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R. Kh. Khamizov[a]; L. I. Mironova[a]; N. A. Tikhonov[a]; A. V. Bychkov[a]; A. D. Poezd[ab]
[a] V. I. VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY OF RUSSIAN ACADEMY OF SCIENCES, MOSCOW, RUSSIA [b] PHYSICAL DEPARTMENT OF M. V. LOMONOSOV, MOSCOW STATE UNIVERSITY, MOSCOW, LENINSKIE GORY, RUSSIA

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Recovery of Pure Magnesium Compounds from Seawater by the Use of the Effect of Isothermal Supersaturation in the Ion-Exchange Process

R. KH. KHAMIZOV, L. I. MIRONOVA, N. A. TIKHONOV, A. V. BYCHKOV, and A. D. POEZD

V. I. VERNADSKY INSTITUTE OF GEOCHEMISTRY AND ANALYTICAL CHEMISTRY OF RUSSIAN ACADEMY OF SCIENCES
KOSYGIN STR. 19, MOSCOW 117975, RUSSIA;
PHYSICAL DEPARTMENT OF M. V. LOMONOSOV
MOSCOW STATE UNIVERSITY
MOSCOW, LENINSKIE GORY, RUSSIA

ABSTRACT

The effect of high supersaturation of magnesium carbonate solutions in an ion-exchange bed is displayed on treatment of (Mg^{2+}-Na^{+}) forms of carboxylic resins in the column with solutions of sodium carbonate and sodium bicarbonate. Upon leaving the column the supersaturated eluate decomposes with formation of coarse-grained crystals of nesquegonite: $MgCO_3 \cdot 3H_2O$. The sorption scheme of isolating pure magnesium compounds from seawater by means of the effect of isothermal supersaturation was advanced and tested on a pilot-plant scale. The proposed process includes stages of isolation of calcium using natural and manufactured zeolites and isolation of magnesium using carboxylic ion-exchange resins. The mathematical model of the dynamics of the ion-exchange process with supersaturation is developed.

INTRODUCTION AND BACKGROUND

At present there is a large variety of commercially useful traditional methods for the production of magnesium and its compounds by precipitation of magnesium hydroxide from seawater (1). In spite of that, serious efforts are being made to elaborate new effective technologies, including sorption methods which are advantageous from the ecological point of

view (2). The first interesting way to isolate magnesium from seawater was developed by Bauman (Dow Chemical Co.) (3). This process consisted of stages of sorption of the magnesium ions on strongly acidic cation-exchange resins such as Dowex-50, desorption of the magnesium salt by the concentrated solution of sodium chloride, and subsequent extraction of product by the organic agents. A limitation of this method is that the strongly acidic resins (sulfonated copolymers of styrene and divinylbenzene) show a low selectivity and low capacity to the Mg^{2+} ions from seawater. The equilibrium capacity of Dowex-50X8, for example, to Mg^{2+} from seawater is less than 1.0 meq/mL as compared to the total capacity of the exchanger of 2.5 meq to 1 mL of the resin's bed.

Some selectivities to the magnesium ion sorbents were elaborated (4–6). Macroporous anion-exchangers such as Dowex-MWA-1 with microcrystals of $MgX_2 \cdot 2Al(OH)_3$ (X = halogen), dispersed in the pores, and sorbents based on calcium titanyl oxalates are examples. These materials are not yet widely used and commercially available. Among the weakly acidic carboxyl ion-exchangers, copolymers of methyl methacrylate and divinylbenzene, e.g., KB (Russia), Amberlite IRC-50 (USA), Zerolite-226 and Zeocarb (UK), appear to be the most promising because of their selectivity and capacity for Mg^{2+} during sorption from complex solutions with an excess of sodium ions. However, in such cases the problem is to find a convenient regeneration technique. In agreement with the previously proposed process of recovery of magnesium on carboxylic resins (7, 8), seawater freed of calcium by the use of natural zeolites is passed through a sorption column which is part of a countercurrent ion-exchange system of three columns with the resin KB-4. A portion of sorbent loaded with Mg^{2+} to equilibrium capacity (2.7 meq/mL) is transferred to a desorption column where it is treated with a solution of HCl and then moved to a regeneration column where it is treated with a solution of NaOH. The regenerated resin in the Na-form is placed back into the sorption column. In spite of the high efficiency of this process, it has some limitations related to the expenditure of chemical agents. The total chemical balance of the process requires two equivalents of alkali and one equivalent of acid per one equivalent of magnesium hydroxide produced.

We considered the possibility of developing a rather inexpensive and effective sorption process for the recovery of magnesium from seawater. Such a possibility became evident after finding the effect of isothermal supersaturation of magnesium carbonate solutions in the resin's bed (9). Concentrated solutions of alkali metals carbonates, usually mixtures of Na_2CO_3 and $NaHCO_3$, when passed through a column with the (Mg^{2+}-Na^+)-form of carboxylic resin, do not precipitate the $MgCO_3$ in the bed of the sorbent but form supersaturated solutions which are spontaneously

decomposed outside the column. The efficient desorption of magnesium ions with the concomitant regeneration of the Na^+-form of cationic resins is thus achieved due to the formation of low-dissociated magnesium compounds. The total material balance of the process is consistent with the input of one equivalent of sodium carbonate per one equivalent of the final solid magnesium carbonate produced. Some experimental and computer calculated data obtained during the development of the project are presented in this article.

EXPERIMENTAL

Materials

The sorbents listed in Table 1 were used in this study:

KB-4 and KB-4P2: Methyl methacrylate ion-exchange resins crosslinked with 6 and 2.5% of divinylbenzene, respectively are manufactured in Russia.

Clin.: Natural zeolite clinoptilolite from the Tedzami deposit (Georgia) with an active mineral content of over 90%.

Zeol.: Synthetic zeolite of the A-type and manufactured in Russia.

The model solutions and natural seawater from the Sea of Japan listed in Table 2 were used.

Substances of "reagent grade" were used for the preparation of the model solutions.

