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Influence of Solution Acidity on the Sorption of Fission Radionuclides by Titanium Phosphate

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We have studied a relationship between the sorption of fission radioactive nuclides by titanium phosphate and the solution acidity. The fission fragments, such as ⁹²Sr, ⁹⁷Zr, ⁹⁷Nb, ¹³³I, ¹³⁵I, ¹³⁹Ba, ¹⁴²La, ¹⁴³Ce were obtained from ²³⁵U fission by thermal neutrons and accumulated in an aqueous solution. An M-10 electron accelerator at Uzhgorod National University, was employed for this reaction. It is shown that titanium phosphate sorbes intensely ¹³⁷Cs at pH ≥ 9 ; ⁹²Sr at pH $\approx 6-12$; ¹⁴²La and ¹⁴³Ce (III) – at pH $\approx 2-7$; while ⁹⁷Zr, ⁹⁷Nb, and ¹⁴³Ce(IV) can be sorbed only from highly acidic solutions with pH < 2 , and only in the case of rapid change of the solution acidity. The high sorption of ⁹²Sr isotopes shows that titanium phosphate can also be used to concentrate strontium trace. The processes which take course on the absorbent surface when pH changes (hydrolysis, dissociation of $-H_2PO_4^-$ and $-HPO_4^{2-}$ groups, substitution of the phosphate groups with the hydroxyl groups) also make a great influence on the sorption of fission radioactive nuclides. In some cases (e.g., sorption of ¹⁴²La) the processes, occurring on the absorbent surface, play a significant role.

Key words: titanium phosphate, solution acidity, fission fragments, hydrolysis, gamma-spectrometry.

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Nuclear fission of ²³⁵U results in the formation of fission radionuclides such as ⁹²Sr, ⁹⁷Zr, ⁹⁷Nb, ¹³³I, ¹³⁵I, ¹³⁹Ba, ¹⁴²La, ¹⁴³Ce along with other fragment elements [1]. The behavior of fission radio nuclides in some physico-chemical processes, including the process of sorption in inorganic ion exchangers is of a considerable scientific interest [2-5]. Here we report on the studies of fission radioactive nuclide sorption by titanium phosphate from aqueous solutions with different pH. The choice of titanium phosphate is determined by a number of factors. It is an ion exchanger with amphoteric properties being widely used for potable water purification as well as for radionuclide concentration. A certain role for the sorbent choice was played by the fact that Ti is capable of formation of coordination compounds with oxygen-containing ligands. This ability of Ti is essential since the fission radionuclides exist in aqueous solutions as aqua- or hydroxo-complexes [2].

The methodology of obtaining the solution of the fission radioactive nuclides with the density around 10^{-14} mole/l is described in detail in ref. [5]. The fission fragments, such as ⁹²Sr, ⁹⁷Zr, ⁹⁷Nb, ¹³³I, ¹³⁵I, ¹³⁹Ba, ¹⁴²La, ¹⁴³Ce were obtained from ²³⁵U fission by thermal neutrons and accumulated in an aqueous solution. An M-10 electron accelerator at Uzhgorod National University, was employed for this reaction. The concentration of each element by the end of irradiation was about 10^{-14} mole/l. The determination of each radionuclide content

was performed using γ -spectrometry. The γ -radiation spectra from the solution were measured by a Ge(Li) spectrometer. The concentration of a certain fission fragment was determined from the intensity of the corresponding maximum in the γ -spectrum. The half-life period and the irradiation conditions were taken into account. The detected pulse sum in the spectral maximum S is related to the radionuclide activity N directly after the irradiation as:

$$N = (S/q\epsilon Tm) \times (1/\exp(-\lambda t_1) - \exp(-\lambda t_2)) \quad (1)$$

where ϵ – is the general efficiency of registration of γ -quanta; q – is the quantum efficiency of the corresponding γ line; λ – is the decay constant; $t_1 = T_{dec}$, $t_2 = T_{dec} + T_m$ where T_{dec} is the time interval between the end of the irradiation session and the beginning of the spectrum measurement, T_m – is the spectrum measurement time.

The sorption analysis was started 30 minutes after the radiation exposure. The aqueous solution with the fission fragments was divided into several portions 20 ml each, to one of which no sorbent was added. Sorption under dynamic conditions was studied using a 60-70 mm high column of sorption glasses, 5 mm in diameter, the sorbent mass being 600 mg, the solution feed rate 2,5 ml/min. According to the technique described in ref. [6], the sorption column was washed by the solution under investigation without the sorbed elements to remove the impurities which could have been sorbed by titanium

