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Batch study of ^{85}Sr adsorption from synthetic seawater solutions using phosphate sorbents

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Abstract Sorption of the ^{85}Sr radionuclide from model seawater solutions on phosphate sorbents was studied. Sorbents were synthesized using natural dolomite by various methods. Effects of salinity and pH of solutions on the degree of sorption and the distribution coefficient of the ^{85}Sr were investigated. Hydrolytic stability, phase transformation of sorbents in model seawater solutions and change of the pH_{pzc} were established with the aim of identifying factors, which influence on the sorption efficiency towards the ^{85}Sr radionuclide. The best sorption parameters in all range of salt concentration were obtained for sorbent containing tertiary calcium and magnesium phosphates and magnesium–ammonium phosphates.

Keywords Sorption · Ca and Mg phosphates · ^{85}Sr · Modeling seawater · Competing ions

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Introduction

High risk of radiation for human health makes continuous interest in finding effective methods for radionuclides immobilization. Depending on the level of radioactivity, sources, and volume of pollution different methods are used for immobilization of radionuclides, details of which are summarized in some review papers: precipitation, evaporation, solvent extraction, membrane technique, filtration, sorption and ion-exchange [1–4]. Each method has its advantages and limitations in use, so studies are underway in all these areas.

Currently, sorption technologies are developed very intensively for the decontamination of liquid radioactive waste (LRW) containing strontium radionuclides. The study of novel sorbents for strontium removal is the subject of research around the world. Due to the chemical and thermal stability and radiation resistance inorganic sorbents are the most promising materials for these purposes. One of the main required characteristics for sorbents is the high selectivity towards radionuclides due to the complex composition of LRW. Depending on chemical composition, LRW can be classified to low-salt (e.g. rinsing waters with salt concentration < 1 g L^{-1}) and high-salt (e.g. decontamination solutions, ion-exchange regeneration solutions with salt concentration > 1 g L^{-1}) [5].

At the present time there is a number of sorbents that demonstrate sorption-selective properties towards Sr^{2+}-ions in saline solutions, e.g. natural and synthetic zeolites [4–7] and other raw materials [8–10], composite magnetic nanoparticles [11], manganese oxides [12], titanates and titanosilicates [5, 6, 13–15] etc.

Selective removal of Sr^{2+}-ions from solutions with high salinity is a challenging task. One problem of strontium radionuclides removal from LRW is the presence of

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competing ions in solutions, especially calcium [5, 6, 8–14], magnesium [9–11, 14] and sodium [6, 8–12, 14, 15] that reduce the uptake of strontium. Another problem is the formation of strontium complexes with strong organic complexing ligands that lowers strontium sorption affinity [9]. These substances like oxalic acid and oxalates, citrate, Trilon B and others are often used as anti-fouling or decontamination reagents and at the technology end-point they become the component of LRW.

High characteristics for strontium sorption and ion exchange were shown by phosphate sorbents [16]. Most of the works are devoted to the sorption study of hydroxyapatite (HA) as the most common representative of calcium phosphates which is the main mineral component of bone tissue [7, 16–23]. Non-apatite calcium phosphates are much less studied [7, 24]. Despite the fact that the presence of competing ions negatively affects on the targeted ions sorption by phosphate sorbents, their use for the immobilization of radionuclides appear to be very promising because of the sorption capacity persistence in salt solutions, high affinity to strontium ion, its durable retention due to the formation of insoluble compounds, high performance in a wide pH range, especially in alkaline medium. The advantages of phosphate sorbents also include their safety for the environment and the possibility of using local natural resources to produce such sorbents in large quantities.

In particular, carbonate-containing minerals, such as calcite, can be used for obtaining of HA both of stoichiometric composition [25] and calcium deficient HA with incorporation of carbonate groups [26]. In some studies, the calcium oxide is obtained from calcium carbonate via its calcination, and then is neutralized with phosphoric acid [18, 28, 29]. In addition to the inorganic raw materials renewable organic resources also can be used, as for example in the case of sorbent Apatite II derived from fish bones [16, 17], and biogenic HA produced by bacterium *Serratia* sp. [19, 20].

The possibility of textural and morphological properties varying (degree of crystallinity, size of crystallites, porous structure) is a feature of HA and non-apatite calcium phosphates that determines their sorption capacity [21, 25, 27–29]. The sorption mechanism of Sr on HA is investigated in details. It has been showed that the sorption capacity of HA depends on its crystallinity [19, 22], morphology [21], solubility [22] and point of zero charge [18, 23]. According to the previous works, the dominant mechanism of Sr^{2+}-ions sorption on HA is ion exchange, due to the similarity of the ionic radii of Ca^{2+} and Sr^{2+}-ions [18, 21] and specific sorption mechanisms [18].

Calcium phosphates of non-apatite structure, as well as magnesium phosphates have been less studied as sorbents [7, 24, 30, 31]. Although the tertiary and hydrogen calcium and magnesium phosphates also show high sorption capacity, binding of ions occurs via the mechanism of dissolution–precipitation or ion exchange reactions. As the result of this interaction, the molar ratio of the extracted ions to ions released into solution can be increased to 1.3, 1.5 or 2 times depending on the concentration and pH of the initial solution [31]. Rokita et al. [24] found a fundamental difference in the mechanism of interaction of calcium phosphates with metal ions, for example Sr^{2+}, depending on their structure. It was shown that during the removal of Sr^{2+} ions by phosphate with apatitic structure, strontium atoms are preferentially incorporated in fourfold calcium positions, while in the case of amorphous calcium phosphate and dicalcium phosphate dihydrate all calcium sites may be occupied by strontium atoms.