Experimental Procedures

The ion-exchange experiments were carried out in glass columns with fritted plates (the specific parameters of each particular run are indicated

TABLE 1
Characteristics of Sorbents

No.	Sorbent	Particle size (cm)	Total exchange capacity[a] (meq/g)	Total exchange capacity[b] (meq/mL)
1	KB-4	0.025–0.05	9.0	3.0
2	KB-4P2	0.025–0.05	9.6	2.5
3	Clin.	0.05–0.20	2.1	2.0
4	Zeol.	0.02–0.05	4.0	3.6

[a] Total exchange capacity per unit mass of air-dried sorbent.

[b] Total exchange capacity per unit bed volume of Na^+-form sorbent in 0.55 M NaCl.

TABLE 2
Composition of Solutions

No.	Solution	Concentrations of ions (eq./L)							
		Na^+	Mg^{2+}	Ca^{2+}	K^+	Sr^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
1	Model solution 1	0.45	0.12	—	—	—	0.57	—	—
2	Model solution 2	0.43	0.12	0.02	—	—	0.57	—	—
3	Seawater	0.40	0.11	0.019	0.01	9×10^{-4}	0.49	0.05	0.0015

in the legends to the figures). A method of direct frontal analysis was employed for the data collecting in the following way: a solution with an initial concentration of a component C_0 (meq/mL) and with a flow rate v (cm^3/h) was passed through the column with a sorbent bed volume w (mL) and porosity ϵ. Eluting solution aliquots of volume V_i (mL) were collected, and the component content C_i, where i is the number of aliquot, was measured. The equilibrium coefficient of exchange of components A and B was determined by the formula

$$K_B^A = \left(\frac{a_A}{C_{0_A}}\right)^{1/Z_A} \left(\frac{C_{0_B}}{a_B}\right)^{1/Z_B} \tag{1}$$

The selectivity factor was calculated by the formula

$$\alpha_B^A = \frac{a_A}{C_{0_A}} \frac{C_{0_B}}{a_B} \tag{2}$$

where Z is the ion charge and a_A is an equilibrium capacity of unit volume of the sorbent bed (meq/mL) to component A, determined as

$$a_A = \frac{[V_e - V_0]C_{0_A} - \sum_{i=1}^{i=n} (V_i - V_{i-1})C_{A_i}}{w} \tag{3}$$

where V_e is the total volume of n-fractions until equilibrium is reached (up to quantitative agreement between concentrations of ions in the input and output solutions):

$$V_0 = V_f + w\epsilon \tag{4}$$

where V_f is the volume of liquid in the column above and below the sorbent bed.

For a binary mixture:

$$a_B = a_0 - a_A \tag{5}$$

where a_0 is the total capacity of sorbent per unit volume of bed (meq/mL).

The maximum errors of this method, as determined by the accuracy of analytical techniques used, were $\Delta a/a \leq 0.05$; $\Delta K/K \leq 0.1$.

In order to refine the equilibrium parameters and to draw the breakthrough curves of desorption, a displacement method was applied in the following way: a desorbing solution was passed through a column with a sorbent previously worked up to equilibrium by the model solutions or seawater. Aliquots of the eluate were collected, and their compositions were measured.

The equilibrium coefficient was determined as

$$K_B^A = \left(\frac{\bar{C}_A}{C_{0_A}}\right)^{1/Z_A} \left(\frac{C_{0_B}}{\bar{C}_B}\right)^{1/Z_B} \tag{6}$$

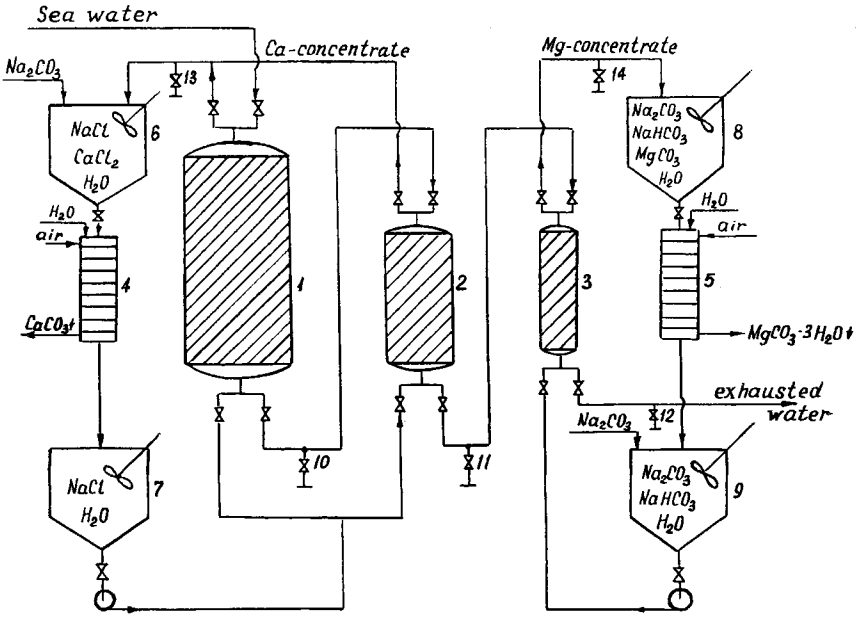

FIG. 1 Pilot plant for recovery of magnesium from seawater. 1–3: columns with sorbents. 1: Clin., l = 162.5 cm, s = 615.4 cm^2. 2: Modified Zeol., l = 95.5 cm, s = 314 cm^2. 3: KB-4, l = 100 cm, s = 140 cm^2. 4 and 5: Polymer filters. 6 and 7: Tanks, 0.5 m^3. 8 and 9: Tanks, 0.15 m^3. 10–14: Sampling points.

where $\overline{C}_A$ and $\overline{C}_B$ are the average concentrations of components A and B in the total volume of eluate. The maximum error of this method is $\Delta K/K \leq 0.05$.

A pilot study with natural seawater was carried out by using the basic scheme shown in Fig. 1.