Table 1

Sorption of the ^{235}U fission fragments from the solutions with different pH

Fission Fragment	K						
	solutions						
	HCl pH=2	HNO ₃ pH=2	Na ₂ CO ₃ pH=7.2	H ₂ O (distilled)	Wat./Eth mixture (42%)	Ammonium b.s.	KOH pH=12
^{142}La	0.54	0.57	0.50	0.43	0.535	0.01	0.12
^{97}Zr	0.17	0.27	0.02	0.13	0.16	0.11	0.04
^{97}Nb	0.39	0.50	0.27	0.13	0.63	0.22	0.25
^{140}Ba	0.44	0.35	0.35	0.64	0.655	0.63	0.47
^{143}Ce	0.08	0.12	0.00	0.12	0.52	0.03	0.10
^{92}Sr	0.24	0.24	0.78	0.84	0.79	0.91	0.71
^{137}Cs	0.00	0.00	0.00	0.00	0.00	0.89	0.67

phosphate from the air. From the experimental activities, the coefficients K of the element extraction from the solution (hereinafter – the sorption coefficients) were calculated as

$$K = (N_0 - N) / N_0 \quad (2)$$

where N – is the radionuclide activity in the water solution after the sorption process; N_0 is the activity of the same radionuclide in the solution which has been out of contact with the sorbent.

The sorption in acidic medium was studied from two solutions: HCl and HNO₃ (pH ~ 2), in near-neutral medium close to from several solutions: distilled water (free from carbon dioxide pH = 7), sodium carbonate (pH = 7.2), 42% water/ethanol mixture (pH = 6.7). As alkaline medium we used ammonium buffer solution (pH = 9) and KOH (pH = 12) solution.

The study of the sorption process (Table 1) shows a dependence of the sorption coefficients on the medium acidity.

The solution acidity strongly affects the general state of the reacting system. Inorganic amorphous titanium phosphate in the H form with Ti/P ratio 1 was used throughout the experiments. The sorbent structure can be explained as polymeric combinations of the following groups: $\equiv \text{Ti-O-Ti} \equiv$, $\equiv \text{Ti-OH}$, $-\text{H}_2\text{PO}_4^-$, $-\text{HPO}_4^{2-}$, $-\text{PO}_4^{3-}$ etc. The Ti/P ratio 1:1 means that the sorbent has a certain amount of tertiary hydrogen, for which the dissociation degree is low enough, being revealed at pH close to 7. This means that ion exchange due to this hydrogen will be weak, taking place only in a neutral or weak alkaline medium. With the pH increase, the anion-exchange capacity of the titanium phosphate decreases: at pH = 7 it equals to 30-40% of the initial anion-exchange capacity (which was measured at pH = 2) [7].

In an acidic medium the fission fragment adsorption on glass is minimal. But, it increases with the solution pH; and the process becomes irreversible for Zr at pH > 2, for Nb at pH > 3, for La, Ru, Y at pH > 5.5–6 [2]. Besides, with the further increase of pH of the solution in the

absorbent matrix, the phosphoric acid starts to substitute the OH groups actively [8].

At pH = 2, considerable sorption coefficients were observed for ^{139}Ba , ^{142}La , and ^{97}Nb . Since the radionuclides under study are the products of nuclear fission reaction, they get into the solution with the electron deficiency. In the acidic conditions, the elements under investigation will have rather high oxidation rates and thus will coordinate a number of H₂O molecules around themselves. In that case the O–H bonds in aqua-complexes become unequal and thus predisposed to dissociation. As far as titanium phosphate has amphoteric properties, it can absorb negative aqua ions of polyvalent elements, such as ^{97}Nb . On the other hand, ^{97}Nb has a precursor ^{97}Zr with considerable half-life (1020 min) [1]. But the influence of the irradiation conditions on the sorption processes needs further detailed investigation.

Sorption of the alkali (^{137}Cs) or alkaline-earth (^{92}Sr) elements by titanium phosphate in an acidic medium is rather weak (zero in the case of ^{137}Cs). Divalent ^{139}Ba (as well as ^{92}Sr) can be contained in aqueous solutions in the form of hydrated cation – $\text{Ba}(\text{H}_2\text{O})_4^{2+}$ ($\text{Sr}(\text{H}_2\text{O})_4^{2+}$). The sorption coefficient of barium in an acidic medium is higher than that of strontium which has the similar properties. Moreover, the pH increase has less influence on the sorption of barium isotopes than for strontium isotopes (the sorption coefficients for ^{92}Sr grow with the pH increase). This may be ascribed to the larger weight and bigger ionic radius of ^{139}Ba in comparison with ^{92}Sr ; or maybe the ion-exchange centers of the titanium phosphate better correspond to the barium ion size. According to [9], the phases of barium or strontium phosphate or hydrophosphate were not found on the surface of amorphous phosphate sorbents. So, the sorption of ^{139}Ba and ^{92}Sr took place without interaction between these elements and the sorbent surface acidic groups ($-\text{H}_2\text{PO}_4^-$, $-\text{HPO}_4^{2-}$, $-\text{PO}_4^{3-}$). Their sorption could be achieved by hydrated titanium dioxide phase which is always present in amorphous titanium phosphate [10,11].