Using the ability of calcium phosphates to participate in exchange reactions with polyvalent metals ions in aqueous solutions it is possible to obtain substituted phosphates, in which the presence of impurity ions in the structure may increase their reactivity. In this way, sorbent Apatite II with Na^+ ions has high reactivity towards numerous metal ions [16, 17]. Use of dolomite (calcium–magnesium carbonate) as a raw material makes it possible to obtain a magnesium containing calcium phosphates [32]. It is important to note that magnesium is a major impurity elements included in the structure of bone tissues and teeth, which ensures its higher reactivity [33].

Studies of the effect of magnesium addition to the composition of HA on removal efficiency of Cd^{2+} ions showed a significant increase in the sorption capacity with increasing of Mg^{2+} content and a higher value of enthalpy of ion exchange between Mg^{2+} and Cd^{2+} than that between Ca^{2+} and Cd^{2+} [34]. In previous works [35, 36] we found high efficiency of Ca-, Mg- and Ca–Mg phosphate sorbents of non-apatite structure in the processes of stable and radioactive Sr^{2+} ions removal both from aqueous solutions and model groundwater with hardness (in the presence of $CaCl_2$). Sorption materials consisting Ca–Mg phosphates were synthesized from dolomite as a cheap and widespread natural raw materials representing a mixture of Ca and Mg carbonates. It was found that Mg phosphates retained a capacity for Sr^{2+} ions up to 100 mg g^{-1} in 0.05 M $CaCl_2$ solution.

The aim of this work was to study the efficiency of Ca–Mg phosphate sorbents based on dolomite for radionuclide ^{85}Sr removal from aqueous solutions modelling seawater depending on the salt content in the wide range of pH. It was important to determine the influence of competing ions in the solution on the stability of Ca–Mg phosphate sorbents and the effect of the surface changes of sorbents on their selectivity towards ^{85}Sr removal from solutions with high salinity.

Experimental

Preparation of sorbents

The dolomite used was from the Ruba (Belarus, Vitebsk region) deposit with the following chemical composition (wt%): SiO_2 1.1, Fe_2O_3 0.4, Al_2O_3 0.5, CaO 30.3, MgO 20.0, SO_3 0.4, K_2O 0.2, Na_2O 0.1 and calcination loss 47.0. For the synthesis of sorbent with a high content of calcium and magnesium phosphates and high sorption properties it was previously suggested to activate the natural dolomite by its calcination at 800 °C. This allows to remove organic impurities contained in the natural dolomite, and to decompose dolomite to the magnesium oxide and calcium carbonate, that will significantly increase its activity in interaction with nitric and phosphoric acid.

The first sorbent (PD-1) was obtained after 24 h of activated dolomite stirring with a 20% phosphoric acid at dolomite:phosphoric acid weight ratio of 1:3. In order to prepare the second sorbent (PD-2), activated dolomite was dissolved in concentrated nitric acid, thereafter Ca and Mg phosphates were precipitated by ammonium phosphate at pH 10. The synthesis was realized by a slow controlled titration (5 mL s^{-1}), and after total addition of the ammonium phosphate solution the suspension was stirred during 24 h. After the aging and washing with distilled water, the precipitate of Ca–Mg phosphate was rinsed with ethanol. Replacement of intermicellar liquid (water–ethanol) allows to obtain the sorbent with a more developed mesoporous structure, because ethanol has a lower value of the surface tension comparing to water. By this means, sorbent PD-1 represents a mixture of Ca–Mg hydrogen phosphates with the approximate composition (Mg,Ca)HPO$_4$·xH$_2$O and PD-2 represents a mixture of Ca–Mg tertiary phosphates with the total formula (Mg,Ca)$_3$(PO$_4$)$_2$·yH$_2$O. More details can be found elsewhere [32]. Sample PD-3 was obtained using soft non-acid method after 16 h of activated dolomite stirring with 0.2 M NaH$_2$PO$_4$ with dolomite:NaH$_2$PO$_4$ ratio of 1.4:33 g mL^{-1} [37]. Theoretical calculations suggest that this quantity is enough for full interaction between magnesium oxide and sodium phosphates.

Analytical methods

XRD patterns were collected on a DRON-3 powder diffractometer (CuKα radiation, $2\theta = 10°–60°$) (Burevestnik, Russia). Phase identification of the samples was carried out using XRD standard base JCPDS PDF2. The file number is provided in figure caption in the brackets.

The sorption and texture properties of the sorbents were assessed by isotherms of low temperature (−196 °C) physical adsorption–desorption of nitrogen, measured by the volumetric method on an ASAP 2020 MP surface area and porosity analyser (Micromeritics, USA). The surface area of pores per unit mass of the solid or the specific surface area were determined by the single point (A_{sp}) according to Brunauer–Emmett–Teller (BET) theory (A_{BET}). The single point method was used to calculate not only the specific surface area A_{sp}, but also the adsorption and desorption volumes ($V_{sp.ads}$ and $V_{sp.des}$) of pores and their average adsorption and desorption diameters D_{ads} and D_{des}. The relative error in determination of the pore volume was ± 1% for the surface area and ± 15% for the pore size.

For elemental composition analysis the sorbents were dissolved in 6 M nitric acid. Total calcium and magnesium concentrations were determined using complexometric EDTA-titration and magnesium concentration was determined using an atomic-absorption technique. The concentration of PO_4^{3-} was analyzed spectrophotometrically as phosphovanadomolybdate complex at $\lambda = 440$ nm.

