Recovery of Strontium Ions with Calcium and Magnesium Phosphates from Aqueous Solutions against the Background of CaCl₂

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Abstract—The ability of calcium and magnesium phosphates of different compositions to selectively take up ions of stable strontium and of ^{85}Sr radionuclide from calcium-containing solutions (0.05 M CaCl₂), including those containing complexones (EDTA, HEDP), was studied. In the presence of 0.05 M CaCl₂, the sorption capacity of calcium phosphates for strontium ions decreases by a factor of 8–10. Magnesium phosphates and magnesium-containing sorbents prepared from natural dolomite preserve up to 90% of the sorption capacity (80–100 mg g^{-1}) in the presence of CaCl₂ and complexones, compared to salt-free aqueous solutions, and the ^{85}Sr distribution coefficient against the background of 0.05 M CaCl₂ is $(1.1–1.3) \times 10^2$ cm^3 g^{-1}. The mechanism of different behavior of calcium and magnesium phosphate sorbents toward strontium ions was suggested, and the effect of HEDP and EDTA on the strontium uptake by these sorbents was revealed.

Keywords: calcium and magnesium phosphates, hydroxylapatite, strontium, sorption, liquid radioactive waste

Inorganic sorbents are considered today as the most promising sorbents for removing long-lived strontium radionuclides from liquid radioactive waste (LRW) because of their relatively high selectivity to strontium ions and high levels of chemical durability and of heat and radiation resistance [1–3]. One of the most effective inorganic sorbents for Sr is hydroxylapatite, with which the distribution coefficient (K_d) of Sr radionuclides in aqueous solutions can reach values of the order of 10^5 [4–6]. According to our data [7–9], other calcium phosphates such as tricalcium phosphate and calcium hydrophosphate, and also magnesium phosphates, along with hydroxylapatite, also exhibit high ability to take up polyvalent metal ions, including Sr ions, from aqueous solutions. The ^{85}Sr distribution coefficient in aqueous solutions on these phosphate sorbents exceeds 5×10^3 cm^3 g^{-1}.

However, real LRWs are multicomponent aqueous solutions of complex chemical composition, containing large amounts of Na$^+$, Ca^{2+}, and Mg^{2+} cations, and also

surfactants and complexones, including disodium dihydrogen ethylenediaminetetraacetate (EDTA) and 1-hydroxyethane-1,1-diphosphonic acid (HEDP) [10, 11]. It is known that the ability of the overwhelming majority of the known sorbents to selectively take up Sr radionuclides decreases considerably in salt solutions, especially in those containing calcium: The ^{85}Sr distribution coefficient on mixed Mn(III, IV) oxide decreased by a factor of 36 in the presence of 0.01 M Ca(NO₃)₂ (from 40 000 to 1100 cm^3 g^{-1}) relative to the adsorption from a 0.1 M NaNO₃ solution, and for synthetic chabazite the ^{85}Sr distribution coefficient decreased by a factor of 200 under the same conditions (from 5000 to 250 cm^3 g^{-1}) [12].

In this connection, we studied the ability of calcium- and magnesium-containing phosphate sorbents to selectively take up ions of stable Sr and of ^{85}Sr radionuclide in the presence of CaCl₂ and complexing agents: EDTA and HEDP.

EXPERIMENTAL

As investigation objects we used synthetic calcium and magnesium phosphates of different compositions: acidic [$CaHPO_4$ (calcium hydrophosphate CHP) and $MgHPO_4 \cdot 3H_2O$ (magnesium hydrophosphate trihydrate, MHP)], neutral [$Ca_3(PO_4)_2 \cdot 2H_2O$ (tricalcium phosphate dihydrate, TCP)], and basic [$Ca_{10}(PO_4)_6 \cdot (OH)_2$ (hydroxylapatite, HA)]. All the phosphates were prepared by chemical precipitation from solutions by standard procedures [13]. Also, as in the previous study [9], we performed experiments with mixed calcium and magnesium phosphates prepared by phosphatization of natural dolomite. These products consisted of a mixture of acidic (PD-1) and neutral (PD-2) calcium and magnesium phosphates.

