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Sorption behavior and speciation of Am^{III} in orthophosphates of rare-earth elements

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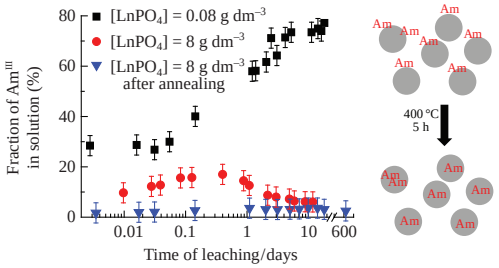
It has been found that leaching of Am^{III} from the surface after the sorption is characterized by slow kinetics; over 10 days are required to reach a dynamic equilibrium in the system. The leaching process is accompanied by the formation of Am-containing phosphate phase on the sorbent surface. Annealing the sample at 400 °C for 5 h after sorption results in incorporation of the sorbed cation into the sorbent structure, which allows subsequent leaching to be reduced considerably.



Operation of nuclear fuel cycle plants results in permanent accumulation of large amounts of radioactive waste (RW).[1] To date, a number of countries have accepted a fractionation of RW containing long-lived radionuclides and immobilization of these RW into solid matrices (glasses, concretes, mineral-like matrices).[2–4] High-level radioactive wastes (HLRW) containing radioactive cesium and strontium, among other radionuclides, are vitrified. This is an industrial technology that currently exists in various countries, including France, Russia, Great Britain, USA, Belgium, India, Japan, *etc*. High restrictions concerning the content of α-emitting radionuclides, especially Am^{III} and Cm^{III} isotopes, are imposed on the RW to be vitrified since glass matrices are unstable under this type of radiation. The main drawback of glass matrices is that they undergo devitrification upon heating due to radiation.[5] This phenomenon impairs the initial parameters of the matrix. In particular, the leaching rate of components increases. Therefore, development of methods for americium and curium isolation from HLRW for vitrification is an important task.

It can be accomplished using the materials that would simultaneously extract these radionuclides and serve as matrices for RW disposal. Rare-earth element (REE) phosphates, especially monazite, are promising inorganic materials that can be used for Am^{III} and Cm^{III} extraction. REE orthophosphates demonstrate high sorption properties towards Am^{III}.[6] Furthermore, the physicochemical properties of REE orthophosphates allow one to assume that the spent sorbent can become a matrix for Am^{III} disposal. The purpose of this work was to determine the processes that occur during the acid leaching of Am^{III} after sorption on REE orthophosphate ($LnPO_4$) samples with monazite structure. The understanding of these processes is important for determining the possibility of using REE orthophosphates for Am^{III} extraction from aqueous solutions and its subsequent disposal.

As it was shown previously, the sorption of Am^{III} on lanthanide orthophosphates is a pH dependent reaction[6] that however does not depend on the solution ionic strength. This behavior is characteristic of Am^{III} sorption on various minerals giving inner-sphere complexes with functional groups on the surface. Figure 1 shows the variation of Am^{III} sorption on monazite surface at various pH values and at two concentrations of the solid phase: 0.08 and 8 g dm^{-3}. It is evident that an increase in the solid phase concentration raises the sorption considerably [Figure 1(*a*)]. However, the same experimental results in K_d-unit [Figure 1(*b*)]

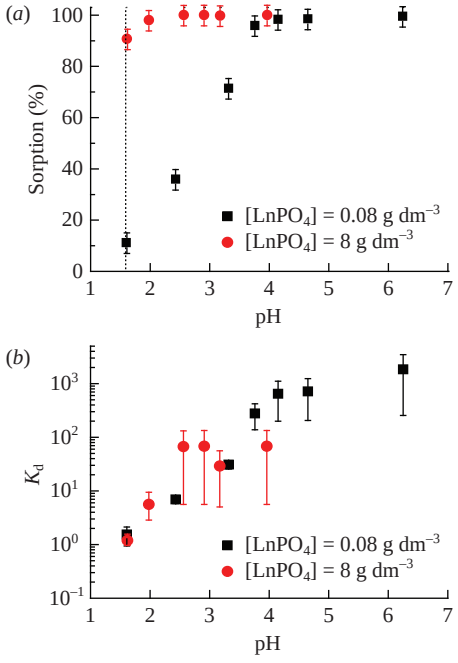


Figure 1 Dependence of Am^{III} sorption on monazite surface *vs*. pH at various concentrations of the solid phase. The dashed line shows the pH of subsequent leakage. ([Am^{III}] = 1×10^{-9} mol dm^{-3}, I = 0.01 M $NaClO_4$).

