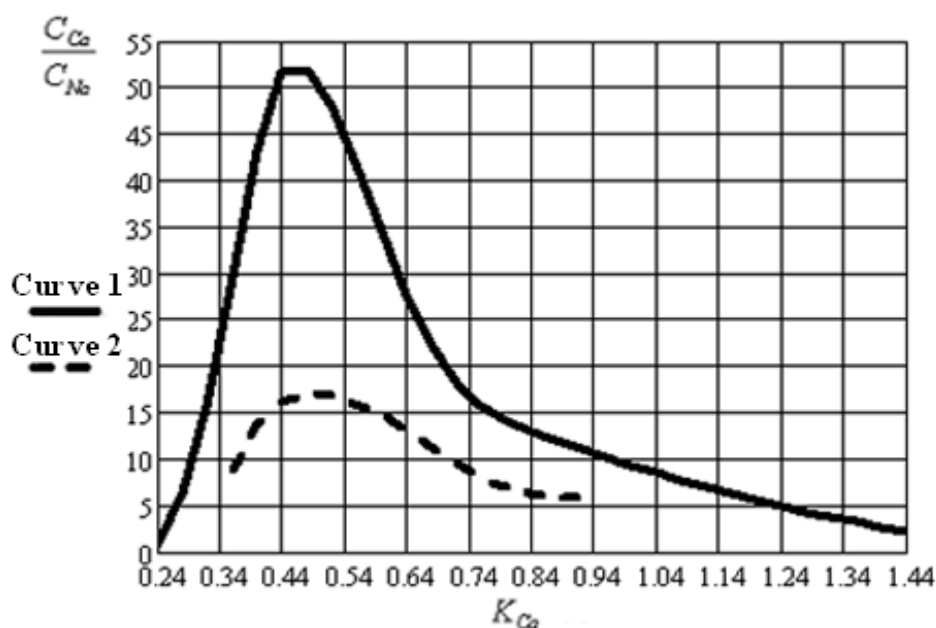
Figure 4. Dependence of the maximal value of C_{Ca}/C_{Na} in the initial solution, on different values of K_{Ca} for different values of mass transfer coefficients, when the cyclic process is possible. Curve 1: β=20 1/hr; curve 2: β=10 1/hr.
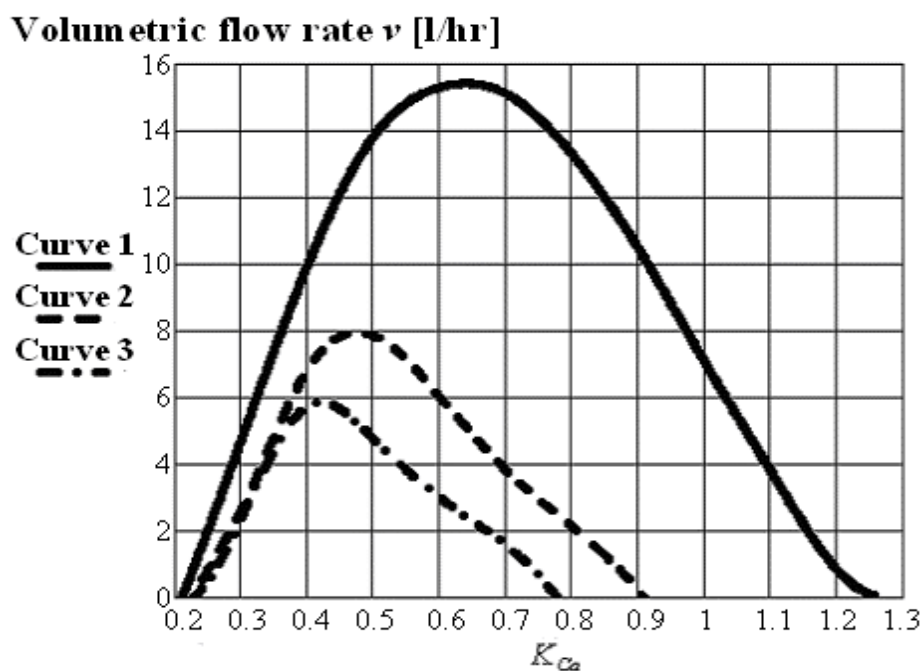

Figure 5. Dependences of maximal flow rate (above which the SS-process is instable) on K_{Ca} for fixed initial concentrations. Curve 1: C_{Na}=0.01 mol/l, C_{Ca}=0.048 mol/l; Curve 2: C_{Na}=0.002 mol/l, C_{Ca}=0.052 mol/l; Curve 3: C_{Na}=0.001 mol/l, C_{Ca}=0.0525 mol/l.

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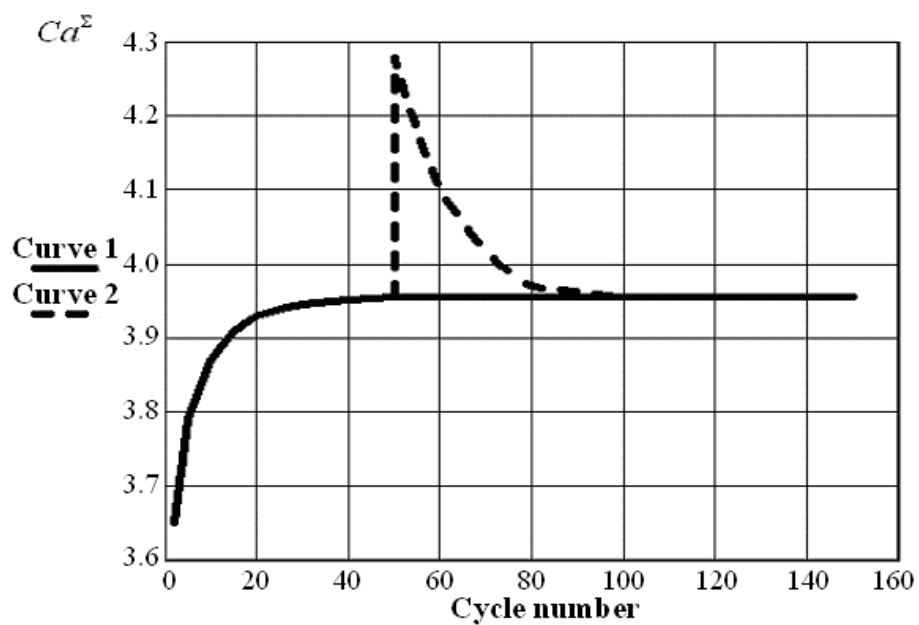
Figure 6. Total amount of calcium in the column after the sorption stage dependently on a cycle number: Curve 1: unperturbed cyclic process. Curve 2: cyclic process perturbed at the 50th cycle.