The ability of the synthesized sorbents to take up Sr cations was studied under static conditions at the ratio $V/m = 250$ cm^3 g^{-1} using stable Sr and ^{85}Sr radionuclide. In the first case, the sorption of Sr ions was performed from strontium nitrate solutions with the Sr^{2+} concentration in the interval 100−2000 mg L^{-1}. The Sr concentration in solutions before and after the contact with the sorbents (24 h) was determined with an AAS Contr AA 300 atomic absorption spectrometer (Germany).

When studying the ^{85}Sr uptake by phosphate sorbents, the ^{85}Sr activity concentration in the solution before (A_{init}, kBq cm^{-3}) and after the sorption (A_{fin}, kBq cm^{-3}) was studied with an MKS AT1315 γ,β-ray spectrometer. After that, the degree of recovery (S, %) and the distribution coefficient (K_d, cm^3 g^{-1}) of ^{85}Sr were calculated.

To examine the effect of calcium cations on the Sr recovery, the solutions were prepared with the addition of CaCl$_2$ (pure grade) to a concentration of 0.05 M. The complexone solutions were prepared from EDTA disodium salt (chemically pure grade) and HEDP (technical grade); their content in the model solution was 1×10^{-3} M. When using complexones in the experiments, we initially prepared a mixture of calcium chloride with the addition of EDTA or HEDP. This mixture was allowed to stand for 24 h at the chosen pH value (pH 5.0), after which Sr was added. Then, a weighed portion of the sorbent was added to the solution. The choice of pH 5.0 of the initial solutions is governed by creation of the conditions for predominant formation of metal–ligand complexes, with the formation of hydroxo complexes reduced to a minimum [14].
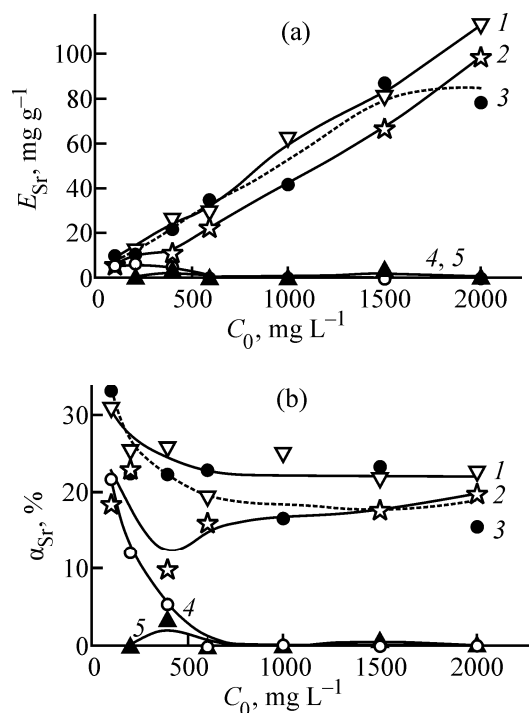

Fig. 1. (a) Sorption isotherms and (b) degrees of recovery of Sr^{2+} ions with (*1*) PD-2, (*2*) PD-1, (*3*) MHP, (*4*) TCP, and (*5*) HA samples from Sr(NO$_3$)$_2$ solutions containing 0.05 M CaCl$_2$. (E_{Sr}) Sorption capacity for Sr^{2+} ions, (α_{Sr}) degree of recovery, and (C_0) initial concentration of Sr^{2+} in model solutions.

To analyze the chemical and phase transformations occurring in the course of the Sr sorption, we performed X-ray diffraction (XRD) analysis of the sorbents before and after the contact with model solutions. The diffraction patterns were taken with a DRON-3 installation using CuK_α radiation (2θ range 10°−70°).

