

An XPS Study of Interaction of Neptunyl(V) in Aqueous Solution with Goethite (α -FeOOH)

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Abstract—Sorption and physicochemical state of Np on the goethite (α -FeOOH) surface were studied. The oxidation state of Np on the α -FeOOH surface was studied by the liquid extraction. The neptunium complexes formed on the surface were studied by X-ray photoelectron spectroscopy. The ionic and elemental composition of the goethite surface and NpO_2^+ complexes with α -FeOOH were determined from the XPS data. No Np(IV) and Np(VI) compounds were detected. Neptunyl(V) Np(V)O_2^+ forms complexes with the surface groups of α -FeOOH. The equatorial plane of these complexes is occupied by the oxygen atoms of α -FeOOH and water and/or carbonate group CO_3^{2-} .

Migration, bioavailability, and hence toxicity of radionuclides depend on their physicochemical state in the environment [1]. The mobility of radionuclides is essentially determined by processes occurring on the mineral–natural water interface (sorption, redox reactions) and types of radionuclide complexes formed on the surface of minerals and suspended particles. Neptunium mainly occurs in nature in the form of neptunyl(V) ion NpO_2^+ . This is a linear dioxo cation with the formal charge of +1. Since the electron density on the central atom is low, NpO_2^+ is relatively inert chemically and hence readily migrates in the environment. Under these conditions, it can be reduced to Np(IV) or oxidized to Np(VI)O_2^{2+} [2].

Goethite is an abundant iron-containing mineral having high sorption capacity for heavy metal ions and radionuclides [3–5]. In this work we studied sorption of Np(V)O_2^+ on the goethite (α -FeOOH) surface and the surface complexes of neptunyl(V) by both liquid–liquid extraction allowing separation of neptunium species in different oxidation states and by X-ray photoelectron spectroscopy (XPS). The latter method is used to determine the physicochemical state of radionuclides in the environment. Reduction of Cr(VI) to Cr(III) on the goethite surface by Fe(II) traces [6] and interaction of uranyl with calcite and diabase [7] were studied by XPS previously.

EXPERIMENTAL

Goethite (α -FeOOH, sample I) was prepared by the procedure in [8]. $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (50 g, chemically pure grade) was dissolved in double-distilled water (825 ml). A 2.5 M KOH solution (200 ml) was added. The resulting solution was heated at 60°C for 24 h with continuous stirring. The precipitate was washed several times with double-distilled water and acetone and dried at 40°C for 2 days. For sorption experiments, an α -FeOOH suspension was prepared.

Sample II was prepared as follows. A goethite suspension (0.0374 g of sample I with $1.6 \times 10^{18} \text{ nm}^2$ free surface area of the mineral and $5.2 \times 10^{-6} \text{ mol}$ of the sorption centers) was placed in a centrifugation tube, and a supporting electrolyte (0.1 M NaClO_4) was added. Then $^{237}\text{Np(V)}$ was added in an amount corresponding to approximately 10^{-6} M total Np concentration. The pH was adjusted at 7.2 ± 0.2 , and the solution was continuously stirred for several days. The mother liquor was separated by centrifugation at 6000 rpm. After that, an aliquot of the mother liquor was taken. The total neptunium concentration in the solution was measured. The neptunium redox speciation was determined by liquid–liquid extraction with a 0.5 M solution of dibenzoylmethane in toluene by the procedure in [9]. Only Np(V) species were detected. After the sorption experiments with the same sample

Oxidation state of neptunium (Np^{n+}) and binding energy of electrons (E_b , eV) in samples I–III and neptunium compounds [10]

Sample*	Np^{n+}	MO	$\text{Fe}2p_{3/2,1/2}$ **	$\text{Fe}3s$	$\text{Np}4f_{7/2,5/2}$	$\text{O}1s$	$\text{C}1s$
I ($\alpha\text{-FeOOH}$)		6.9, 22.9	711.6(719.8) 725.1(733.4)(743.3)	93.6, 101.0		530.3, 531.5	285.0 288.6
II ($\alpha\text{-FeOOH} + \text{Np}^{n+}$)	Np^{6+}	7.1, 23.7	711.9(720.2) 725.5(733.4)(743.1)	94.2, 101.2	403.6, 415.2	530.5, 531.5 533.1	285.0 288.3
III ($\alpha\text{-FeOOH} + \text{Pu}^{n+}$)		6.4, 23.4	712.0(720.2) 725.5(733.4)(743.0)	94.5, 101.5		530.4, 531.7 533.7	285.0 289.0
NpO_2	Np^{4+}				402.5, 414.3	529.7	284.5
$\text{RbNpO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Np^{5+}	2.9 (Np5f) 5.4, 27.0			403.6, 415.3	531.5 533.5	285.0
$\text{Cs}_2\text{NpO}_2(\text{CH}_3\text{COO})_3$	Np^{5+}	2.3 (Np5f) 4.3, 27.2			403.0, 414.6	531.5	285.0 288.3
$\text{Cs}_3\text{NpO}_2\text{Cl}_4$	Np^{5+}	2.5 (Np5f) 4.9, 26.2			403.4, 415.2	531.6	285.0
$\text{Cs}_2\text{NpO}_2\text{Cl}_4$	Np^{6+}	3.3 (Np5f) 5.3, 25.8			404.6, 416.4	531.9	285.0
$\text{NaNpO}_2(\text{CH}_3\text{COO})_3$	Np^{6+}	3.4 (Np5f) 5.9, 24.2 26.0			405.2, 417.0	532.0	285.0 288.8

