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Clean Ion-Exchange Technologies. 2. Recovery of High-Purity Magnesium Compounds from Seawater by an Ion-Exchange Isothermal Supersaturation Technique

Ruslan Kh. Khamizov,[†] Dmitri Muraviev,*,[‡] Nikolai A. Tikhonov,[§] Anna N. Krachak,[†] Tatyana I. Zhiguleva,[†] and Olga V. Fokina[†]

Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Science, Kosygin Str. 19, 117975 Moscow, Russia, Department of Analytical Chemistry, Autonomous University of Barcelona, E-08193 Bellaterra (Barcelona), Spain, and Physics Department, Lomonosov Moscow State University, 119899 Moscow, Russia

This paper reports the results obtained by studying the ion-exchange isothermal supersaturation (IXISS) of magnesium carbonate solutions which is observed during elution of Mg^{2+} from carboxylic resin equilibrated with decalcinated seawater (artificial or natural) with either 2 M NH_4HCO_3 or with the mixture of 1.5 M Na_2CO_3 and 0.6 M $NaHCO_3$. Crystallization of supersaturated solution in the first case has been shown to lead to the formation of previously unknown complex ammonium–magnesium carbonate. The results of X-ray, chemical, and differential thermal analyses have allowed the proposal of the following formula for the new magnesium compound: $(NH_4)_2Mg(CO_3)_2 \cdot 5H_2O$. In the second case, crystallization of magnesium carbonate leads to the formation of a pure phase of nesquegonite: $MgCO_3 \cdot 3H_2O$ of 99.9% purity. Samples of MgO obtained after annealing ammonium–magnesium precipitates at 773 K contain less than 10^{-3}% of impurities.

Introduction

At present, around 25% of overall world production of magnesium stems from hydromineral resources such as seawater, underground brines, and so forth (Khamizov et al., 1995). The traditional magnesium-from-seawater technology includes mixing the raw seawater in special reservoirs with lime milk and then filtering, roasting, and treating the $Mg(OH)_2$ slurry with HCl. This is followed by evaporation, drying, and electrolysis (so-called "lime process"; Mero, 1965; Horne, 1969). Despite its profitability the traditional lime process fails to satisfy modern ecological standards. Consequently, new alternative technologies based on sorption and ion-exchange methods are being developed (Khamizov et al., 1995; Muraviev et al., 1996).

In the first communication of this series, we have demonstrated successful application of the ion-exchange isothermal supersaturation (IXISS) effect for designing highly efficient and ecologically clean ion-exchange technology for manufacturing chlorine-free potassium fertilizers (Muraviev et al., 1997a). The IXISS phenomenon, discovered for the first time by Muraviev (Muraviev, 1979), is observed in a number of ion-exchange systems where ion-exchange separation is accompanied by simultaneous concentration of the target substance in the interstitial space of ion-exchange column up to and beyond the level exceeding its solubility at a given temperature (Muraviev et al., 1979; Muraviev and Saurin, 1980; Muraviev and Gorshkov, 1982; Muraviev et al., 1982; Khamizov et al., 1996; Tikhonov, 1995; Muraviev et al., 1997b). The present communication is dedicated to the development of IXISS-based clean ion-exchange technology for recovery of high-purity magnesium compounds from seawater, which can be considered as a competitive alternative to the existing large-scale magnesium-from-seawater industrial processes.

The cycle of investigations being carried out in Russia is directed to the development of a practically wasteless complex technology of seawater processing, which combines recovery of valuable mineral components (more than 12 elements) from seawater with production of desalinated water as a byproduct (see Khamizov et al., 1995 and refs 15 and 19–21 therein). This technology includes a magnesium-recovery stage, which on one hand, must be adapted to the flowsheet of the whole process, and on the other hand, allows for the production of sufficiently pure magnesium compounds. For obvious reasons the lime process cannot be used within such a complex technology because of the high calcium content in the water to be processed and desalinated. A possible solution could be a substitution of lime with an alkali ("alkali process"; Khamizov et al., 1991), but this version of the process fails from an economical viewpoint. Magnesium precipitation with sodium carbonate ("soda process"; Mironova and Khamizov, 1994) seems eco-

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* To whom correspondence is addressed.

† Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Science.

‡ Autonomous University of Barcelona.

§ Lomonosov Moscow State University.

nomically reasonable, but is complicated by the low magnesium content in the initial seawater. The possibility of introducing a modified soda process into the complex technology flowsheet appeared with the discovery of IXISS of magnesium carbonate in the resin bed (Khamizov et al., 1995, 1996).

The present study was addressed (1) to study the formation and stability of supersaturated MgCO$_3$ solutions in columns using the IXISS technique, (2) to study the desorption efficiency of different IXISS-active stripping agents applicable for the yielding of high-purity magnesium compounds from seawater, and (3) to isolate and to study a pure solid phase of unknown ammonium−magnesium carbonate.