RESULTS AND DISCUSSION

The isotherms of strontium sorption by the synthesized calcium and magnesium phosphates from aqueous solutions in the presence of 0.05 M CaCl$_2$ are shown in Fig. 1a. Comparison of the sorption isotherms shows that all the calcium phosphates in salt solutions have low values of Sr adsorption (5−10 mg g^{-1}) throughout the examined concentration range (100–2000 mg L^{-1}). For the magnesium-containing sorbents (MHP, PD-1, PD-2), however, the pattern is essentially different (Fig. 1a, curves *1–3*). These sorbents exhibit high sorption capacity, 80–100 mg g^{-1}. For acidic magnesium phosphate, the sorption capacity for Sr in the presence of CaCl$_2$ decreases

Degrees of recovery (S) and distribution coefficients (K_d) of ^{85}Sr in its sorption from aqueous solutions of different compositions onto various sorbents at V/m = 250 cm^3 g^{-1}

Sample	Solution composition							
	H$_2$O		CaCl$_2$		CaCl$_2$ + EDTA		CaCl$_2$ + HEDP	
	S, %	$K_d \times 10^{-2}$, cm^3 g^{-1}	S, %	$K_d \times 10^{-2}$, cm^3 g^{-1}	S, %	$K_d \times 10^{-2}$, cm^3 g^{-1}	S, %	$K_d \times 10^{-2}$, cm^3 g^{-1}
CHP	56	3.2	6	0.2	4	0.1	8	0.2
TCP	57	3.3	7	0.2	6	0.2	11	0.3
HA	92	38.0	10	0.3	14	0.4	16	0.5
MHP	75	7.5	34	1.3	31	1.1	32	1.2
PD-1	37	1.5	12	0.4	12	0.3	14	0.4
PD-2	97	99.3	31	1.1	34	1.3	35	1.4

relative to salt-free aqueous solutions by a factor of approximately 3 [9]. For example, whereas the strontium uptake by manganese phosphate from aqueous solutions containing 2000 mg L^{-1} Sr was approximately 250 mg g^{-1}, in the presence of 0.05 M CaCl$_2$ the adsorption was about 80 mg g^{-1}. For PD-2 sample, introduction of CaCl$_2$ into the solution does not noticeably influence its ability to take up Sr: The sorption capacity reaches 100 mg g^{-1}.

As seen from Fig. 1b, the degree of recovery of Sr ions with magnesium-containing sorbents is considerably higher than with calcium-containing sorbents. The degree of recovery of Sr ions from solutions with the concentration not exceeding 100–200 mg L^{-1} is about 30%, and at higher Sr concentrations it regularly decreases to 2–3 and 15–20% for calcium- and magnesium-containing sorbents, respectively.

On the whole, there is correlation in the behavior of calcium- and magnesium-containing phosphate sorbents in salt-free aqueous Sr(NO$_3$)$_2$ solutions [9] and in solutions containing 0.05 M CaCl$_2$. In particular, in both cases MHP exhibits the highest capacity for Sr ions, and TCP, the lowest capacity. The above results indicate that magnesium materials, preserving the ability to selectively take up Sr ions from salt solutions, can be promising sorbents for the treatment of natural and process waters to remove Sr, and their further study is of indubitable interest.

It should be noted, however, that the above studies were performed using model solutions with high Sr concentration, up to 2000 mg L^{-1}, whereas real LRWs contain Sr radionuclides in considerably lower concentrations. The sorbent behavior toward macro- and microconcentrations of a sorbate can be essentially different. Therefore, we studied the ability of phosphate sorbents to selectively take up ^{85}Sr from aqueous solutions containing 0.05 M CaCl$_2$, in particular, from those containing also complexing agents: EDTA and HEDP.

The results that we obtained in studying the ^{85}Sr uptake by calcium and magnesium phosphates from aqueous solutions of different compositions are given in the table. Data on the removal of ^{85}Sr from salt-free aqueous solutions are presented for comparison.

As seen from the table, the sorption activity of calcium and magnesium phosphate sorbents in aqueous solutions without additives increases in the order

$$PD\text{-}1 < CHP < TCP < MHP < HA < PD\text{-}2. \quad (1)$$

For example, in ^{85}Sr uptake from aqueous solutions, K_d increases in this series from 1.5×10^2 cm^3 g^{-1} for PD-1 to 99.3×10^2 cm^3 g^{-1} for PD-2, and the mean degree of recovery for the same samples increases from 37 to 97%. The highest sorption capacity in salt-free aqueous solutions is exhibited by MHP, HA, and PD-2: The degree of Sr recovery with these phosphates reaches 97%. The results obtained are fully consistent with the results of studying the ability of these sorbents to take up ions of stable Sr.