* Samples I–III were applied to a scotch tape and the other samples, to an indium support.

** Binding energies of satellites are in parentheses.

was repeated three times, 30% [1.53×10^{-6} mol $^{237}\text{Np}(\text{V})$] of the surface sorption sites of goethite were saturated. Then the mother liquor was separated and the samples were dried in a vacuum for 30–35 h. Sample III containing $^{242}\text{Pu}(\text{V})$ was prepared similarly. The sensitivity of XPS was too low to reliably record the $\text{Pu}4f$ spectrum. However, in this work the surface of this sample was characterized and the Pu sorption was estimated. These data were used to estimate the reproducibility (error) of the spectral measurements.

X-ray photoelectron spectra of samples I–III were recorded on an MK II VG Scientific electrostatic spectrometer in a vacuum (10^{-7} Pa) at room temperature using AlK_α X-ray radiation (1486.6 eV). The resolution determined from the half-width of the $\text{Au}4f_{7/2}$ line was 1.2 eV. The binding energies E_b (eV) were given relative to the binding energy of $\text{C}1s$ electrons of hydrocarbons on the sample surface, taken as 285.0 eV. The determination error of the binding energy was 0.1 eV. The relative intensities were determined with a 10% error [10]. To prepare samples for XPS study, the samples were crushed to fine powder (but not ground) and were applied in the form of dense thick layers onto a scotch tape attached to a titanium support.

The quantitative analysis of the sample surface was based on the fact that the line intensity is proportional to the concentration of atoms in the sample. The relative intensity of the atoms n_i/n_j was calculated from the equation $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where S_i/S_j is the relative intensity (area) of lines of inner electrons of these atoms and $k_{ji} = k_j/k_i$ is an experimental relative coefficient of the sensitivity. In this work we used the following coefficients relative to carbon: 1.00 ($\text{C}1s$); 2.8 ($\text{O}1s$); 8.0 ($\text{Fe}2p_{3/2}$); 0.55 ($\text{Fe}3s$); 9.20 ($\text{Na}1s$); 2.92 ($\text{Cl}2p$); 40.0 ($\text{Np}4f_{7/2}$); and 44.0 ($\text{Pu}4f_{7/2}$) [11]. The sensitivity coefficients of Np and Pu were obtained by extrapolation of the Th and U coefficients [11]. The Np coefficient is consistent within the determination error with $k_{ji}(\text{Np}4f_{7/2}) = 49.2$ determined with a $\text{Cs}_2\text{NpO}_2\text{Cl}_4$ single crystal taking $k_{ji}(\text{Cl}2p) = 2.92$ into account [10]. The coefficient for $\text{Fe}3s$ electrons was calculated from $k_{ji}(\text{Fe}2p)$ and cross sections of the photoeffect [11, 12]. The XPS spectrum of sample II was assigned using spectral parameters of other Np compounds (see table).

RESULTS AND DISCUSSION

To determine the physicochemical state of radio-nuclides in the environment, we used both conven-

tional XPS parameters (binding energies of inner electrons and their line intensities) and the fine structure parameters of valence and inner electrons. Among them are the relative line intensity of Fe3*d* and Np5*f* electrons negligibly involved in chemical bonding; relative binding energies of outer (OMO) and inner (IMO) valence molecular orbitals; multiplet splitting ΔE_{ms} (eV) of inner electronic levels; parameters of fine structure caused by the dynamic effect; and relative energies ΔE_{sat} (eV) of the shake-up satellites in the spectra of inner electrons [13, 14]. These spectral parameters furnish rich information on the physico-chemical state of iron and actinides on the sample surface.