Experimental Section

Materials, Ion Exchangers, and Analytical Methods. Sodium chloride, sodium carbonate, sodium bicarbonate, ammonium carbonate, ammonium bicarbonate, and magnesium chloride of p.a. grade were used as received. Weakly acidic cation exchangers KB-4 and KB-4P2, were commercial ion exchangers (Russian production) of methyl methacrylate type containing 6% and 2.5% of cross-linking (divinylbenzene, DVB), respectively. Strong acid sulfonate cation-exchange resin KU-2 × 8 was also a commercial product (Russian analogue of Dowex-50 × 8 resin) with 8% of cross-linking (DVB). The total ion-exchange capacity of the resins equaled to 4.5 (KU-2 × 8), 9.0 (KB-4), and 9.6 (KB-4P2) mequiv/g. The concentrations of Na$^+$ and Mg^{2+} were determined by the atomic absorption technique using a Saturn-5 (Russia) photometer. The concentration of NH$_4^+$ was determined by potentiometric titration using a formaldehyde method. The relative uncertainty on the determination of ammonium and metal ions was not more than 2%.

Procedure. All experiments on IXISS of MgCO$_3$ solutions were carried out under dynamic conditions in laboratory-scale glass columns in a thermostated room at 298 ± 1 K. The ion exchangers preliminarily underwent conventional conditioning by going through several ion-exchange cycles followed by their conversion into the Mg form by rinsing resins in the Na form either with calcium-free natural seawater (seawater samples from the Sea of Japan) or with the mixture of 0.45 equiv/dm^3 of NaCl and 0.12 equiv/dm^3 of MgCl$_2$. This solution was shown to be an adequate model of decalcinated seawater (Khamizov et al., 1996). Then the columns were rinsed with deionized water from the excess of Mg^{2+} ions and prepared for the magnesium desorption (stripping) cycle. Decalcination of seawater was carried out as reported elsewhere (Khamizov et al., 1995, 1996). The stripping of magnesium was carried out by passing solution of either Na$_2$CO$_3$ + NaHCO$_3$ or (NH$_4$)$_2$CO$_3$ and NH$_4$HCO$_3$ through the bed of resin in the Mg form at a constant flow rate. The concentration and the composition of the Na$_2$CO$_3$ + NaHCO$_3$ mixture, (NH$_4$)$_2$CO$_3$, and NH$_4$HCO$_3$ solutions were varied in a wide range to determine the optimal conditions for IXISS of the magnesium carbonate solution. The supersaturated eluate was collected in portions where the concentrations of Mg^{2+}, NH$_4^+$, or Na$^+$ were determined. After complete crystallization of supersaturated solutions, the crystals were separated from the supernatant, rinsed with a small portion of cold deionized water, and examined by X-ray, chemical, and differential thermal analyses (DTA). The ion-exchange equilibrium was
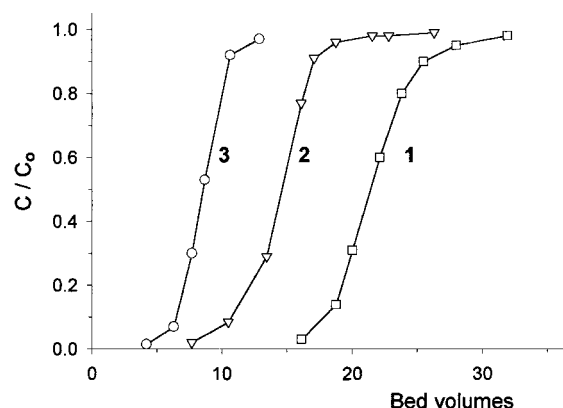

Figure 1. Concentration−volume histories obtained by sorption of Mg^{2+} on carboxylic resins KB-4 (1) and KB-4P2 (2) and sulfonate cation exchanger KU-2 × 8 (3) in Na form from artificial decalcinated seawater.

studied under dynamic conditions in columns by following the conventional procedure.