In a neutral medium, irreversible sorption of the elements under investigation on the glass surface begins. In general, having considered the small amounts of the elements under investigation, the hydrophilic property of the absorbent surface and the results obtained, we can assume that the sorption process for the most of the radioactive nuclides takes place without abiding the rules of ion exchange. In this case not only the absorbent surface and some radioactive nuclide ion interact, but also some active groups of the absorbent surface and aqua or hydrolyzed form of the radioactive nuclide. In the near-neutral medium high sorption coefficients were observed for ^{142}La , ^{139}Ba and ^{92}Sr . It is well known that lanthanum readily forms complexes with phosphoric acid, hence its good sorption by titanium phosphate may be ascribed to this capability. Process of dissociation of the phosphoric acid groups on the surface of titanium phosphate with increasing pH is treated as occurring in two steps: (i) dissociation of the $-\text{H}_2\text{PO}_4^-$ groups (pH = 1–4), (ii) dissociation of the hydrophosphate ($-\text{HPO}_4^{2-}$) groups (pH = 4–6). In this range of pH we observed considerable sorption coefficients for lanthanum isotopes.

In the alkaline medium (in the absorbent matrix phosphoric acid groups start to be replaced with the OH^- groups) lanthanum couples with the phosphoric acid residues into complexes like $[\text{La}(\text{H}_2\text{O})_n(\text{H}_2\text{PO}_4)]^{2+}$ already in the solution, and thus its sorption by titanium phosphate is rather weak. The difference in the sorption coefficients between ^{142}La and ^{143}Ce can be explained due to their different oxidation states. Cerium exists not only in a trivalent state, but also as Ce(IV) . The amount of desorbed phosphate ions from the sorbent surfaces

reaches up to 5 mg/g at pH ≥ 8 [9]. Thus the content of hydroxyl groups increases which causes more intense sorption of ^{92}Sr and ^{137}Cs . The elements which hydrolyze intensely (^{97}Nb , ^{97}Zr , and ^{143}Ce) are contained in the solution in the form of hydroxyl complexes and their sorption by titanium phosphate is quite low.

We have studied a relationship between the sorption of fission radioactive nuclides by titanium phosphate and the solution acidity. It is shown that titanium phosphate sorbes intensely ^{137}Cs only at pH ≥ 9 ; ^{92}Sr at pH ≈ 6 –12; ^{142}La and $^{143}\text{Ce(III)}$ – at pH ≈ 2 –7; while ^{97}Zr , ^{97}Nb , and $^{143}\text{Ce(IV)}$ can be sorbed only from highly acidic solutions with pH < 2 , and only in the case of rapid change of the solution acidity. The high sorption of ^{92}Sr isotopes shows that titanium phosphate can also be used to concentrate strontium trace. An assumption is made that the sorption process for the most of the radioactive nuclides takes place without abiding the rules of ion exchange. The processes which take course on the absorbent surface when pH changes (hydrolysis, dissociation of $-\text{H}_2\text{PO}_4^-$ and $-\text{HPO}_4^{2-}$ groups, substitution of the phosphate groups with the hydroxyl groups) also make a great influence on the sorption of fission radioactive nuclides. In some cases (e.g., sorption of ^{142}La) the processes, occurring on the absorbent surface, play a significant role.

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Вплив кислотності розчину на сорбцію уламкових радіонуклідів фосфатом титану

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Вивчено вплив кислотності розчину на сорбцію ряду уламкових радіонуклідів ^{92}Sr , ^{97}Zr , ^{97}Nb , ^{137}Cs , ^{139}Ba , ^{142}La , ^{143}Ce фосфатом титану. З метою напрацювання уламкових радіонуклідів – продуктів ядерної реакції поділу урану тепловими нейтронами – було використано циклічний прискорювач електронів М-10 встановлений в Ужгородському Національному університеті та мішень окису урану. Показано, що фосфат титану добре сорбує ^{137}Cs при $\text{pH} \geq 9$; ^{92}Sr в інтервалі значень $\text{pH} \approx 6-12$, ^{142}La і ^{143}Ce (III) при $\text{pH} \approx 2-7$, ^{97}Zr , ^{97}Nb та ^{143}Ce (IV) в сильнокислому середовищі $\text{pH} < 2$. Процеси, що відбуваються на поверхні сорбенту із зміною pH (гідроліз, дисоціація $-\text{H}_2\text{PO}_4^-$ та $-\text{HPO}_4^{2-}$ груп, заміна фосфатних груп на гідроксильні) мають значний вплив на сорбцію уламкових радіонуклідів. У деяких випадках, наприклад при сорбції ^{142}La , процеси, що відбуваються на поверхні фосфата титану відіграють визначальну роль.

Ключові слова: фосфат титану, кислотність розчину, уламкові радіонукліди, гідроліз, гамма-спектрометрія.