For studying of ^{85}Sr uptake by phosphate sorbents, the ^{85}Sr activity in the solution before (A_{init}, kBq L^{-1}) and after the sorption (A_{eq}, kBq L^{-1}) was measured by MKS AT1315 γ,β-spectrometer (Atomtex, Belarus). The degree of recovery (S, %) and the distribution coefficient (K_d, cm^3 g^{-1}) of ^{85}Sr were calculated by equations:

$$S = \frac{A_{init} - A_{eq}}{A_{init}} \times 100\% \tag{1}$$

$$K_d = \frac{A_{init} - A_{eq}}{A_{eq}} \times \frac{V}{m} \tag{2}$$

where V is the volume of solution (cm^3), m is the mass of the sorbent (g). The initial activity of ^{85}Sr(NO$_3$)$_2$ aqueous solutions was about 1×10^2 kBq L^{-1}. The pH of the aqueous solutions was measured with a pH-meter OP-208/1 (Radelkis, Hungary).

Batch sorption studies

The batch experiments were conducted by mixing 0.10 g of sorbent with 50 mL of model seawater solutions with ^{85}Sr radionuclide at controlled initial pH in plastic tubes from polyethylene with low sorption capacity (volume 100 mL) on open atmosphere. For pH adjustment HCl (0.1 M) and NaOH (0.1 M) solutions were used. The suspensions were agitated at the temperature 20 °C for 24 h with periodical rotation. After that sorbents were filtered by paper filter (3–5 μm pores) and ^{85}Sr activity was measured by γ, β-spectrometer.

Seawater solutions preparation

The sorption experiments with radionuclide [85]Sr were performed using the stock solution modelling seawater with total salt content 50.0 g L^{-1} and the diluted solutions with salt content 5.0, 10.0, 15.0, 20.0 and 35.0 g L^{-1}. The stock solution was prepared by dissolving alkaline and alkaline-earth chlorides MCl (M = K, Na) or MCl$_2$ (M = Mg, Ca) and MgSO$_4$·6H$_2$O in distillate water. The composition of the stock solution is presented in Table 1. At salt content 35.0 g L^{-1} the composition correspond to real seawater [38] and was used elsewhere [10, 20].

Effects of salt content and pH on the sorption of radionuclide [85]Sr

Influence of salt content on the sorption process was studied in the solutions with various salt concentrations in the range from 0.0 to 35.0 g L^{-1} and radionuclide [85]Sr. The solutions' pH was adjusted to 8.1 ± 0.3.

The batch experiments for studying of pH effect were conducted by mixing of sorbent with model solutions (salt content 35.0 g L^{-1}) at pH range from 2 to 8.5.

Effects of salt content and pH of solutions on the sorbents stability

These experiments were carried out at the same conditions as batch sorption experiments but in absence of radionuclide [85]Sr. After suspension filtration pH of solutions were measured. This technique allows determine the point of zero charge (pH$_{pzc}$) [18, 23]. The sorbents were washed

with distilled water, dried at the temperature 70 °C and then phase composition was studied.

Results and discussion

Characteristics of the sorbents

The sorbents for this study differ in chemical and phase composition. According to chemical analysis (Table 2) and XRD data (Fig. 1) the PD-1 sample is a mixture of calcium and magnesium hydrogen phosphates with gross composition Ca$_2$Mg(HPO$_4$)$_3$·8.7H$_2$O. Sorbent PD-2 is a mixture of calcium, magnesium and magnesium-ammonium secondary phosphates and its composition can be described by formula CaMg$_{1.5}$(NH$_4$)(PO$_4$)$_2$·12.5H$_2$O. PD-3 is a mixture of calcium and magnesium tertiary and hydrogen
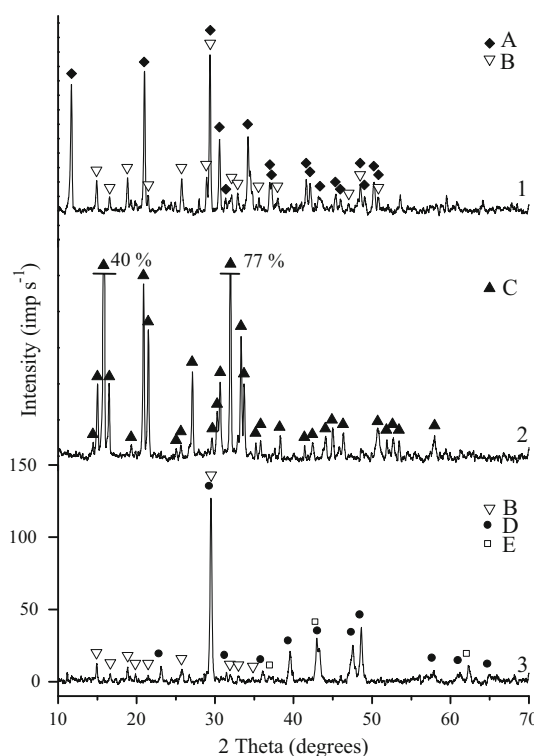
Fig. 1 XRD patterns of PD-1 (1), PD-2 (2) and PD-3 (3). Phases: A—CaHPO4·2H2O [9-77], B—MgHPO4·3H2O [35-780], C—MgNH4PO4·6H2O [71-2089], D—CaCO3 [5-586], E—MgO [78-430]. The same phases are for Fig. 4