Analytical Techniques

Analyses of the ion composition of solutions were performed by atomic absorption in an acetylene-air flame, by atomic emission in a propane-air flame, and by ion chromatography. X-ray analysis was performed on diffractometer DRON-3 with the use of CoK_α radiation.

RESULTS AND DISCUSSION

Preliminary Seawater Processing. Selective Separation of Magnesium and Calcium Ions

A special feature of the carboxylic cation-exchangers used for the extraction of magnesium from seawater is the requirement for the preliminary removal of calcium compounds. This preliminary process determines all the following stages, particularly the possibility of efficient desorption of magnesium compounds and the purity of the final product. On the other hand, it is important to avoid any appreciable collection of magnesium ions by the sorbent in the preliminary stage. Otherwise, this ancillary sorbent loses part of its capacity for calcium, the desired magnesium product is lost.

The requirements of the ancillary sorbent can be easily estimated. For example, in order to obtain losses of the desired component within a 3–5% limit of the initial content in solution 2 or in seawater (Table 2), it is necessary to use a sorbent with selectivity factor values within $25 \leq \alpha_{Mg}^{Ca} \leq 30$.

Our tests of some sorbents for the separation processes of Ca^{2+} and Mg^{2+} from seawater showed the following values of α_{Mg}^{Ca}: Dowex-50X8 = 2.5, KB-4 = 2.1, Clin. = 3.4, and Zeol. A = 4.5. These examples demonstrate the complexity of the problem.

We found that several successive treatments of zeolites with seawater and a concentrated solution of sodium chloride lead to their modification at the sacrifice of irreversible sorption of magnesium ions (10).

Data shown in Figs. 2 and 3 and in Table 3 demonstrate that the modification of Zeol. A is practically complete after three cycles of treatment in the dynamic conditions. This treatment includes sorption of Ca^{2+} and Mg^{2+} from the model solution 2 and desorption with 3 M NaCl. That the

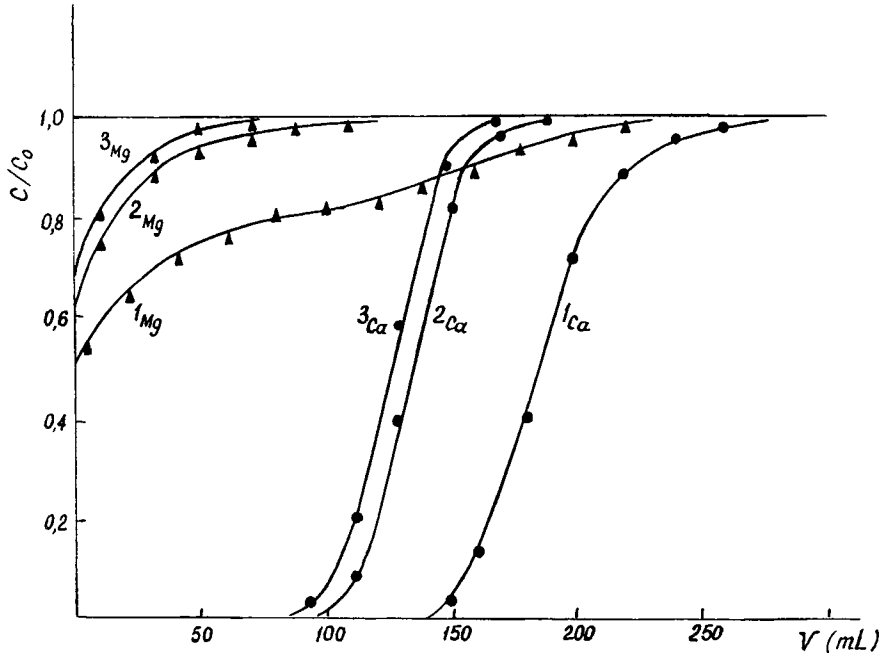

FIG. 2 Breakthrough curves of sorption of Mg^{2+} and Ca^{2+} ions from model solution 2 on zeolite A, 1–3 cycles. Sorbent bed: l = 10.7 cm, s = 0.56 cm^2, w = 6 cm^3. Flow rate: v = 10 cm^3/h (v/w = 1.67 h^{-1}).

sorption processes became reversible is indicated by the close values of the sorption and desorption parameters. The average value of the selectivity factor for the modified sorbent is $\alpha_{Mg}^{Ca} \approx 27.3$.

As shown in Fig. 2 the modified zeolite provides almost complete purification from Ca^{2+} of more than 18 relative volumes of model solution 2 per one sorbent bed volume within one cycle. In this process the content of magnesium in the refined solution is reduced to no more than 4% of its initial value.

For the selective separation of Ca^{2+} and Mg^{2+} in desalination processes, special sorbents, e.g., Activit, Taylor-made cationic resins, are used. They are analogous to sulfonated copolymers of styrene and divinylbenzene, but they have more than one sulfonic acid group per one aromatic ring in their structures (11).

As compared with our results, the "supersulfonated" cationic resins provide for the purification of 30–40 relative volumes of seawater within