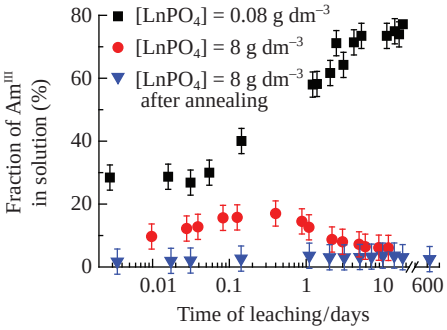


Figure 2 Kinetics of Am^{III} leaching from monazite surface at various concentrations of the solid phase and after annealing at 400 °C for 5 h.

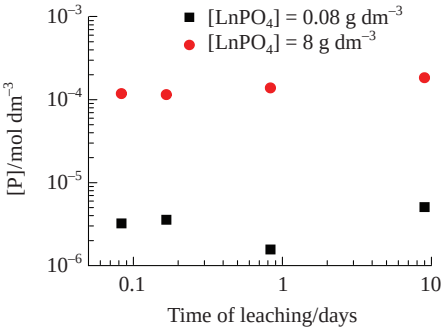


Figure 3 Phosphorus content in solution containing various concentrations of lanthanum orthophosphate at pH 1.6.

reveal that the increasing of sorption is in proportion to the increment in the solid phase concentration.†

To clarify the mechanisms of Am^{III} binding with the surface, we performed experiments on its leaching from the surface after sorption with dilute perchloric acid at pH 1.6 (Figure 2). Upon leaching from a suspension of solid phase (0.08 g dm^{-3}) about 30% Am^{III} passes into solution in the first two hours. In case of interaction by the reversible chemisorption mechanism, desorption of cations usually occurs quickly and quantitatively within the first hours. However, here we observe a more complex mechanism. The second region of the kinetic plot of leaching is characterized by a slow increase in the Am^{III} concentration. The time required for establishing a dynamic equilibrium is longer than 10 days.

The leaching from a suspension of solid phase (8 g dm^{-3}) occurs by a different mechanism. It is evident from the plot of sorption *vs*. pH at the same concentration of the solid phase (Figure 1) as in the case of reversible sorption, pH decrease to 1.6 should drops the sorption to 90% in the new system, hence the leaching should reach *ca*. 10%. However, the experimental data indicate a more complicated leaching behavior: the Am^{III} concentration in the solution first increases to *ca*. 20%, then decreases to 5% under dynamic equilibrium conditions (Figure 2). This behavior contradicts the assumption about a reversible sorption reaction and indicates that a number of concurrent processes occur during the leaching procedure. To identify these processes, the content of phosphorus was measured in similar suspensions (Figure 3). One can see that the phosphorus content in solutions containing suspensions with various solid phase concentrations and the same pH values vary by several orders of magnitude. Thermodynamic calculations indicate that the concentration of phosphate ions in the system should range within 10^{-6}–10^{-5} M, depending on the solid phase concentration.[9,10] An increase in the phosphorus content upon the increase in the solid phase concentration may indicate the presence of phosphorus-containing admixtures in the starting monazite sample, as was also determined previously.[9]

Based on these results, it can be assumed that in a system containing monazite (8 g dm^{-3}), Am^{III} that passed into solution within the first hours of leaching is bound to form a new deposit. The system containing 0.08 g dm^{-3} did not show a similar behavior since the phosphate ion concentration in solution was insufficient for deposition. It was repeatedly shown in previous publications that dissolution of phosphates can be accompanied by formation of new phases on a matrix surface.[11–14] In particular, it is most likely that a new rhabdophane phase is formed during monazite dissolution.[7,15] The formation of a new phase in the course of acid leaching is beneficial for the prospects of utilizing phosphate materials for disposal in a geologic repository since it prevents the leakage of a radionuclide into ground water.