Table 1 Composition of modeling seawater solution

Component	Concentration, g L^{-1} (mol L^{-1})	
Na$^+$	15.39 (0.669)	10.77 (0.468)
K$^+$	0.57 (0.015)	0.40 (0.010)
Mg^{2+}	1.82 (0.075)	1.28 (0.053)
Ca^{2+}	0.60 (0.015)	0.42 (0.011)
Cl$^-$	27.77 (0.783)	19.44 (0.548)
SO$_4$$^{2-}$	3.85 (0.040)	2.69 (0.028)
Total salt content (g L^{-1})	50.00	35.00

Table 2 Chemical composition of Ca–Mg phosphate sorbents

Sorbent	Content (mmol g^{-1})						Ca/Mg	(Ca + Mg)/P
	Ca	Mg	NH$_4$	CO$_3$	PO$_4$	H$_2$O		
PD-1	3.91	1.99	–	–	4.93	17.39	1.96	1.20
PD-2	1.84	3.07	1.52	–	3.78	23.70	0.60	1.50
PD-3	5.27	5.09	–	4.65	1.56	7.78	1.04	6.65

Table 3 Adsorption and textural properties of Ca–Mg phosphate sorbents

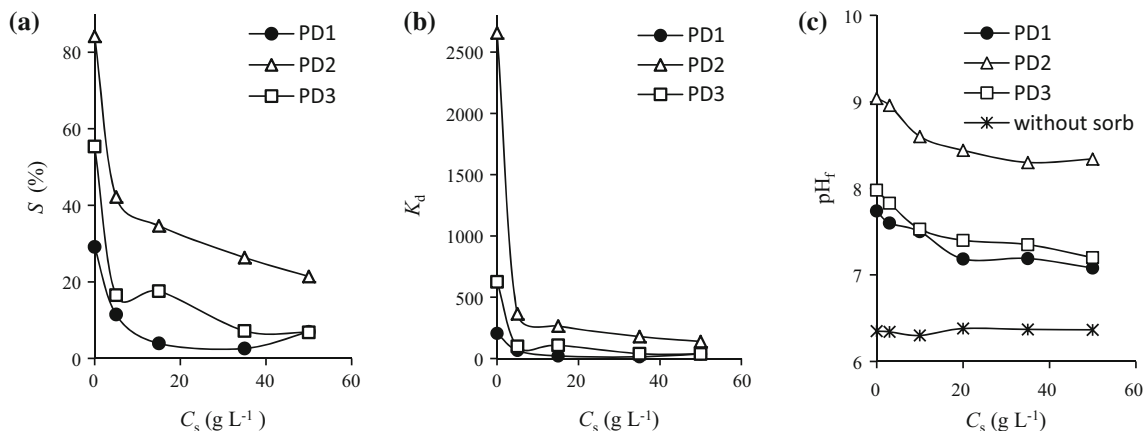| Sample	Specific surface area ($m^2\ g^{-1}$)		Pore volume ($cm^3\ g^{-1}$)		Pore size (nm)	
	A_{sp}	A_{BET}	$V_{sp.ads}$	$V_{sp.des}$	D_{ads}	D_{des}
PD-1	19	22	0.069	0.080	14	16
PD-2	49	54	0.182	0.238	15	19
PD-3	15	17	0.041	0.043	11	12

Fig. 2 Effect of salt content C_s on the degree of sorption of ^{85}Sr (**a**), distribution coefficient (**b**) and the pH changes of solutions after contact with sorbents (**c**)

phosphates, calcium carbonate and magnesium oxide with composition of $Ca_{0.6}Mg_x(PO_4)_y(HPO_4)_{1.6-y}(CaCO_3)_{4.7}$ $(MgO)_{5.1-x}\cdot 7\cdot 8H_2O$. The diffraction pattern of the PD-2 sorbent shows only the magnesium-ammonium phosphate because this compound is characterized by a high degree of crystallinity and is confirmed by corresponding intensive reflections, while the calcium and magnesium tertiary phosphates obtained by precipitation method are amorphous compounds and their reflexes are absent.

Table 3 shows the differences in the porous structure parameters of the obtained sorbents. The highest specific surface area was obtained for PD-2—$A_{sp} = 49$ and $A_{BET} = 54\ m^2\ g^{-1}$. For samples PD-1 and PD-3 the values were about 15–20 $m^2\ g^{-1}$. The sample PD-2 had the highest pore volume 0.182–0.238 $cm^3\ g^{-1}$, which was about 3–4 times higher than for other two sorbents. Distribution data for the average pore sizes indicated that the PD-3 samples had the smallest pore size about 11–12 nm.

Effects of salt content on the sorption of ^{85}Sr

Figure 2a and b show the degree of ^{85}Sr radionuclide sorption by phosphate sorbents from aqueous solutions depending on the salt concentration and the corresponding change of distribution coefficient of ^{85}Sr. Thus, in aqueous solution without background electrolyte sorbent PD-2, which is a mixture of tertiary phosphates of Ca, Mg and

ammonium, is the most active. The degree of ^{85}Sr radionuclide sorption for this sorbent has reached 84% and the distribution coefficient $2.66 \times 10^3\ cm^3\ g^{-1}$. For sample PD-3, obtained under acid-free phosphating, the degree of extraction of ^{85}Sr was 55%, and K_d—$0.63 \times 10^3\ cm^3\ g^{-1}$. The lowest activity towards ^{85}Sr showed sorbent PD-1: $S = 29\%$, $K_d = 0.21 \times 10^3\ cm^3\ g^{-1}$.