The ability of all the sorbents under consideration to take up Sr ions from aqueous solutions against the background of CaCl$_2$ both in the presence of complexones and without them is considerably lower compared to straight aqueous solutions. The distribution coefficient K_d of Sr between the solid and liquid phases in salt solutions is $(0.1–1.4) \times 10^2$ cm^3 g^{-1}, and the degree of recovery is 4–35%. On the other hand, magnesium-containing sorbents, especially MHP and PD-2, considerably surpass calcium phosphates in the sorption activity in salt solutions. The phosphates can be ranked in the following order with respect to the efficiency of the ^{85}Sr uptake from salt solutions:

$$CHP = TCP < HA < PD\text{-}1 < MHP \approx PD\text{-}2. \quad (2)$$
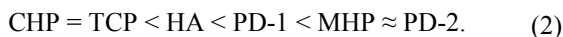
Comparison of series (1) and (2) shows that the most effective sorbent for Sr among calcium phosphates, HA, exhibits no selective properties and does not noticeably take up ^{85}Sr against the background of $CaCl_2$. It is known that HA is an inorganic ion exchanger and that it takes up ions via reaction (3)

$$Ca_{10}(PO_4)_6(OH)_2 + xSr^{2+} \rightarrow Ca_{(10-x)}Sr_x(PO_4)_6(OH)_2 + xCa^{2+},$$
$$(3)$$
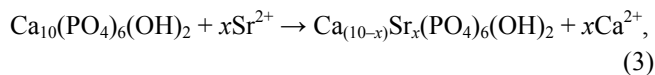
where $x = 0{-}10$.

In calcium-containing solutions, the equilibrium of this reaction is shifted to the left up to cessation of the process. It is interesting that the sorption capacity of calcium phosphates, including HA, decreases by a factor of 8–10 in going from salt-free solutions to calcium-containing aqueous solutions, whereas the sorption capacity of magnesium-containing phosphates decreases by a factor of only 2–3. This fact suggests more pronounced ability of magnesium sorbents, compared to calcium phosphate sorbents, to selectively take up Sr ions.

As seen from the table, complexones do not noticeably influence the ^{85}Sr uptake against the background of $CaCl_2$, irrespective of the sorbent composition. For all the calcium phosphates except HA, the presence of EDTA and HEDP in the salt solution affects the degree of Sr recovery and the distribution coefficient insignificantly, compared to the salt solution without complexone. We can note a slight increase in the degree of ^{85}Sr recovery with TCP in the presence of HEDP: from 31 to 35%, respectively. The effect of complexones on magnesium sorbents is similar: The presence of EDTA and HEDP in $CaCl_2$ solution only weakly influences their sorption properties.

To better understand the mechanism of strontium sorption by calcium and magnesium phosphates, we studied previously the physicochemical transformations of sorbents in the $CaCl_2$–complexone–sorbent systems [15]. According to the data obtained, calcium phosphates do not undergo noticeable transformations in $CaCl_2$ solutions. Magnesium phosphates in $CaCl_2$ solutions completely transform into the corresponding calcium phosphates irrespective of the presence of complexones. As shown by the calculations, a 0.05 M $CaCl_2$ solution used in this study contains calcium ions in a twofold excess relative to the amount required for this transformation. In the case of TMP, weakly crys-

tallized TCP is formed, and MHP transforms into calcium hydrophosphate dihydrate (CHP). The transformation of TMP into TCP is also confirmed by the XRD and IR data. Because of complete transformation of magnesium phosphates into calcium phosphates in $CaCl_2$ solutions, it could be expected that the sorption characteristics of calcium and magnesium phosphates in $CaCl_2$ solutions would be the same. Nevertheless, the sorption capacity of calcium and magnesium phosphates in salt solutions is essentially different. We believe that the main cause of the observed features of the sorption uptake is the participation of Sr ions in recrystallization of magnesium phosphates into calcium phosphates and higher sorption activity of the freshly formed phase.