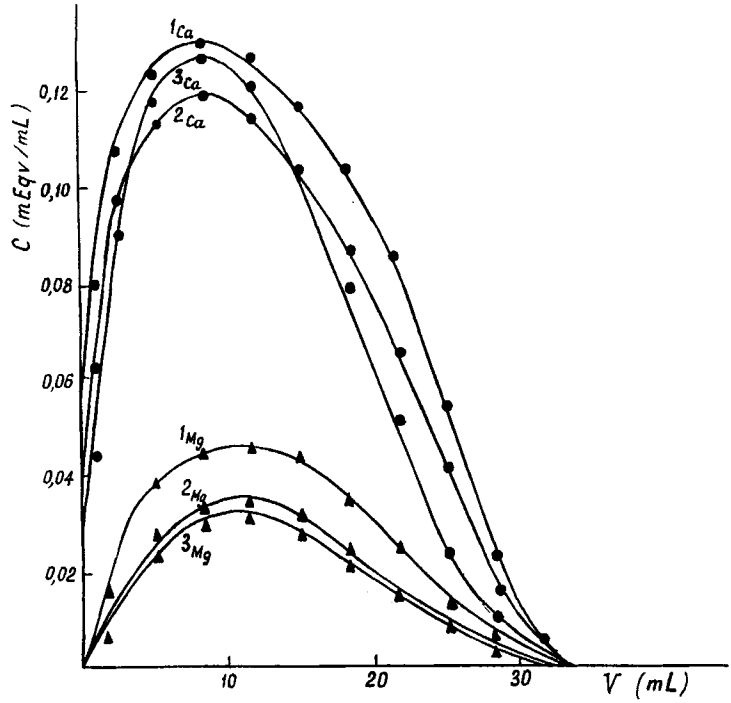

FIG. 3 Breakthrough curves of desorption of Mg^{2+} and Ca^{2+} ions from the zeolite, 1–3 cycles. Flow rate of 3 N NaCl: 3 cm^3/h (0.5 h^{-1}).

one cycle. At the same time, the modified zeolites are advantageous with respect to the total expenditures of NaCl and to magnesium losses at the stage of seawater purification from calcium. The main practical advantage of modified zeolites is their easy availability and relatively low price. Our preliminary studies show that in the described process, it is even possible

TABLE 3
Equilibrium Parameters of Separation of Ca^{2+} and Mg^{2+} in the Cyclic Process: Sorption from Solution 2 (S) and Desorption with 3 M NaCl Solution (DS)

	1st cycle		2nd cycle		3rd cycle	
Parameters	S	DS	S	DS	S	DS
a_{Ca}(meq/mL)	0.610	0.479	0.449	0.432	0.416	0.412
a_{Mg}(meq/mL)	0.630	0.157	0.115	0.098	0.092	0.090
α_{Mg}^{Ca}	5.82	18.30	23.41	26.45	27.10	27.50

to utilize zeolites Na-A which were developed for the purification of gases in the chemical industry (10).

The use of a modified zeolite in combination with natural ones leads to an increase in the efficiency of the modified zeolite. The clinoptilolite partially removes Ca^{2+} from seawater in addition to mechanical filtration and the elimination of iron and other heavy metals. The results of the pilot-plant experiments shown in Fig. 4 demonstrate that within one cycle more than 20 relative volumes of seawater can be purified from calcium with one volume of the modified zeolite.

By using alternated beds of Clin. and Zeol. for preliminary seawater processing as shown in Fig. 1, the desorption of Ca^{2+} and the regeneration of sorbents can be performed with an NaCl solution which can be returned to the process in every cycle after $CaCO_3$ precipitation with the equivalent amount of Na_2CO_3.

Recovery of Magnesium Compounds with Carboxylic Cation Exchangers. Effect of Supersaturation

Since the data described above showed the possibility of quantitative removal of calcium ions from seawater, further laboratory studies were carried out with the model solution 1 containing sodium and magnesium

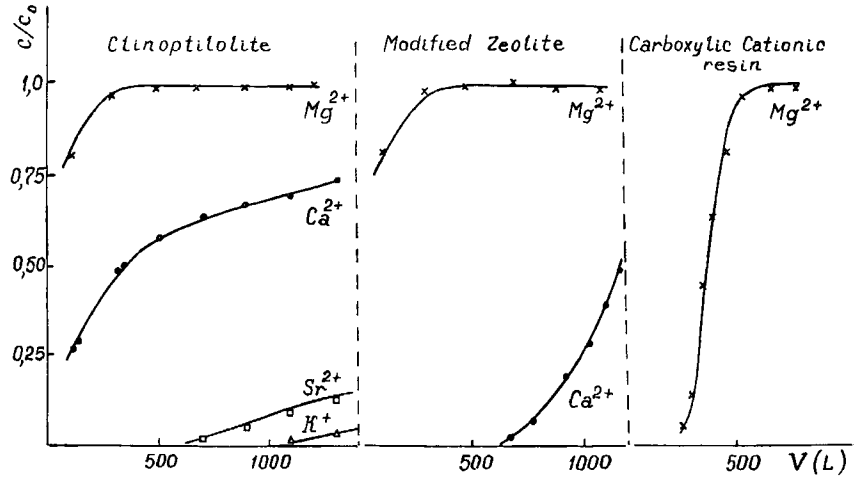

FIG. 4 Breakthrough curves of sorption of metal ions from seawater on the different sorbent beds of the pilot plant at a flow rate of 100 L/h. Sampling points 10, 11, and 12 on Fig. 1.

chlorides (Table 2). Some results of sorption experiments with the exchange of Mg^{2+} and Na^{+} on the carboxylic cationic resins are presented in Fig. 5 and Table 4.

The efficiency of the sorption process can be enhanced through a cross-linking increase in the resin structure. As shown in Fig. 5 (Curve 1), exhaustive extraction of magnesium from more than 20 relative volumes of solution 1 can be practically achieved by one volume of KB-4 in the single sorption cycle.

A variety of solutions of sodium carbonate, sodium bicarbonate, and their mixtures were tested to find the optimal conditions of magnesium desorption and sorbents regeneration (Fig. 6). Initially the main idea of these experiments was to provide complete desorption of magnesium and regeneration of the Na^{+}-form of the cationic resin through the formation of poorly soluble magnesium carbonate. Contrary to expectations, in none of the experiments did precipitation occur in the sorbent bed.