Introducing cations and anions modelling seawater to ^{85}Sr radionuclide solution leads to the decrease of ^{85}Sr sorption by all sorbents. Even the solutions with minimal salt concentration (5.0 $g\ L^{-1}$) suffers a sharp decrease in sorption degree to 42% for PD-2, 16.7% for PD-3 and 11.5% for PD-1. The subsequent increase of salt concentration from 5.0 to 50.0 $g\ L^{-1}$ does not cause sharp decrease in the degree of sorption, reaching at the end point values of 21.4, 6.8 and 7.0% for PD-2, PD-3 and PD-1, respectively. Similar changes occur with the value of the distribution coefficient.

Figure 2c shows the changes of the background pH of the solutions after contact with the sorbents. It demonstrates that all the sorbents increase the pH of salt solutions in comparison with the initial solution without sorbents. Changes in the pH_f values relative to the initial pH of solutions are less for sorbents PD-1 and PD-3, than for the sorbent PD-2. Moreover, increase of the concentration of salt solution leads to the decrease of ΔpH that can be explained by the suppression of sorbent hydrolysis in the solution.

The comparison of obtained results with the data of [36] for the sorption of the [85]Sr radionuclide on the background of CaCl₂ suggests that Na⁺ ions have much less influence on the degree of [85]Sr radionuclide sorption comparing to Ca²⁺ ions. Thus, in more mild conditions—with V/m ratio 250 mL g⁻¹ and a saline background 0.5 g of Ca²⁺ ions per 1 g of sorbent, the degree of sorption for PD-1 and PD-2 decreased from 37 and 97% in water to 12 and 31% in the presence of 0.05 M CaCl₂. The similar results of the influence of different alkali and alkaline earth metals cations on the extraction of the [85]Sr radionuclide were obtained for sorbents with apatite structure [7, 18, 20], that is explained by the greater affinity of Ca²⁺ ions to the surface than others (Mg²⁺, Na⁺, K⁺) [18].

Effect of pH on sorption of [85]Sr

Effect of initial solutions pH for the [85]Sr sorption was studied in model solution with a salinity 35.0 g L⁻¹, which corresponds to the salt content in seawater. The change in the degree of sorption and distribution coefficient depending on pHₛ solution is shown on Fig. 3a and b, which demonstrate different characters for the studied sorbents. So, for the most active phosphate sorbent PD-2, the maximum sorption efficiency in relation to the radionuclide is in the range of pH 3–9. The degree of [85]Sr sorption is about 25%. At pH less than 3, the degree of soprption of the radionuclide decreases rapidly and is slightly more than 5%. The change in the distribution ratio is similar and the maximum value in the alkaline solution is 0.18×10^3 cm³ g⁻¹. For samples PD-1 and PD-3 the dependence of degree of [85]Sr sorption on the pH of the initial solution has an extreme character. The maximum absorption falls to the range of pH 5–6 and is 8 and 13% for PD-1 and PD-3 respectively. At pH below 3.0 and above 6.0 sorption effeciency is reduced 3 times for PD-1, and 2

Fig. 4 XRD patterns of PD-1 (a), PD-2 (b) and PD-3 (c) after aging ▶ in water without salt (1) and in solution modeling seawater with salt content 10.0 g L⁻¹ (2), 35.0 g L⁻¹ (3–5) at pH 2 (4), 6 (1–3) and 8 (5)

times for PD-3. Thus, minimum sorption of [85]Sr varies from 3% for PD-1 to 6.2% for PD-2 and PD-3 in the most acidic solutions for all sorbents. At pH 8.5 the sorption efficiency of the sorbents, with the exception of PD-2, is significantly reduced.

pH$_f$ of model solutions after contact with all three sorbents rised with increasing pH$_s$ of initial solutions, and graphics pH$_f$ versus pH$_s$ (Fig. 3c) are similar to S versus pH$_s$ (Fig. 3a) and K_d versus pH$_s$ (Fig. 3b) for all three sorbents.

Effects of salt content and solutions pH on the sorbents stability

The results of the effect of initial solutions pH (for the model solution with salt content of 35.0 g L⁻¹) and the salt concentration on the changes in pH after contact with the sorbents in the absence of radionuclides are present on Figs. 2c and 3c. Together with the results of the phase composition of the sorbents after contact with model solutions (Fig. 4) allow to assume stability characteristics of the sorbents in the considered conditions.

The pH of the aqueous extract of sorbents without the background electrolytes for all samples is increasing with the greatest increase (ΔpH about 2.7) observed for PD-2, while for PD-1 and PD-3, this difference is much smaller— 1.4 and 1.6, respectively (Fig. 2c). The increase of salt content in solution is accompanied by pH decrease 0.68–0.78.
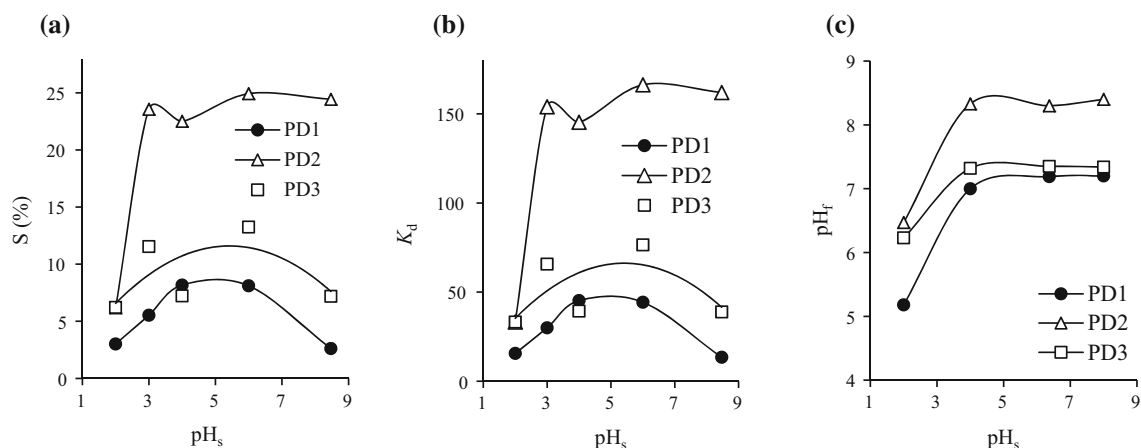