Results and Discussion

The typical breakthrough curves (normalized) of magnesium sorption from natural or artificial seawater on KU-2 × 8, KB-4, and KB-4P2 resins in the Na form are shown in Figure 1. As seen, the sorption of magnesium proceeds effectively (sorption fronts are sufficiently sharp) on all resins studied. This indicates to sufficiently high selectivity of both sulfonate (KU-2 × 8) and carboxylic (KB-4 and KB-4P2) resins toward Mg^{2+} versus Na$^+$. This conclusion is consistent with the results on the determination of selectivity factors for Na$^+$−Mg^{2+} exchange on carboxylic resins of different types from artificial and natural seawater (Khamizov et al., 1996; Muraviev et al., 1996). Nevertheless, the comparison of selectivity factors of Na$^+$−Mg^{2+} exchange (α_{Na}^{Mg}) on the resins under study, determined under identical conditions from decalcinated seawater, testify to the favor of KB-4 resin. Indeed, respective α_{Na}^{Mg} values are equal to 16.7 (KB-4), 9.4 (KB-4P2), and 3.1 (KU-2 × 8). The same conclusion follows from the comparison of resin capacities for Mg^{2+} (under given experimental conditions), which are equal to 2.7 (KB-4), 2.0 (KB-4-P2), and 1.0 (KU-2 × 8) mequiv per cm^3 of resin bed in the column. Figure 2 shows the typical concentration−time history obtained by the desorption of magnesium from KB-4 resin with the Na$_2$CO$_3$ + NaHCO$_3$ mixture (curve 1). During elution, magnesium carbonate does not precipitate in the column and remains as a stable supersaturated solution (with $\gamma \approx$ 5) at least over a period of 72 h. Removal of this solution from the column leads to spontaneous crystallization of the desorbed magnesium carbonate, which is readily separated from the supernatant by filtration or sedimentation. The induction period of crystallization strongly depends on temperature. Thus, at 273−278 K the supersaturated eluate remains stable during 1 day. At ambient temperature the crystallization starts in 1−2 h after collecting the product solution while at 310 K magnesium carbonate starts to precipitate ~5 min after the heating is finished (see below). During the stripping of magnesium the ion exchanger appears to be completely regenerated (converted into the desired Na form) and is prepared for the next magnesium sorption−desorption cycle. The results of the X-ray
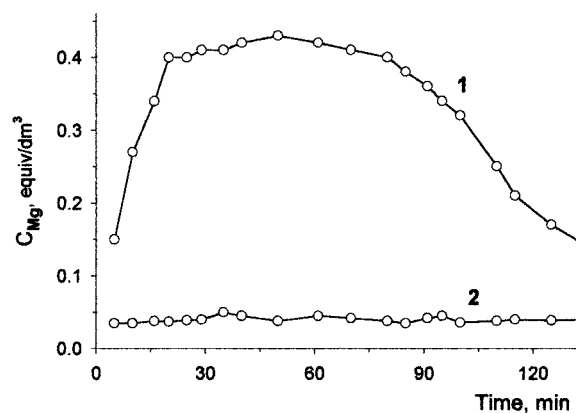
Figure 2. Concentration–time history of desorption of Mg^{2+} with 1.5 M Na_2CO_3 + 0.60 M $NaHCO_3$ (1) from KB-4 resin preloaded with decalcinated natural seawater at 293 K. Conditions: resin bed height = 33.1 cm; column cross-section area = 30 cm^2; solution flow rate = 2.3 dm^3/h. Curve 2 corresponds to Mg^{2+} concentration in a supernatant after crystallization of supersaturated solution samples (see text).

analysis of the crystals obtained (Khamizov et al., 1996) testify to the formation of a pure phase of nesquegonite: $MgCO_3 \cdot 3H_2O$. Unlike magnesite ($MgCO_3$), the nesquegonite crystals are calcium free. Hence, more than a 99.9% purity magnesium compound was obtained even from incompletely decalcinated seawater.

The yield of $MgCO_3 \cdot 3H_2O$ appears to depend on the conditions of crystallization of the supersaturated eluate collected. Thus, the crystallization at ambient temperature has been shown to give ~70% yield of the product in one desorption cycle (Khamizov et al., 1996). The residual magnesium content in the supernatant under these conditions depends on the time of crystallization and usually remains at the level of 0.08−0.10 equiv/dm^3 after several hours. The increase of crystallization time to 14−16 h allows for decreasing Mg^{2+} concentration in the supernatant to ~0.04−0.05 equiv/dm^3 but is technologically inconvenient. The fast increase of temperature in the crystallizer (during 10 min from ~290 to ~310 K) allows for substantial increasing of the rate of crystallization. As a result, the concentration of Mg^{2+} in the supernatant drops to 0.04 mequiv/dm^3 within 10−15 min and the yield of the product rises up to >90%. Curve 2 in Figure 2 corresponds to the residual Mg^{2+} concentration in the eluate samples collected (see curve 1) after short-term heating followed by crystallization of $MgCO_3 \cdot 3H_2O$.