Certain increase in the sorption activity in uptake of Sr ions against the background of $CaCl_2$ in the presence of HEDP may be associated with the effect of HEDP on the crystallization processes occurring in the course of chemical transformation of magnesium phosphate into calcium phosphate. As we found previously, complexones interact with surface ions of calcium and magnesium of all the tested sorbents and influence the occurring chemical transformations. In the presence of EDTA, calcium phosphate formed in the heterogeneous chemical reaction is crystalline. Joint action of $CaCl_2$ and HEDP results in active transformation of the initial MHP and TMP phases into X-ray amorphous compounds. Thus, the freshly precipitated amorphous calcium phosphate formed in the process is characterized by larger surface area and higher sorption activity. As a result, we observe a slight (by several percents) but stably reproducible increase in the degree of recovery and distribution coefficient of ^{85}Sr in $CaCl_2$–HEDP–magnesium phosphate systems compared to $CaCl_2$–EDTA–magnesium phosphate systems. In addition, positive effect in the presence of HEDP may be due to specific features of complexation with Ca^{2+} ions, because HEDP, in contrast to EDTA, can form chelate rings with several cations simultaneously [16], thus reducing the effect of excess Ca^{2+} ions.

Figure 2 shows the X-ray diffraction patterns of the initial samples of MHP, PD-1, and PD-2 and of the products formed after the Sr sorption in the presence of $CaCl_2$. The X-ray diffraction patterns of HA and TCP are not given, because calcium phosphates do not undergo noticeable changes in the course of contact with model solutions.

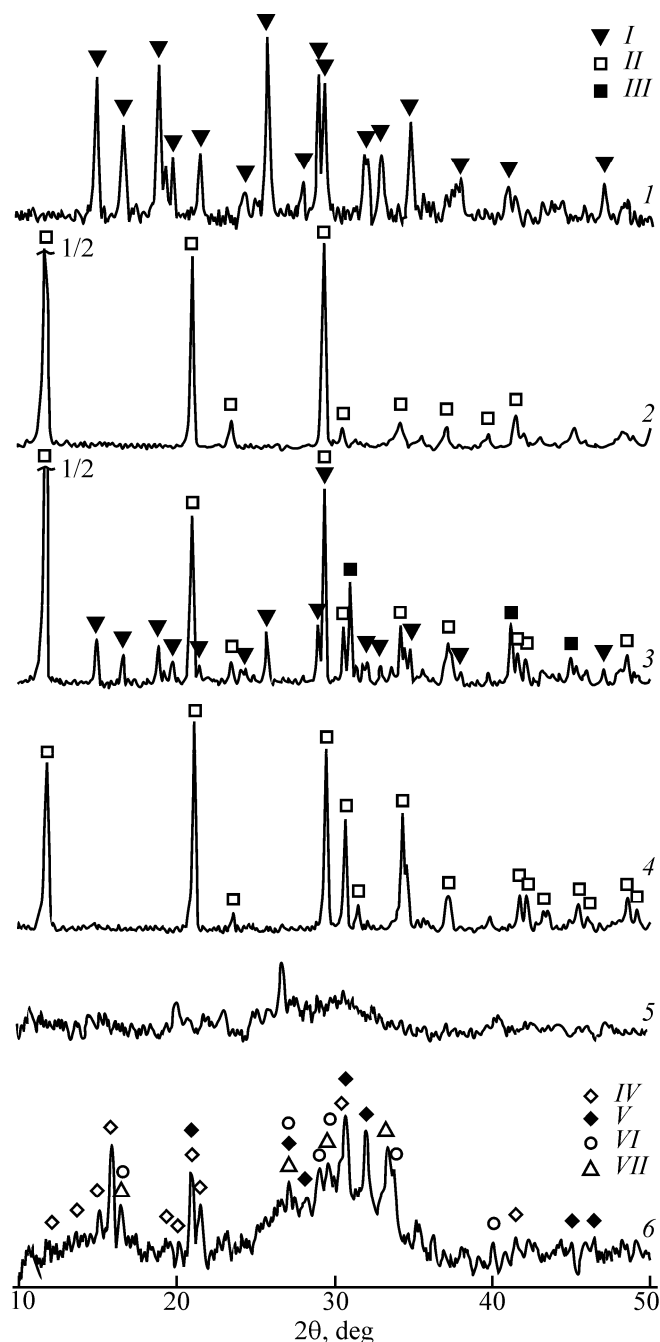The XRD data confirm the occurrence of recrystal-