Fig. 3 Effect of pH of initial solutions (pHs) with salt content of 35.0 g L⁻¹ on the degree of sorption (a) and distribution coefficient (b) of [85]Sr and on the pH changes of solutions after contact with sorbents (c)
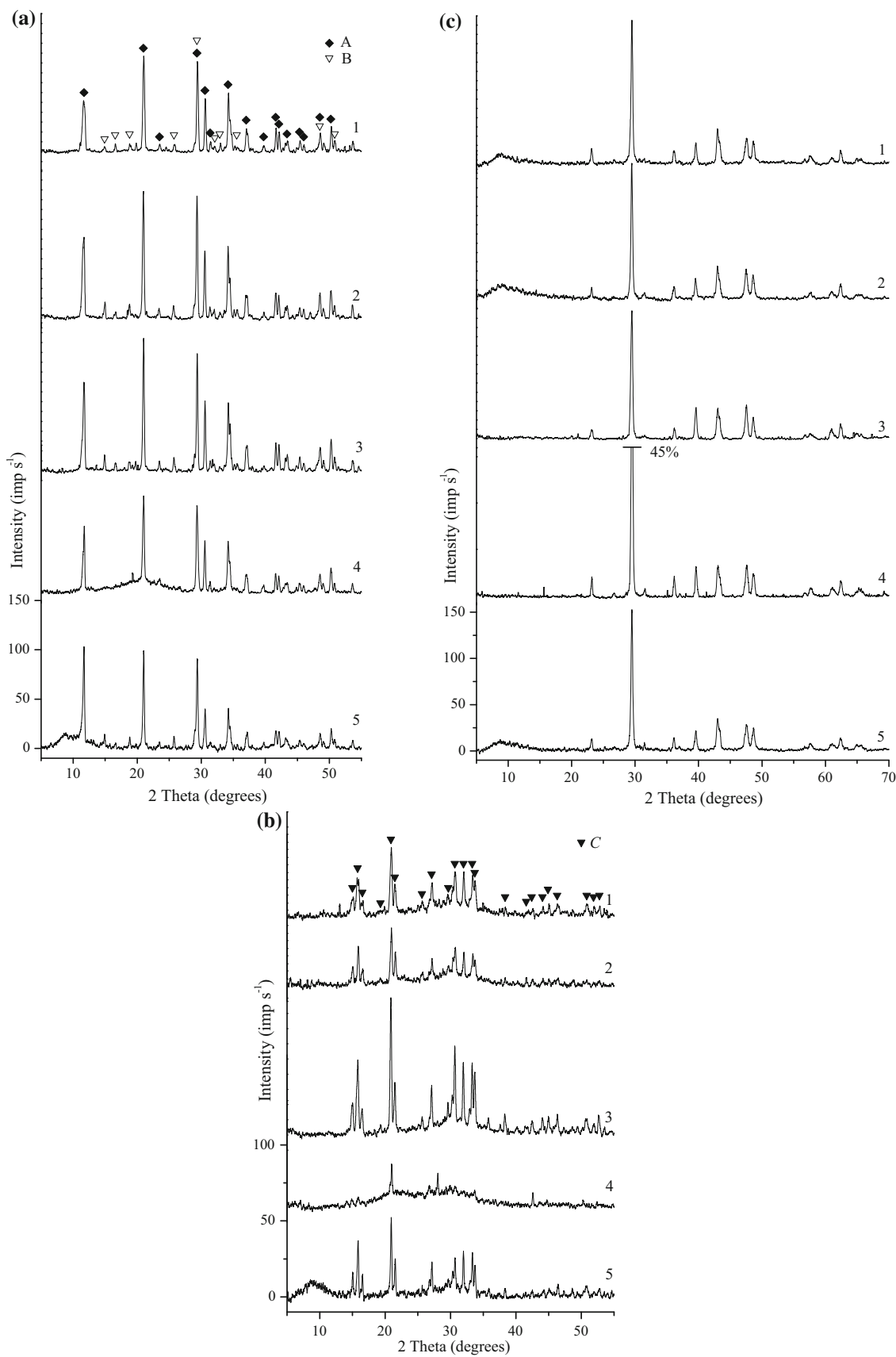
Table 4 Sorption properties of different materials towards strontium ions