A variety of IXISS-active stripping agents have been tested in a series of experiments on the desorption of Mg^{2+} from KB-4 resin (Muraviev et al., 1997b). The choice of the IXISS-active eluents was based on the following considerations:

1. The IXISS-active stripping agent must be bearing, on one hand, the desired counterion to combine the desorption of the product with the regeneration of the ion exchanger. On the other hand, it also must contain an appropriate co-ion to provide the formation of a stable supersaturated solution of a low-solubility compound (the product) and to shift the ion-exchange equilibrium in the system to the desired direction. This can be illustrated by a Na^+-Mg^{2+} exchange reaction on a carboxylic resin, which can be written as follows:

$$(R-COO^-)_2Mg^{2+} + 2Na^+ \leftrightarrow 2R-COO^-Na^+ + Mg^{2+} \tag{1}$$
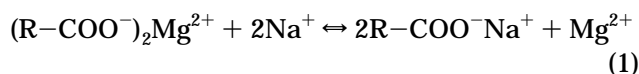
The equilibrium in reaction 1 can be quantitatively characterized by the equilibrium coefficient, $K_{Mg^{2+}}^{Na^+}$:

$$K_{Mg^{2+}}^{Na^+} = \frac{Q_{Na}(C_{Mg})^{1/2}}{(Q_{Mg})^{1/2} C_{Na}} \tag{2}$$

where C and Q are the concentrations of ions in the solution and resin phases, respectively. For chloride or sulfate media $K_{Mg^{2+}}^{Na^+}$ is known to be <1 (Khamizov et al., 1996; Muraviev et al., 1996). If reaction 1 proceeds in a carbonate media, for example, when the resin in the Mg form is treated with a Na_2CO_3 (or Na_2CO_3 + $NaHCO_3$) solution (C_0, mol/dm^3), it is coupled with the formation $MgCO_3$, which can be described by the solubility product of $MgCO_3$, L_{MgCO_3}, as follows:

$$L_{MgCO_3} = C_{Mg^{2+}} C_{O_3^{2-}} \tag{3}$$

In the case when $MgCO_3$ forms a stable supersaturated solution, where magnesium carbonate exists in an associated (molecular) form at a concentration C_M mol/dm^3 exceeding γ times the solubility of $MgCO_3$, C_S, at a given temperature, eq 3 can be rewritten in the following form:

$$L_{MgCO_3} = C_{Mg^{2+}}(C_0 - C_M) \tag{4}$$

By introducing $C_M = \gamma C_S$, and after substitution of C_{Mg} from (4) into (2), one obtains

$$K_{Mg^{2+}}^{Na^+} = \frac{Q_{Na}(L_{MgCO_3})^{1/2}}{(Q_{Mq})^{1/2} C_0 (C_0 - \gamma C_S)^{1/2}} \tag{5}$$

As follows from eq 5, at constant C_0, C_S, and L_{MgCO_3}, $K_{Na^+}^{Mg^{2+}}$ increases with γ and may reach sufficiently high values ($\gg1$), as $\gamma \to C_0/C_S$. Equation 5, derived for the first time by Muraviev, can be rewritten in a more general form for the displacement of the divalent metal ion (e.g., Mg^{2+}) from the resin with an IXISS-active stripping agent bearing a monovalent counterion (e.g., Na^+) as follows:

$$K_{Sss}^{Dis} = \frac{Q_{Dis}}{(Q_{Sss})^{1/2}} \frac{L^{1/2}}{C_0 (C_0 - \gamma C_S)} \tag{6}$$

where "Dis" and "Sss" superscript and subscript denote the displacer and the product (substance under supersaturation, respectively), C_0 is the concentration of the displacer solution, L is the solubility product of the target compound (product), C_S is the solubility of the product at a given temperature, and γ is the supersaturation degree of the product solution. Note that Muraviev's equation (eq 6) is the fundamental equation describing the shift of ion-exchange equilibrium in IXISS systems of different types.

2. The successful application of the IXISS effect requires, on one hand, maximum stability of the supersaturated solution in the interstitial space of the column during the ion-exchange treatment cycle and, on the other hand, fast decomposition (crystallization) of this solution after its removal from the column. In the case of inorganic substances a unified interpretation of the IXISS phenomenon must be based (at least at the moment) on general principles of the aggregative stability of dispersion systems (Friedrichsberg, 1984; Peters

et al., 1974; Pankow, 1991), adapted to the particular ion-exchange systems.

3. The following main factors may influence the stability of dispersions of precrystalline molecular aggregates in the interstitial space: (1) an effective charge of the polymolecular aggregate, which is due to the sorption of either counter- or co-ions on the particle surface and (2) the ionic strength of the media, which may strongly influence the coagulation (crystallization) conditions (Friedrichsberg, 1984; Peters et al., 1974; Pankow, 1991).