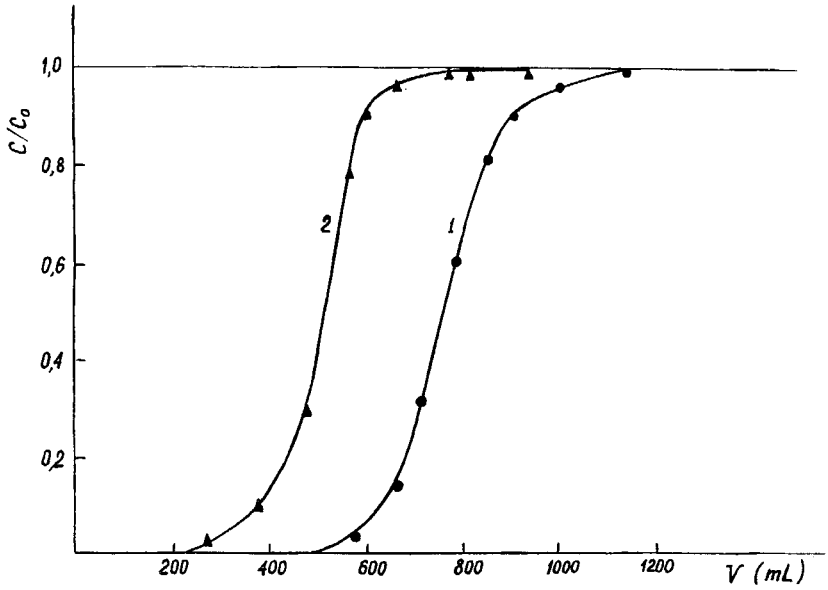

FIG. 5 Breakthrough curves of sorption of Mg^{2+} from the model solution 1 on the Na^{+} form of carboxylic resins KB-4 (1) and KB-4P2 (2). Initial (i) and final (f) parameters of the resin beds: (1) s = 1.9 cm^2, l_i = 20 cm, l_f = 18.3 cm; (2) s = 1.9 cm^2, l_i = 20 cm, l_f = 16.4 cm. Flow rate: 330 cm^3/h (v/w_i = 8.7 h^{-1}).

TABLE 4
Equilibrium Characteristics of Sorption of Mg^{2+} by Na^+-forms of Carboxylic Resins

Parameters	KB-4P2	KB-4
a_{Mg}(meq/mL)	2.00	2.70
a_{Na}(meq/mL)	0.80	0.60
α_{Na}^{Mg}	9.38	16.88
K_{Na}^{Mg}	2.30	3.56

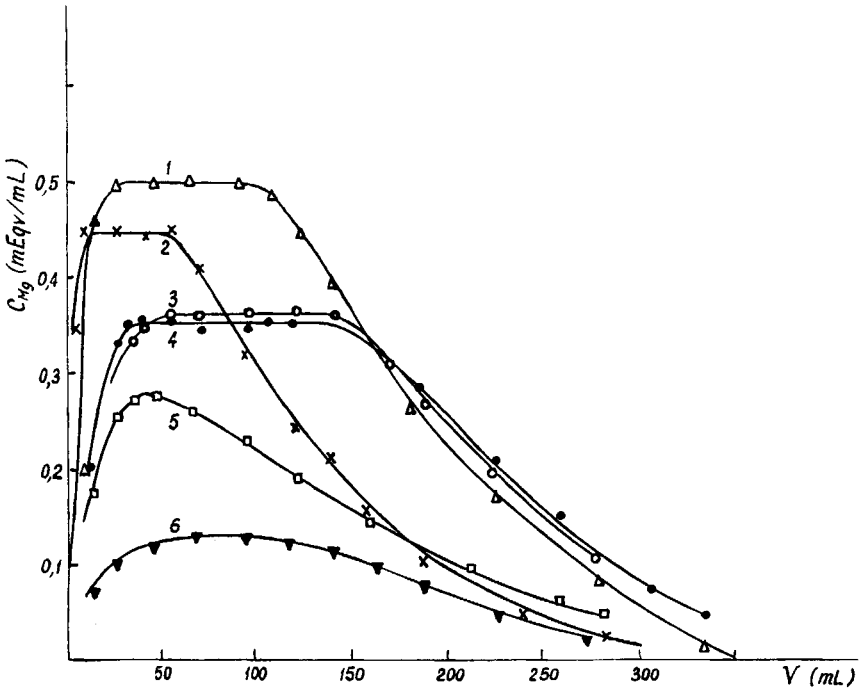

FIG. 6 Breakthrough curves of Mg^{2+} desorption from the carboxylic resins KB-4 (1, 3, 4, 5) and KB-4P2 (2). Recovery agents: (1, 2) 1.5 M Na_2CO_3 + 0.59 M $NaHCO_3$; (3, 4) 1.5 M Na_2CO_3; (5) 1 M $NaHCO_3$. Relative flow rates (v/w): (1, 2, 3, 5) 2.2 h^{-1}; (4) 5 h^{-1}; (6) Mg^{2+} concentration in solutions after the breakdown of supersaturated solutions according to Curve 1.

Additional investigations were performed in the following manner: The desorption processes were stopped at some intermediate stages, corresponding to certain points on the breakthrough curves shown in Fig. 6. The solution was removed from the column by compressed air pressure, and x-ray analyses of sorbent beads from different zones of the bed were performed. No crystallization processes in the resins (within the sensitivity of the instrument) were detected, at least over a period of 72 hours.

On the other hand, in the desorption processes the eluates decomposed upon leaving the columns, and precipitation took place with the formation of coarse-grained crystals (0.2–2 mm). The crystallization process started in 0.5–5 hours and was completed in the next 3 hours. The time taken for crystallization to start depended on the total magnesium concentration in the eluate, and the process was markedly accelerated with a temperature increase. At present the problem of the crystallization kinetics requires further investigation.

It is evident that in the ion-exchange process studied, the effect of isothermal supersaturation of slightly soluble magnesium compounds takes place.

A rather stable supersaturation is difficult if not impossible to accomplish in the ordinary way in a solution volume by mixing solutions of sodium and magnesium salts at concentrations corresponding to the largest ones on the breakthrough curves in Fig. 6. Our experiments with solutions of $MgCl_2$ (0.2–1 mol/L), Na_2CO_3 (1–1.6 mol/L), and $NaHCO_3$ (0–0.6 mol/L) showed rapid precipitation of complex mixtures of magnesium carbonates (with the structures of magnesite and nesquegonite), magnesium hydroxide-carbonate, and magnesium hydroxide.