Sorbents	m/V (g mL^{-1})	Competing ions/composition	Concentration (mol L^{-1})	State of strontium/concentration (mol L^{-1})	S (%)	Sorption (mg g^{-1})	K_d (mL g^{-1})	References
HA (bioceramics)	1/100	Ca^{2+}/CaCl$_2$	1×10^{-5}– 1×10^{-2}	Sr^{2+}/1×10^{-1}	–	–	516–5	[21]
HA (for liquid chromatography)	1/100	Ca^{2+}/CaCl$_2$	1×10^{-5}– 1×10^{-2}	Sr^{2+}/1×10^{-1}	–	–	1885–17	[21]
HA (prepared by a wet chemical precipitation)	1/100	Ca^{2+}/CaCl$_2$	1×10^{-5}– 1×10^{-2}	Sr^{2+}/1×10^{-1}	–	–	42–1	[21]
HA (biogenic, amorphous)	1/150	Na$^+$/NaCl	2×10^{-4}–2	Sr^{2+}/1×10^{-3}	66.2–44.9[a]	8.7–5.9	–	[20]
	1/150	Ca^{2+}/CaCl$_2$	2×10^{-4}–2	Sr^{2+}/1×10^{-3}	76.1–5.8[a]	10–0.76	–	[20]
HA (commercial nano-sized, crystalline)	1/150	Na$^+$/NaCl	2×10^{-4}–2	Sr^{2+}/1×10^{-3}	16.0–9.9[a]	2.1–1.3	–	[20]
	1/150	Ca^{2+}/CaCl$_2$	2×10^{-4}–2	Sr^{2+}/1×10^{-3}	27.4– < 0.15[a]	3.6– < 0.020	–	[20]
HA (biogenic, amorphous)	1/150	Seawater/ Na$^+$ (0.450 mol L^{-1}) Mg^{2+} (0.052 mol L^{-1}) Ca^{2+} (0.009 mol L^{-1})	90% of salt content	Sr^{2+}/1×10^{-3}	17.5[a]	2.3	–	[20]
HA (commercial nano-sized, crystalline)	1/150	The same	90% of salt content	Sr^{2+}/1×10^{-3}	1.6[a]	0.21	–	[20]
Clinoptilolite	1/150	The same	70% of salt content	Sr^{2+}/1×10^{-3}	0	0	–	[20]
HA (low-crystalline)	1/200	Na$^+$/NaNO$_3$	5×10^{-4}– 5×10^{-3}	Sr^{2+}/2×10^{-3}	42.5–40.5	–	–	[18]
		Ca^{2+}/Ca(NO$_3$)$_2$	5×10^{-4}– 5×10^{-3}	Sr^{2+}/2×10^{-3}	37.6–24.0	–	–	[18]
HA	1/250	Ca^{2+}/CaCl$_2$	5×10^{-2}	^{85}Sr/~ 10 kBq mL	10	–	30	[35]
Ca–Mg phosphate based on dolomite:								
PD-1	1/250	Ca^{2+}/CaCl$_2$	5×10^{-2}	^{85}Sr/~ 10 kBq mL	12	–	40	[35]
PD-2	1/250	Ca^{2+}/CaCl$_2$	5×10^{-2}	^{85}Sr/~ 10 kBq mL	31	–	110	[35]
PD-1	1/250	Na$^+$/NaCl	1.7×10^{-1}	Sr^{2+}/3×10^{-2}	99.2[a]	217.6	–	[41]
PD-2	1/250	Na$^+$/NaCl	1.7×10^{-1}	Sr^{2+}/3×10^{-2}	99.2[a]	196.5	–	[41]
PD-1	1/500	Modelling seawater: Na$^+$ (0.468 mol L^{-1}) Mg^{2+} (0.053 mol L^{-1}) Ca^{2+} (0.011 mol L^{-1})	14–100%	^{85}Sr/~ 10 kBq mL^{-1}	11.5–7.0	–	66–13	This work
PD-2	1/500	The same	14–100%	^{85}Sr/~ 10 kBq mL^{-1}	42.2–26.4	–	365–179	This work

[a]Calculated from C initial, V/m and sorption, mg g^{-1}

Such behavior of the sorbents can be explained by their different chemical composition, and complex multicomponent structure. The observed pH values of the solutions after contact with the sorbents are the cumulative results of many processes. The phosphate anion has a strong tendency to protonation of [39, 40]. Protonation of the phosphate and hydrophosphate anions included in the composition of the sorbents leads to alkalization of the solution.

At the same time, other components of sorbents undergo hydrolysis, in particular magnesium oxide and calcium carbonate.

The sorbent PD-1 is more homogeneous in the anionic composition, therefore in the aqueous medium mainly the protonation of hydrophosphate anion. As a result, at higher phosphorus content in the composition of this sorbent compared to the PD-2 (Table 2), the rise in pH is much smaller. Sorbents PD-2 and PD-3 are complex compounds with several anions and magnesium oxide. Phosphorus compounds are represented as the phosphate groups PO_4^{3-} and hydrophosphate HPO_4^{2-}. However, despite of the lowest phosphorus content of this sorbent, the pH change is strongly contributed by the hydrolysis of carbonate groups and magnesium oxide. As a result, solution has higher pH than after the contact with the sorbent PD-1.

Introduction of electrolytes into the solution causes a decrease in the degree of phosphate ions protonation due to the formation of associates with background cations [39], and it leads to a suppression in hydrolysis, which leads to the pH decrease in comparison with the system in a salt-free medium.

The character of the pH change depending on pH of initial solutions allows to define such an important property of the surface of the sorbent as the pH point of zero charge (pH_{pzc}). Based on the pH curves of equilibrium from initial solutions for all sorbents are allocated two plots (Fig. 3c). At lower initial values pH_s up to 4 increase in pH due to the processes of protonation and hydrolysis is observed, and in the interval pH_s 4–8 the final pH_f values for all sorbents remain constant, corresponding to the values pH_{pzc}. The highest value of pH_{pzc} is shown by a sorbent PD-2, for which pH_{pzc} is 8.4. Sorbents PD-1 and PD-3 have values of 7.2 and 7.3, respectively.