If, for example, component A is desorbed from an ion exchanger by an IXISS-active stripping agent BC (where C is a co-ion) and forms a slightly soluble compound AC in the interstitial space of the column, the charge sign of AC aggregates (micellae) will be the same as that of co-ions if an excess of C versus A ions exists in the interstitial space. In this case the sorption of the micellae on the surface of the ion-exchanger beads becomes impossible and a stabilizing action of the resin bed toward supersaturated solution can be expected. On the other hand, in the presence of an excess of A ions in the interstitial solution, the charge sign of AC aggregates will coincide with that of counterions and fast decomposition of the supersaturated solution is observed due to the sorption of micellae on the surface of the ion exchanger followed by crystallization of the AC component.

Results of electromigration experiments carried out with supersaturated solutions of different compositions (including magnesium carbonate) prior to their crystallization substantiate the formation of charged micellae and allow for the detection of the sign of their effective charge. Decomposition of supersaturated solutions in all experiments carried out has been observed on one of two electrodes. Hence, this technique can be applied for forecasting the stabilizing/destabilizing effect of the given ion exchanger toward supersaturated solutions of different composition. Nevertheless, this point requires a stricter theoretical interpretation, and we intend to continue our investigation on the subject

The results of our experiments demonstrate the possibility of carrying out stable IXISS-based ion-exchange processes at $\gamma \leq 5-10$, which can be applied for the recovery of high-purity magnesium compounds from seawater. A comparison of the stripping efficiency of sodium carbonate−bicarbonate eluents of different compositions has shown that the optimal composition of $Na_2CO_3-NaHCO_3$ mixture corresponds to $1.5-1.6$ mol/dm^3 of Na_2CO_3 and $0.4-0.6$ mol/dm^3 of $NaHCO_3$. At present a large-scale pilot plant using the countercurrent version of an IXISS-based process for the recovery of more than 300 ton of high-purity magnesium carbonate from seawater per year has started to be operating in the Vladivostok region of Russia. The block scheme of the completely automated pilot-scale unit, adequately imitating (in the fixed-bed mode of operation) the Vladivostok plant at 1:1000 scale is shown in Figure 3. The raw seawater is preliminary decalcinated by also using the IXISS technique (for details see Khamizov et al., 1996). During the sorption stage calcium-free seawater passes over 2.5 h from the top to the bottom at the flow rate of 10 dm^3/h through two of the three columns C_1-C_3 loaded with 1 dm^3 of KB-4 resin in the Na form. At the same time the third column is working in the regeneration (magnesium-stripping) mode of operation. After conversion of resin in the Mg
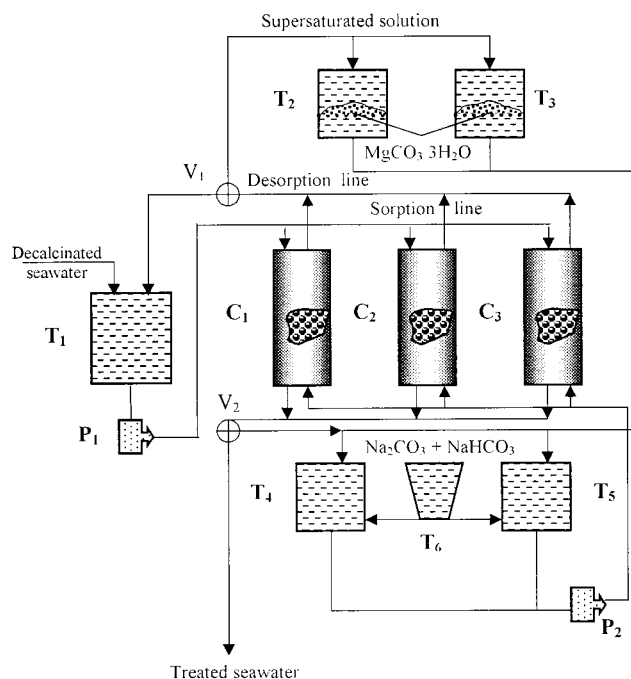

Figure 3. Schematic diagram of experimental pilot unit for recovery of high purity magnesium compounds from seawater (see text): ion-exchange columns C_1-C_3; solution tanks T_1-T_6; solution pumps P_1 and P_2; automatic valves V_1 and V_2.

form the columns are treated from the bottom to the top with a stripping solution of $Na_2CO_3-NaHCO_3$ mixture (containing also a residual $MgCO_3$ from recycled stripping solution) at a flow rate of 2.3 dm^3/h. Ca-free seawater, displaced from the columns, is directed to tank T_1 until the appearance of supersaturated eluate, which is in turn directed to tanks T_2 and T_3 (crystallizers) by reswitching the automatic valve V_1. Tanks T_2 and T_3 are supplied with heating and filtration facilities to collect the crystalline product. After crystallization and removal of magnesium carbonate the stripping solution is returned back to tanks T_4 and T_5 for fortification with the desired amount of the $Na_2CO_3-NaHCO_3$ mixture from T_6 and reuse. Then the sorption cycle repeats. The stripping solution displaced from the columns is also returned back to T_4 and T_5 until the appearance of treated seawater in the line that is controlled by the automatic valve V_2. Hence, the process shown in Figure 3 is absolutely wasteless. All stages of the process are controlled by the computer provided with the specially designed software. The unit is working in an absolutely automatic mode of operation. Note that the results presented in Figure 2 where obtained on the unit shown in Figure 3.