At the same time, it is evident from the results of the x-ray analyses shown in Table 5 that the supersaturated solution in the ion-exchange process discussed decomposes spontaneously to form the pure solid phase of nesquegonite: $MgCO_3 \cdot 3H_2O$.

Breakthrough desorption Curves 1–5 in Fig. 6 represent the total concentrations of magnesium (in the ionic and molecular forms of compounds) in the supersaturated eluates before their decomposition. The most efficient desorbing agents appear to be mixtures of sodium carbonate and sodium bicarbonate at concentrations of 1.5–1.6 and 0.4–0.6 mol/L, respectively. In this case the maximum concentrations of magnesium in the eluates can achieve 0.5 eq/L for cationic resin KB-4 and 0.45 eq/L for KB-4P2. It should be noted that the desorption curves in Fig. 6 were well reproduced in replicated experiments.

Spontaneous breakdown of the supersaturated eluates, corresponding to the "plateau" in Curve 1 of Fig. 6, results in the precipitation of fractions of the dissolved magnesium compound close to three-fourth of the

TABLE 5
The Unit Cell Parameters (a, b, c, β, z), Interplane Distances (d), Reflection Indexes (hkl), and Peak Intensities (I) for Isolated Samples of Magnesium Carbonate Compared to the Data for Nesquegonite from ASTM (12)

Isolated samples of magnesium carbonate			Nesquegonite, ASTM (12)	
hkl	*d*	*I* (%)	*d*	*I* (%)
	Space group $P2_1/n$ a = 12.113 (3) b = 5.364 (3) c = 7.705 (2) β = 90.455° (2) z = 4		Space group $P2_1/n$ a = 12.112 b = 5.365 c = 7.697 β = 90.420° z = 4	
101	6.48	100	6.48	100
200	6.06	4	6.07	2
110	4.90	2	4.91	12
011	4.40	2	4.40	2
111	4.14	2	4.14	4
002	3.85	65	3.85	75
301	3.59	20	3.59	8
	etc.		etc.	

initial concentrations. Curve 6, showing the residual concentrations of magnesium in the solutions over the precipitates of $MgCO_3 \cdot 3H_2O$, is plotted by using points measured 3 hours after visually observed crystallization started.

The results of comparative studies of the desorbing effects of sodium chloride and sodium carbonate are shown in Fig. 7. The graphs obtained clearly demonstrate that exhaustive desorption of Mg^{2+} from the carboxylic resin is not determined by the high concentration of Na^+ in the recovery agent but evidently is related to the formation of low dissociative magnesium compounds.

Mathematical Modeling. Prediction of the Behavior of a Large-Scale Continuous Process

Previously we considered the problems of simulation of ion-exchange dynamics for multicomponent solutions (including seawater) and for different ion-exchange inorganic sorbents and resins (13, 14). Models of ion exchange accompanied by the effect of supersaturation need to be elaborated.

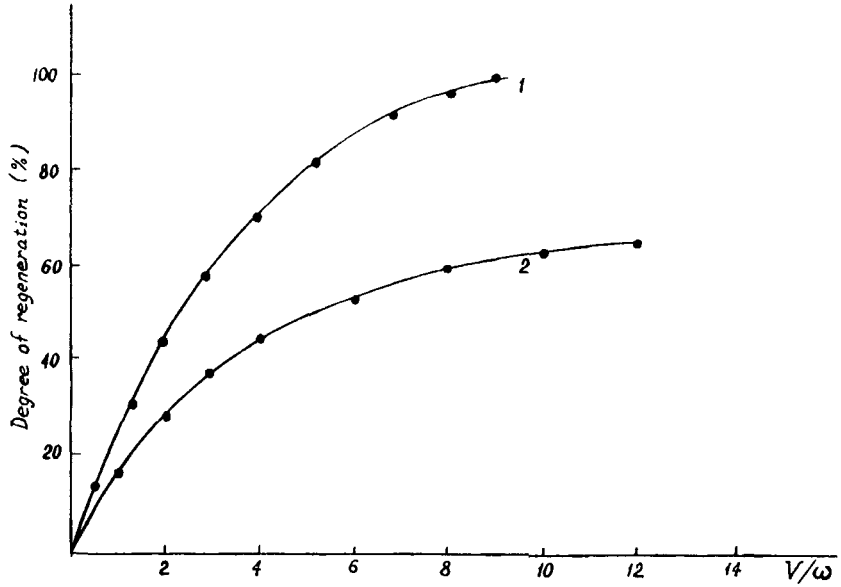

FIG. 7 Degree of regeneration of KB-4 depending on the relative volume (V/w) of recovery agents: (1) 1.5 M Na_2CO_3 + 0.59 M $NaHCO_3$; (2) 4.3 M NaCl.

The breakthrough curves in Fig. 6 (1–4) have some peculiarities from the standpoint of ion-exchange dynamics. They form the "plateau" at the total equivalent concentrations of the desorbed components much less than at the concentrations of the desorbing agents.

Assume the ion-exchange kinetics is described by the well-known equation

$$\partial a_i/\partial t = r(a_i^0 - a_i) \tag{7}$$

where r is the effective kinetic coefficient, a_i^0 is the equilibrium concentration of component i in the resin phase, and a_i is the concentration varying with time. Let $i = 1$ for Mg^{2+} and $i = 2$ for Na^+. The occurrence of the plateau on the desorption curves at the concentrations level $C_2 = C_2|_{pl}$ means that: $\partial a/\partial t = 0$ at $a_i^0 \neq a_i$. This is possible if $r \to 0$ at $C_2 \to C_2|_{pl}$.