In addition to the hydrolysis process solubility of the sorbents influences on their behavior in solutions with different pH. The analysis of X-ray diffraction data of the sorbents after interaction with model solutions with different salinity and pH_s (Fig. 4) confirms the partial dissolution of the sorbents in the solution without background electrolyte, as evidenced by a observable decrease in the intensity of reflexes of all phases in the diffraction patterns (curve 1). For XRD data of the PD-3 sorbent (Fig. 4c) under all conditions of treatment the sorbent is characterized by the presence of reflexes of only calcium carbonate and magnesium oxide, while the reflexes of magnesium hydrogen phosphate are absent. The increase in the concentration of salt in solution is accompanied by the increase in the intensity of reflexes compared with diffraction patterns after treatment in salt-free solution, indicating a decrease in the level of dissolution in the presence of electrolytes. Lowering the pH to 2 causes the greatest changes of the phase composition of the sorbents PD-1 and PD-2 and the almost complete disappearance of the magnesium phosphate reflexes (curve 4).

The obtained data on the stability of the sorbents in model solutions allow to explain the regularities of ^{85}Sr radionuclide sorption from solutions with different salinity and pH-value. It is known that Sr^{2+} ion has very small constant of hydrolysis ($10^{-13.3}$ [23]), therefore, as a rule, it is not hydrolyzed and exists in solution as the divalent cation. As it was established for HA, the binding of these cations takes place most effectively on the surface with a negative charge at establishing pH_f above pH_{pzc} [18, 23]. Given the trace concentration of ^{85}Sr in solution it is possible to compare values pH_{pzc} obtained in the model solution at identical conditions as the experiment on the sorption of the radionuclide, and initial pH for the analysis of sorption processes. So, for the investigated sorbents the values obtained pH_{pzc} increase in the row of PD-1 < PD-3 < PD-2, with the values of 7.2, 7.3, and 8.4, respectively. The sorbents are arranged in the same row by sorption parameters such as degree of sorption and distribution coefficient of ^{85}Sr (Fig. 3b). However, only for sorbent PD-2 value pH_{pzc} exceed pH_s, resulting in the sorption of the radionuclide reaches high values and is practically independent on pH in the range of 3–8.

Higher sorption efficiency of the sorbent PD-3 compared to PD-1 despite the low content of phosphate phases, especially $MgHPO_4$, most active towards ^{85}Sr [35] is facilitated by the presence of $CaCO_3$ and MgO, resulting in a higher value of pH_{pzc}. Decreasing sorption of radionuclides by PD-1 and PD-3 sorbents with increasing pH in model solutions (Fig. 3) can be explained by the lower solubility of the sorbents, which prevents the occurrence of chemical reactions sites on their surfaces.

Comparison with other sorbents

Comparison of the obtained results for ^{85}Sr sorption from solution using phosphate sorbents with literature data should be subject to the conditions of the sorption experiments. So, in this work, the ^{85}Sr radionuclide sorption was studied in conditions close to the natural environment (high salt content and low ratio $m_{sorbent}:V_{solution}$) that is rare in the literature data. This leads to lower values of the degree of ^{85}Sr sorption and K_d for the studied sorbents in comparison

with other inorganic sorbents [5]. Given in Table 4 comparative data on sorption of Sr^{2+} ions mostly in the form of a stable isotope by a variety of sorbents on the basis HA confirms that the most active among the calcium phosphates are compounds characterized by low crystallinity structure or an amorphous state. Such phosphate sorbents are superior to the natural zeolite–clinoptilolite for Sr^{2+} sorption from seawater [20]. Combining data of this study together with presented in [36], we can assume that under similar conditions the sorbent PD-2 according to its sorption characteristics may exceed that described in the literature, and that is why sorbent PD-2 may be of interest for practical applications.

Conclusions

Sorption of ^{85}Sr radionuclide from model seawater solutions was studied on phosphate sorbents with complex chemical composition. It was found that for the studied phosphate sorbents the efficiency of ^{85}Sr sorption from model solutions decreased with salinity increase, due to increase in ionic strength of the solutions and the competing effect of metal cations in the background electrolyte. For sorbent PD-2 containing tertiary calcium and magnesium phosphates and magnesium-ammonium phosphate the highest values for the distribution coefficient K_d (from 2.66×10^3 to 0.14×10^3 cm^3 g^{-1}) and the degree of sorption S (from 84% in salt-free solution to 21% in solution with maximum salt concentration of 50.0 g L^{-1}) were obtained. In solutions similar to seawater composition (35.0 g L^{-1}), these values are 0.18×10^3 cm^3 g^{-1} and 26% respectivly.

The influence of pH on the extraction efficiency of ^{85}Sr is determined by the value of pH$_{pzc}$, which depends on the composition of sorbents and characteristics of the processes of protonation-deprotonation on their surface. For the studied sorbents values pH$_{pzc}$ increased in the row of PD-1 < PD-3 < PD-2, with the values of 7.2, 7.3 and 8.4, respectively. Only for sorbent PD-2 value of pH$_{pzc}$ (8.4) exceeded pH$_s$ in solution with salinity 35.0 g L^{-1}, which ensures the independence of the degree of sorption and distribution coefficient on solution pH in the pH range 3.0–8.5.

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