Another route to increase the purity of magnesium compounds recovered from seawater has been found within the series of experiments carried out with ammonium carbonate and ammonium bicarbonate stripping solutions. Unlike sodium carbonate, ammonium carbonate (or bicarbonate) impurities can be completely removed from the final magnesium product by thermal decomposition that must result in remarkable increase of the product purity. The concentration−volume histories of magnesium desorption with ammonium carbonate and bicarbonate solutions are shown in Figure 4. The shape of breakthrough curves presented in Figure 4 indicates the reversal of KB-4 resin selectivity for the $Mg^{2+}-NH_4^+$ ionic couple in the carbonate media (see eqs 5 and 6 and comments). Indeed, under con-
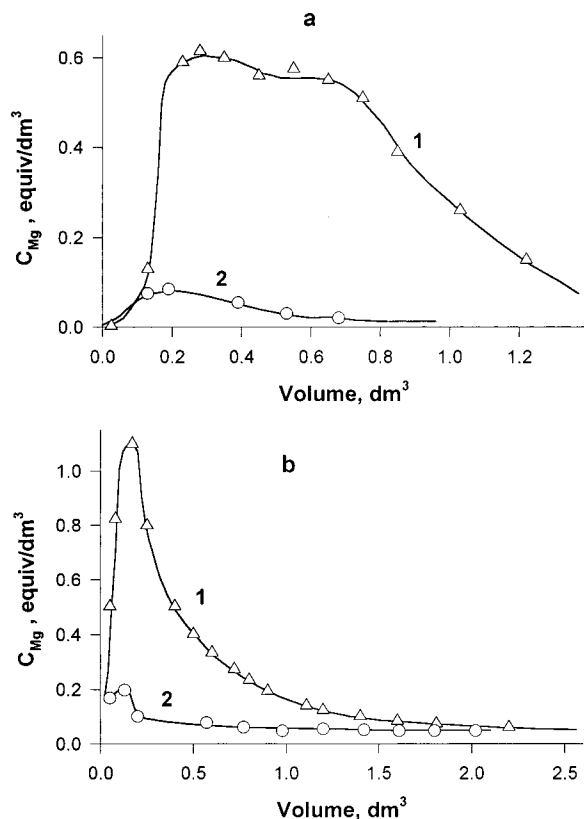
Figure 4. Concentration—volume histories of stripping of magnesium from carboxylic resin preequilibrated with decalcinated natural seawater with 2 M $(NH_4)_2CO_3$ (a) and 2M NH_4HCO_3 (b) solutions. Conditions: resin bed height = 84 cm; column cross-section area = 2.7 cm²; solution flow rate = 1.25 dm³/h. Curves 2 correspond to Mg^{2+} concentration in a supernatant after crystallization of supersaturated solution samples.

ventional conditions (e.g., in chloride media) KB-4 resin manifests high selectivity toward Mg^{2+} versus NH_4^+ ($\alpha_{NH_4}^{Mg} = 12.5$). As seen in Figure 4a, the supersaturation degrees achieved by using ammonium carbonate appear to be much higher in comparison with the sodium carbonate systems (see curve 1 in Figure 2). The first portions of the eluate obtained are characterized by $\gamma = 8-10$, while in the last portions γ rises to 25–30. As a result, the yield of the crystalline magnesium product significantly exceeds 90%. On the other hand, this feature of the ammonium carbonate system makes it technologically inconvenient due to the low stability of supersaturated solutions obtained.

The results of X-ray analysis of precipitates obtained from different portions of the supersaturated eluate collected show the formation of the nesquegonite phase in the first fractions, where γ values are relatively low. In other eluate portions crystallization leads to the formation of two mixed phases containing a minor constituent of magnesium hydroxycarbonate. The major component appeared to be hardly assigned to any known ammonium or magnesium carbonate phases or their derivatives reported in ASTM (ASTM, 1974).

A more stable IXISS process is observed in applying NH_4HCO_3 stripping solutions (see Figure 4b). In all experiments carried out the stripping of magnesium was accompanied by the release of CO_2 in the resin bed; nevertheless, the process was sufficiently stable and well-reproducible. The supersaturation degrees being reached in this process were around $5 < \gamma < 10$.