One of the convenient physical models used to explain this feature can be imagined as shown in Fig. 8. During the desorption process the resin pores are initially filled, and later the resin beads become coated with a microlayer of the hardly permeable (quasi-liquid or quasi-solid) phase, blocking further accumulation of Mg^{2+} in the external solution. This can

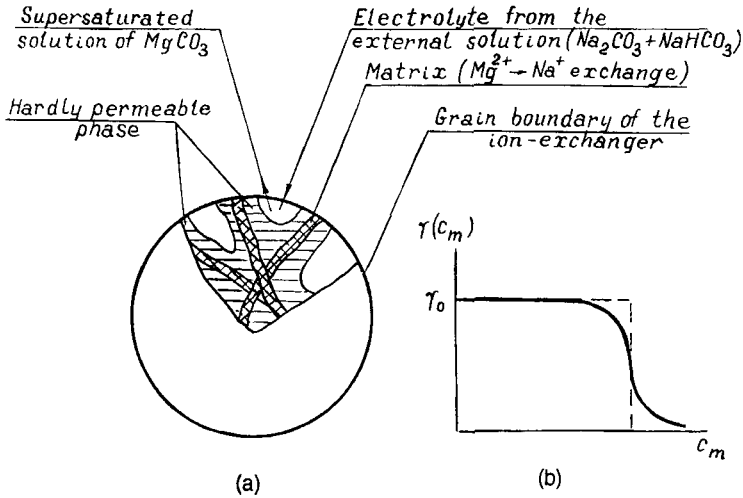

FIG. 8 (a) Model of ion-exchange process in the unit particle with the formation of a supersaturated solution (SS). (b) Change of kinetic coefficient with the concentration of SS in the sorbent phase.

be the result of interaction between CO_3^{2-} and Mg^{2+} ions at some critical concentrations in the resin phase. Figure 8(a) shows a possible visualization of this process in the initial stage.

The degree of coating depends on the degree of supersaturation and on the concentration of $MgCO_3$ in molecular form (C_m). When C_m values are small, only resin pores are filled. The blocked section projections on the bead surface have a small influence on the total exposed area. Correspondingly, r decreases slightly. A similar case takes place at large values of C_m: the microbulges of resin particles become coated. In the intermediate concentration range, r rapidly decreases with C_m. The phenomenon of accumulation of a hardly permeable phase in the resin bed can be considered as analogous to the familiar process of capillary condensation in porous materials.

The convenient exponential form of an equation for r changing with C_m can be used:

$$r = r_0 e^{-(\kappa C_m)^\lambda} \tag{8}$$

where κ and λ determine a family of curves for r. Specific physical meanings are not assigned to these parameters.

On the other hand, C_m is determined by the dissociation law as follows:

$$K_d = \frac{C_1(C_2^0 - C_m)}{C_m} \tag{9}$$

where K_d is the dissociation constant and C_2^0 is the initial equivalent concentration of Na_2CO_3.

The mathematical model of the ion-exchange process dynamics with supersaturation can be defined as a set of equations: (1) in four variables a_1^0, a_2^0 and C_1, C_2; (5) with A = 1 and B = 2; (7) for i = 1 and i = 2; (8), (9), and two partial differential equations for material balance in the column:

$$\epsilon \frac{\partial(C_1 + C_m)}{\partial t} + v \frac{\partial(C_1 + C_m)}{\partial X} + (1 - \epsilon) \frac{\partial a_1}{\partial t} = E \frac{\partial^2(C_1 + C_m)}{\partial X^2} \tag{10}$$

$$\epsilon \frac{\partial C_2}{\partial t} + v \frac{\partial C_2}{\partial X} + (1 - \epsilon) \frac{\partial a_2}{\partial t} = E \frac{\partial^2 C_2}{\partial X^2} \tag{11}$$

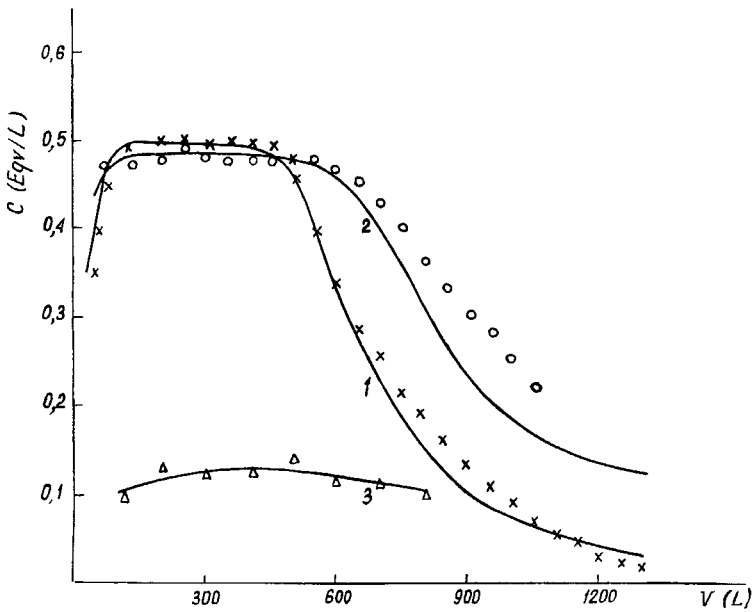

FIG. 9 Experimental points (pilot testing) and designed breakthrough curves of desorption of magnesium compounds from KB-4. (1, 2) 1st and 2nd cycles of desorption; (3) Mg^{2+} concentrations in solutions after the breakdown of SS according to Curve 2.

where X is the coordinate along the axis of the column, and E is the longitudinal dispersion coefficient.

The initial and boundary conditions are

$$C_i|_{t=0} = C_{0i} \qquad (i = 1, 2) \tag{12}$$

$$C_i|_{X=0} = C_{0i}; \qquad \left.\frac{\partial C_i}{\partial X}\right|_{X=l} = 0; \qquad C_m|_{X=0} = 0 \tag{13}$$

where $X = l$ for the outlet of the ion-exchange column.