Annealing a sample of monazite with Am^{III} sorbed on its surface at 400 °C for 5 h strongly affected the acid leaching behavior of the radionuclide (Figure 2). After annealing, nearly

† The sorption experiments were performed using samples of lanthanide orthophosphates. The methods for their synthesis and their characteristics were reported previously.[6]

The experiments were carried out at room temperature. $NaClO_4$ (0.01 M, reagent grade) was used as the background electrolyte. Sorption was performed in plastic flasks (high pressure polyethylene). In an experiment, an aliquot of an Am^{III} solution was added to a flask with lanthanide orthophosphate suspension. A nitric-acid solution containing the ^{241}Am isotope ($T_{1/2}$ = 433 years) was used. After that, the pH was adjusted to the required value using dilute NaOH and $HClO_4$ solutions. The pH values were measured using an In Lab 409 pH-meter (Mettler Toledo). Phases were separated by centrifugation (40000*g*, 15 min, Beckman Allegra). The radioactivity of solutions was measured by liquid scintillation spectrometry (TriCarb 2700TR, Quantulus 1220 PerkinElmer Life and Analytical Sciences).

To determine the leaching kinetics of Am^{III} from $LnPO_4$ in samples with sorption above 95%, the pH of the system was adjusted to 1.6 by addition of a required amount of dilute perchloric acid. Weakly acidic solutions are traditionally used to test the leaching of radionuclides from matrix materials.[7] Solution aliquots were withdrawn at certain time intervals, centrifuged and then used to determine the Am^{III} content in the solution.

Two samples were prepared for XAFS characterization. Lu^{III} (1×10^{-3} mol dm^{-3}) was sorbed on the solid phase $LaPO_4$ (5 g dm^{-3}) at pH 4.9. After the sorption, the solid phase was separated from the solution. One of the samples was then annealed at 400 °C for 5 h. For comparison, the spectra of the original $NdPO_4$ were also obtained. Nd L_3-edge X-ray absorption spectra were measured at the 'Structural Materials Science' station at the Kurchatov Synchrotron Radiation Source.[8] The electron beam energy of the storage ring was 2.5 GeV at 80–100 mA current. X-ray absorption spectra were recorded in 'transmission' mode, *i.e.*, the intensities of the incident and transmitted X-ray beams were measured using ionization chambers. The ionization chambers were filled with an Ar/N_2 mixture in order to reach the optimum signal/noise ratio. The beam size was chosen so as to ensure the sample thickness uniformity along the path of the X-ray beam.

The Lu L_3-edge spectra were collected at the Rossendorf Beamline BM20 of The European Synchrotron (ESRF), Grenoble, France. Lu^{III} was chosen as non-radioactive analogue of the Am^{III} which is also suitable for EXAFS measurement. The incident energy was selected using the ⟨111⟩ reflection from a double water-cooled Si crystal monochromator. Rejection of higher harmonics was achieved by two Rh mirrors at an angle of 2.5 mrad relative to the incident beam. The incident X-ray beam had a flux of approximately 2×10^{11} photons s^{-1} on the sample position. XAFS data were recorded in fluorescence mode using a 13-element high-throughput Ge-detector. The recorded intensity was normalized to the incident photon flux. Data were collected up to k = 10 A^{-1} with a typical acquisition times of 20 min per spectrum. Mass spectrometric measurements of phosphorus in solution were carried out on an Agilent 7500C quadrupole mass spectrometer with inductively coupled plasma (Agilent Technologies). The instrument was controlled using ICP-MS ChemStation software (version G1834B), ^{31}P isotope was used.