Spontaneous crystallization of the supersaturated

Table 1. Comparison of Pattern Parameters of Isolated Unknown Solid Phase vs Pb—Mg and Ba—Mg Carbonates

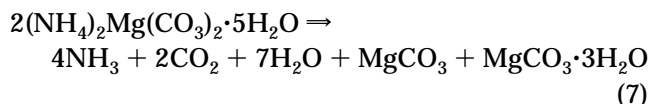| isolated samples		$PbMg(CO_3)_2{}^a$		$BaMg(CO_3)_2{}^a$	
d	I (%)	d	I (%)	d	I (%)
6.06	40	5.52	50	5.58	25
4.47	20	4.13	75	4.21	30
3.82	90	3.79	75	3.86	35
2.98	100	2.97	100	3.02	100
2.65	6	2.62	50	2.66	35
2.35	8	2.46	50	2.29	25
2.21	10	2.25	50	2.16	25
1.93	30	2.11	50	2.10	35

^{a} Data taken from ASTM.

Table 2. Results of DTA Analysis of Solid Ammonium—Magnesium Carbonate Samples

stage no.	decomposition temp. (T_D, °C)	temp. interval (°C)	wt loss (%)
1	120	40–238	63.6
2	257	238–280	0.86
3	317	280–338	1.10
4	407	338–455	16.22

eluate started in 1–2 h after its removal from the column. As seen in Figure 4b, the concentrations of Mg^{2+} in the first two portions of the eluate (see curve 2) are much higher than those in the rest of the fractions due to the different solubility of respective solid phases formed. The results of the X-ray analyses of the precipitate samples indicated the formation of the nesquegonite phase in the first two samples of the eluate, while crystallization of other samples leads to the formation of an unknown solid phase, which is similar to that obtained in the experiments with $(NH_4)_2CO_3$. The pattern parameters of the unknown solid phase appear to be similar to those of some double magnesium carbonates, as follows from the comparison of the data given in Table 1. Results of the differential thermal analysis (DTA) of the unknown solid-phase samples are shown in Table 2.

The chemical analysis of precipitates isolated and air-dried at 35 °C gives the following molar rations: NH_4:Mg:CO_3:H_2O = 1.90:1.08:2.03:5.02. The results of the chemical and DTA analyses allow one to propose the following formula for the unknown compound: $(NH_4)_2Mg(CO_3)_2\cdot5H_2O$ and suggest the following scheme of its thermal decomposition:

stages 1 and 2 (T_D = 120 and 257 °C):

$$2(NH_4)_2Mg(CO_3)_2\cdot5H_2O \Rightarrow$$
$$4NH_3 + 2CO_2 + 7H_2O + MgCO_3 + MgCO_3\cdot3H_2O \quad (7)$$

stage 3 (T_D = 407 °C):

$$MgCO_3\cdot3H_2O \Rightarrow MgCO_3 + 3H_2O \quad (8)$$

stage 4 (T_D = 407 °C):

$$MgCO_3\cdot3H_2O \Rightarrow MgO + CO_2 \quad (9)$$

The validity of this scheme has been confirmed by the results of the X-ray analysis of solid products obtained after sequential thermotreatment of solid samples at 250, 280, 350, and 500 °C.

Ion-exchange synthesis of double ammonium—magnesium carbonate in the system involving carboxylic resin in the Mg form (R_2—Mg) and NH_4HCO_3 solution

can be described by the following reaction:

$$R_2-Mg + 4NH_4HCO_3 + 3H_2O \Longrightarrow$$
$$2R-NH_4 + (NH_4)_2Mg(CO_3)_2{\cdot}5H_2O{\downarrow} + 2CO_2{\uparrow} \quad (10)$$
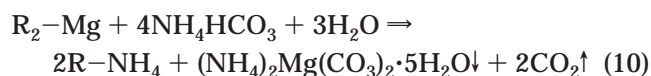
Reaction 10 can also be used for the manufacture of highly pure magnesium compounds from seawater by using an ammonium bicarbonate stripping solution instead of sodium carbonate−bicarbonate mixtures (see Figure 3). Samples of MgO obtained after annealing ammonium−magnesium precipitates at 500 °C contain less than 10^{-3} mass % of impurities.

In conclusion, we would like to emphasize that complex ammonium−magnesium carbonate cannot be isolated under conventional conditions, for example, by precipitation from $MgSO_4$ or $MgCl_2$ solutions with concentrated $(NH_4)_2CO_3$ or NH_4HCO_3 solutions (Nekrasov, 1967). The results of X-ray analysis of precipitates obtained after decomposition of supersaturated solutions in such systems testify to the formation of the mixture of magnesium carbonate and hydroxycarbonate phases. Hence, the ion-exchange synthesis of solid $(NH_4)_2Mg(CO_3)_2{\cdot}5H_2O$ is the first successful application of the IXISS effect for obtaining unknown inorganic compounds.