Fig. 2. X-ray diffraction patterns of (*1*, *2*) MHP, (*3*, *4*) PD-1, and (*5*, *6*) PD-2 (*1*, *3*, *5*) before and (*2*, *4*, *6*) after interaction with a $Sr(NO_3)_2$ solution ([Sr^{2+}] = 2000 mg L^{-1}). (2θ) Bragg angle. Phase designations: (*I*) $MgHPO_4 \cdot 3H_2O$, (*II*) $CaHPO_4 \cdot 2H_2O$, (*III*) $CaMg(CO_3)_2$, (*IV*) $Mg_5(CO_3)_4 \cdot (OH)_2 \cdot 8H_2O$, (*V*) $Ca_2Sr_8(PO_4)_6(OH)_2$, (*VI*) $Sr_9Mg(HPO_4)(PO_4)_6$, and (*VII*) $(Sr_{0.9}Ca_{0.1})_3(PO_4)_2$.

lization of magnesium-containing phosphates. For example, in the course of sorption of strontium cations in the presence of $CaCl_2$, sorbents based on acidic phosphates (MHP, PD-1) virtually completely transform

into CHP dihydrate. The absence of Sr-containing phases is most probably associated with isomorphous substitution of strontium ions for calcium ions without changes in the crystal structure of CHP dihydrate 17].

The complexity of the occurring processes is manifested more clearly in the case of uptake of strontium ions from a calcium-containing solution by a sorbent based on neutral calcium and magnesium phosphates (PD-2). The X-ray diffraction pattern of the forming product contains, along with reflections of mixed calcium strontium and magnesium strontium phosphates of complex composition, also reflections of the basic magnesium carbonate phase and of a weakly crystallized phase (two broad reflections at 2θ ≈ 15° and 30°), which can be tentatively identified as double phosphate $Ca_{2.86}Mg_{0.14}(PO_4)_2$. The presence of mixed calcium strontium and magnesium strontium phosphates as the main sorption products suggests direct participation of Sr ions in the transformation of magnesium phosphates into calcium phosphates.

Thus, we have studied the ability of calcium and magnesium phosphates of different compositions to selectively take up ions of stable Sr and of ^{85}Sr radionuclide from solutions containing 0.05 M $CaCl_2$, including solutions that also contain complexones (EDTA, HEDP). The sorption capacity of calcium phosphates in 0.05 M $CaCl_2$ solutions is 8–10 times lower than that in salt-free solutions and does not exceed 5–10 mg g^{-1}, and the ^{85}Sr distribution coefficient is in the range $(0.2–0.3) \times 10^2$ cm^3 g^{-1}. Magnesium and magnesium-containing sorbents obtained from natural dolomite exhibit high sorption-selective properties in the presence of $CaCl_2$, preserving more than 90% of the sorption capacity compared to salt-free aqueous solutions (80–100 mg g^{-1}), with the ^{85}Sr distribution coefficient in the range $(1.1–1.3) \times 10^2$ cm^3 g^{-1}. The mechanism responsible for different behavior of magnesium and calcium phosphates in sorption of strontium ions in the presence of $CaCl_2$ was suggested. The sorption-selective characteristics of magnesium phosphate sorbents are due to participation of strontium ions in recrystallization of magnesium phosphates into calcium phosphates, and also to the increased sorption activity of the freshly formed calcium phosphate phase. The sorption of magnesium phosphate sorbents slightly increases when the solutions contain 0.05 M $CaCl_2$ in combination with 1×10^{-3} M HEDP. The presence of 1×10^{-3} M EDTA in the solution does not noticeably influence the ^{85}Sr sorption. Different effect

of HEDP and EDTA on the Sr sorption with the phosphate sorbents studied is due to the inhibiting effect of HEDP on the crystallization of calcium phosphate formed by interaction of magnesium phosphates with the model solution.

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Translated by G. Sidorenko