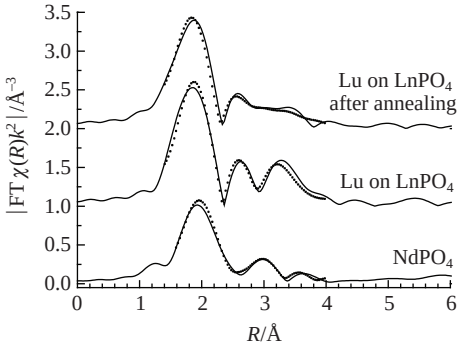


Figure 4 Fourier transform amplitudes for the samples studied (the simulations are dotted curves).

no leaching is observed for over 500 days. There are also no indications that dissolution/deposition processes occur. Thus, sample annealing after sorption prevents radionuclide leaching under mild acidic conditions.

Changes in the physicochemical forms of the sorbate before and after annealing were determined by X-ray absorption spectroscopy. Since work with relatively high concentrations of radioactive isotopes required for spectral methods is difficult, in this study we prepared samples with a stable lutetium isotope, *viz*. two samples of Lu^{III} sorbed on $LaPO_4$ surface. After sorption, one of the samples was annealed at 400 °C for 5 h. The spectrum of Nd in a sample of $NdPO_4$ was also obtained for comparison. The Fourier transform amplitudes for the samples studied, along with the simulation results, are presented in Figure 4.

The monazite crystal structure belongs to monoclinic one; as a result, a low-symmetry environment of REE atoms is observed in it. This is clearly seen in the spectrum of the $NdPO_4$ sample, whose simulation well agrees with crystallographic data. A sample after sorption (Lu on $LnPO_4$) has an environment with a higher symmetry than a sample after sorption followed by annealing (Lu on $LnPO_4$ after annealing). Simulations of experimental spectra (Table 1) also indicate that the local environment of Lu atoms in the sample after annealing is much more similar to the local environment of REE atoms in the $LnPO_4$ structure as compared to the sample after sorption.

Thus, it has been shown that Am^{III} is characterized by slow leaching from REE orthophosphate surfaces after sorption. Under certain conditions, Am^{III} leaching can be accompanied by the formation of a new phase, presumably rhabdophane, which improves the characteristics of REE orthophosphates in potential applications as matrices for radionuclide disposal. Upon annealing a sample at 400 °C for 5 h after sorption, the sorbed cation is incorporated into the sorbent structure, which allows the subsequent leaching to be reduced considerably. This property opens prospects to use orthophosphates of rare-earth elements not only as a sorbent but also as a material for long-term storage of radionuclides.

This study was supported by the Russian Science Foundation (project no. 14-13-01279). $NdPO_4$ EXAFS spectrum measurement was performed at the unique scientific facility Kurchatov Synchrotron Radiation Source supported by the Ministry of Education and Science of the Russian Federation (project code RFMEFI61917X0007).

Table 1 Structural parameters of the samples studied, as obtained by processing of EXAFS spectra.[a]

Sample	Path	*N*	*R*/Å	σ/Å^2	Fitting parameters
$NdPO_4$	Nd–O	6.8	2.48	0.008	R_f = 1.0%
	Nd–P	3.0	3.28	0.008	*k*-range 2.0–9.0
	Nd–P	3.9	3.69	0.008	*R*-range 1.6–4.0
	Nd–Nd	3.9	3.93	0.02	
Lu on $LnPO_4$	Lu–O	9.5	2.34	0.008	R_f = 2.6%
	Lu–P1	2.6	3.03	0.004	*k*-range 2.0–9.5
	Lu–P2	3.6	3.80	0.004	*R*-range 1.4–4.0
	Lu–La	5.7	3.87	**0.01**[b]	
Lu on $LnPO_4$ after annealing	Lu–O	9.0	2.43	0.009	R_f = 1.4%
	Lu–P1	1.6	3.26	0.004	*k*-range 2.0–9.5
	Lu–P2	1.5	3.70	0.004	*R*-range 1.4–4.0
	Lu–La	5.0	4.10	**0.01**[b]	

[a] *N* is the coordination number, *R* is the distance, and σ is the Debye–Walter factor coefficient. [b] The values shown in bold digits were obtained from simulations.

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