Acknowledgment

Literature Cited

ASTM. *Selected Powder Diffraction Data for Minerals,* 1st ed.; ASTM: Philadelphia, PA, 1974.

Friedrichsberg, D. A. *Colloid Chemistry*, 2nd ed.; Khimia: Leningrad, 1984 (Russian).

Horne, R. A. *Marine Chemistry. The Structure of Water and the Chemistry of Hydrosphere*; Wiley: New York, 1969; pp 444−46.

Khamizov, R. Kh.; Mitchenko, T. E.; Bronov, L. V.; Senyavin, M. M.; Ezbekov, A. A.; Postolov, L. E. Method for Manufacturing Mineral Compounds from Seawater. Inventor Certificate of USSR 1,678,771, 1991.

Khamizov, R. Kh.; Muraviev, D.; Warshawsky, A. Recovery of Valuable Mineral Components from Seawater by Ion Exchange and Sorption Methods. In *Ion Exchange and Solvent Extraction. A Series of Advances*; Marinsky, J., Marcus, Y., Eds.; Marcel Dekker: New York, 1995; Vol. 12, Chapter 3.

Khamizov, R. Kh.; Mironova, L. I.; Tikhonov, N. A.; Bychkov, A. V.; Poezd, A. D. Recovery of Pure Magnesium Compounds from Seawater by the Use of the Effect of Isothermal Supersaturation in the Ion-Exchange Process. *Sep. Sci. Technol.* **1996**, *31* (1), 1.

Mero, J. L. *The Mineral Resources of the Sea*; Elsevier: Amsterdam, 1965; pp 34−39.

Mironova, L. I.; Khamizov, R. Kh. Method for Production of Mineral Compounds from Seawater. Patent Russ. Fed. 2,00,-476, 1994.

Muraviev, D. Ion Exchange Isothermal Supersaturation of Amino Acid Solutions. *Zh. Fiz. Khim.* **1979**, *53*, 438 (Russian).

Muraviev, D.; Saurin, A. D. Sorption Isotherm of Aspartic Acid on Cation Exchanger KU-2 × 8 from Unsaturated and Supersaturated Solutions. *Zh. Fiz. Khim.* **1980**, *54*, 1271 (Russian).

Muraviev, D.; Gorshkov, V. I. Purification of L-Glutamic Acid from Racemate Admixture by Ion Exchange Isothermal Supersaturation. *Zh. Fiz. Khim.* **1982**, *56*, 1560 (Russian).

Muraviev, D.; Gorshkov, V. I.; Medvedev, G. A.; Ferapontov, N. B.; Kovalenko, Ju. A. Ion Exchange Purification of Glutamic Acid from Mineral Salts in Countercurrent Columns. *Zh. Prikl. Khim.* **1979**, *52*, 1183 (Russian).

Muraviev, D.; Gorshkov, V. I.; Fesenko, S. A. Ion Exchange in Supersaturated Solutions. I. Study of Stability of Supersaturated Amino Acid Solutions in Contact with Ion Exchangers of Different Types. *Zh. Fiz. Khim.* **1982**, *56*, 1567 (Russian).

Muraviev, D.; Noguerol, J.; Valiente, M. Separation and Concentration of Calcium and Magnesium from Seawater by Carboxylic Resins with Temperature Induced Selectivity. *React. Funct. Polymers* **1996**, *28*, 111.

Muraviev, D.; Khamizov, R. Kh.; Tikhonov, N. A.; Krachak, A. N.; Zhiguleva, T. I.; Fokina, O. V. Clean Ion-Exchange Technologies. 1. Synthesis of Chlorine-Free Potassium Fertilizers by Ion-Exchange Isothermal Supersaturation Technique. *Ind. Eng. Chem Res.* **1997a**, in press.

Muraviev, D.; Khamizov, R. Kh.; Tikhonov, N. A. Dynamics of Ion Exchange in Supersaturated Solutions. *Langmuir* **1997b**, *13* (26), 7186−7191.

Nekrasov, B. V. *Inorganic Chemistry*; Khimia: Moscow, 1967; Vol. 2, pp 275−277.

Pankow, J. F. *Aquatic Chemistry Concepts*; Lewis: Chelsea, 1991; pp 644−656.

Peters, D. G.; Hayes, J. M.; Hieftje, G. M. *Chemical Separation and Measurements. Theory and Practice of Analytical Chemistry*; Saunders Co.: New York, 1974; pp 212−220.

Tikhonov, N. A. Modelling the Isothermal Supersaturation in a Sorbent, *Comput. Maths Math. Phys.* **1995**, *35*, 375.