Computations of the desorption processes were performed with the use of experimental parameters except for the dissociation constant of magnesium carbonate in the resin phase (K_d) and parameters κ and λ. Their values were determined from the inverse problem solution with the use of data of pilot-plant testing. Figure 9 compares experimental and calculated

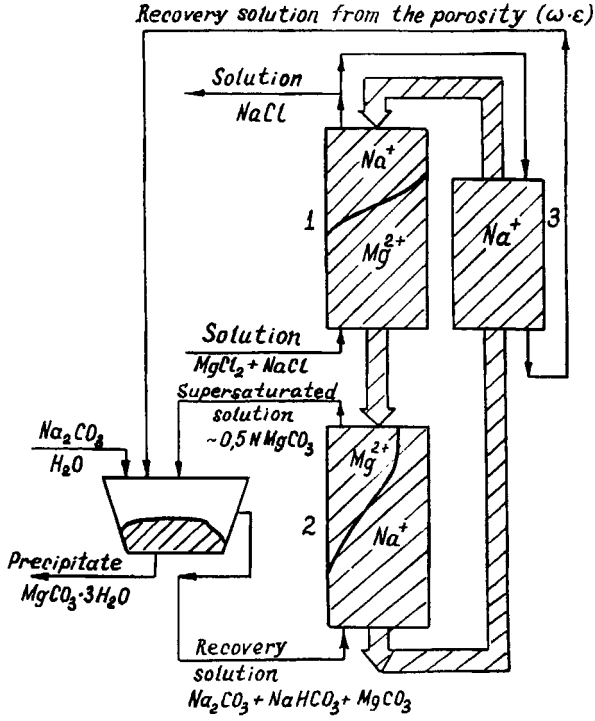

FIG. 10 Ion-exchange countercurrent process of magnesium recovery with sorption (1), regeneration (2), and electrolyte replacement (3) columns.

breakthrough curves. Curve 2 demonstrates the desorption process wherein the regeneration agent (1.5 M Na_2CO_3 + 0.6 M $NaHCO_3$ + 0.06 M $MgCO_3$) recovered after the previous cycle (with the remainder of dissolved magnesium compound) is used. The specific values of the main parameters of the proposed model are: $\epsilon = 0.35$, $a_0 = 3.0$ eq/L, $r_0 = 3\ h^{-1}$, $K_d = 3.7$ eq/L, $K_2^i = 3.56$, $E = 0.4\ m^2/h$, $\kappa = 5.1$ L/eq, $\lambda = 8$.

The ion-exchange process of magnesium compound recovery from seawater with the use of the supersaturation effect can best be designed as the countercurrent scheme shown in Fig. 10. At present, a large-scale pilot plant based on this design (with a potential output of more than 300 ton per year of pure magnesium compound) is under construction in the Far-East region of Russia (8). Seawater freed of calcium is passed with a flow rate v_S through sorption Column 1 with ion-exchange resin KB-4 ($w = 2\ m^3$) until magnesium appears in the eluting solution. Then a portion of resin (w_{eq}) loaded with Mg^{2+} to its equilibrium capacity is transferred into desorption Column 2 and treated with the recovery solution (Na_2CO_3 + $NaHCO_3$ + $MgCO_3$) at flow rate v_d. Then the resin is transferred to Column 3 for the replacement of electrolyte in the porosity volume. The

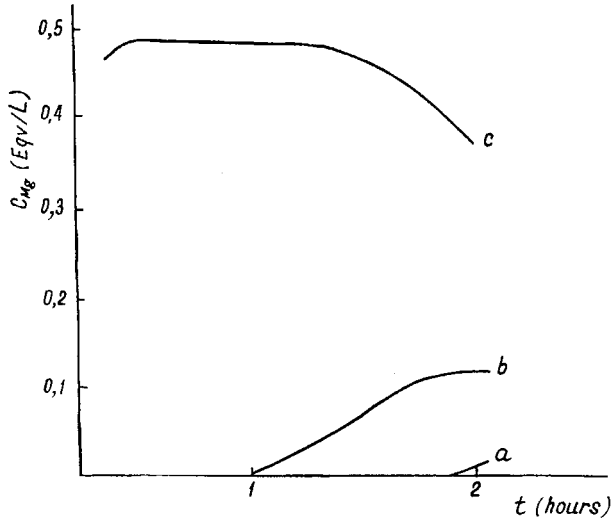

FIG. 11 Calculated breakthrough curves of sorption (a) and desorption (c) for Columns 1 and 2 in Fig. 10, respectively, at steady-state conditions; (b) assumed sorption curve for the lower half of Column 1.

regenerated ion-exchanger is transported back to the sorption column. In fact, all processes in Columns 1–3 occur concurrently, but the resin portion w_{eq} is transferred in a circle at regular time intervals t_i.

Figure 11 shows the calculated breakthrough curves for the cyclic coupled processes of sorption and desorption in Columns 1 and 2 after steady-state conditions are established. The rational parameters for these processes are: $w_{eq} = 1\ m^3$, $v_S = 11\ m^3/h$, $v_d = 2.5\ m^3/h$, $t_i = 2$ hours. The optimal desorption degree in one cycle is 70%; the total recovery of magnesium from seawater is more than 90%.

CONCLUSIONS

The effect of supersaturation of magnesium carbonate solutions in the ion-exchange process is demonstrated. A new sorption process for the recovery of magnesium compounds from seawater is developed on the base of this phenomenon.

The proposed process includes a new solution for the problem of separating Ca^{2+} and Mg^{2+} ions by the use of modified zeolites and allows pure magnesium carbonate to be produced.

This process eliminates the difficulties related to the separation of phases and avoids ecological problems as compared with traditional methods.

A mathematical model of the dynamics of the ion-exchange process involving supersaturation is developed and used to predict the rational conditions for a large-scale continuous process.

FURTHER COMMENTS

Dr. D. Muraviev from Moscow State University was the first to find the effect of isothermal supersaturation of amino-acids solutions in ion-exchange processes and to use this effect for the solution of specific separation problems.

Our preliminary studies showed the possibility of creating high supersaturation (10–50 times) solutions of magnesium compounds upon treatment of the Mg^{2+} form of carboxylic resins with concentrated solutions of ammonium carbonates. This permitted us to prepare some previously inaccessible double salts of magnesium by the ion-exchange method.

Further investigations will be required to reveal the general character of this effect in ion-exchange processes and its use for different applications.

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