Spectra of weakly bound electrons. The valence band of goethite (α -FeOOH, sample I) appears in the range from 0 to 40 eV and consists of the OMO band from 0 to 15 eV and IMO band from 15 to 40 eV (Fig. 1a). The O2*s* line is relatively broad [half-width $\Gamma(O2s) = 4.4$ eV], whereas the half-width of the complex O1*s* line is only $\Gamma(O1s) = 2.6$ eV. This indicates that O2*s* atomic orbitals are involved in MO. Indeed, from the uncertainty relationship $\Delta E \Delta \tau \sim h/2\pi$ (where ΔE is the half-width of the level from which an electron was removed, $\Delta \tau$ is the lifetime of the hole, and h is Planck's constant) it follows that, if the O2*s* level were atomic, the half-width of the O2*s* line would be smaller than that of the O1*s* line, which is not the case. The mechanism of formation of the fine structure of the spectra of different elements including lanthanides in the range of binding energies from 0 to 50 eV was systematically studied in our previous work [13]. We found that inner valence MOs can be effectively formed in this range under certain conditions. Based on these results, we suggest that the line in the O2*s* region is assigned to electrons of valence MOs.

The valence band of α -FeOOH is mainly due to the Fe3*d*,4*s*- and O2*s*,2*p* electrons forming MOs. The structure of the OMO spectrum is mainly caused by interaction of the Fe3*d*,4*s* and O2*p* electrons, and the structure of IMO, by interaction of the Fe3*d*,4*s* and O2*s* electrons [13]. Since the electronic configuration of iron atom is $\{Ar\}3d^64s^2$ (where $\{Ar\}$ is the electronic configuration of argon) and the photoeffect cross section of the Fe3*d* electrons is substantially higher than that of the O2*p* electrons [12], the Fe3*d*⁵ photoelectrons of the Fe(III) ion in the ground state should make the major contribution to the intensity of the OMO line (Fig. 1a). Unfortunately, it is difficult to estimate quantitatively the relative intensity of this line and the number of weakly bound Fe3*d* electrons

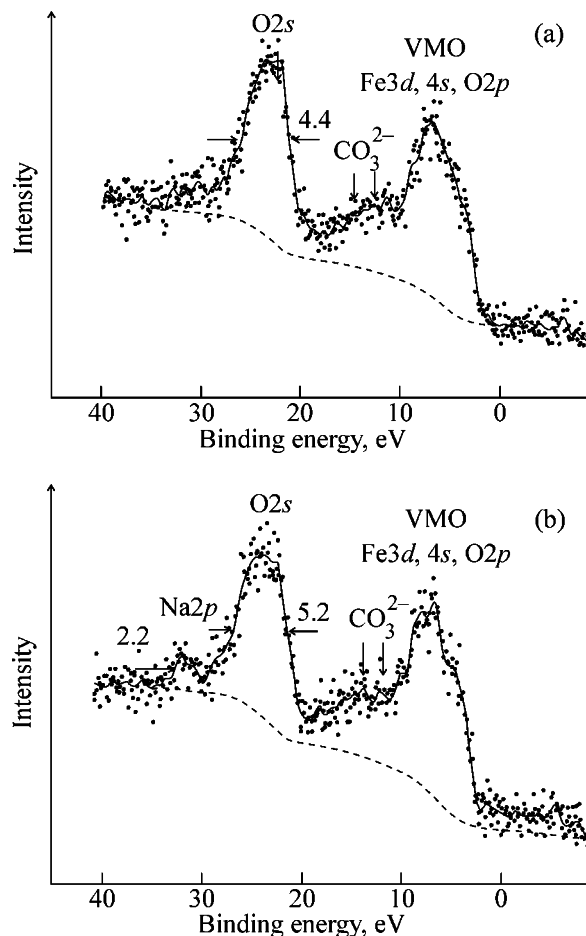


Fig. 1. XPS spectra of low-energy electrons of (a) goethite α -FeOOH (sample I) and (b) products of interaction of goethite with $Np(V)O_2^+$ in an aqueous solution (sample II).

from the spectrum. The weak band at 12–14 eV can be due to MO electrons of the carbonate anion CO_3^{2-} [13].

The low-energy electron spectrum of the interaction products of goethite with neptunyl(V) (sample II) slightly differs from that of the initial sample owing to modification of the sample I surface under the action of the solution (Fig. 1b). In this case, the line at $E_b \sim 2.5$ eV assigned to the Np5*f* electrons negligibly involved in the chemical bonding should appear. The area under this line is proportional to the number of the Np5*f* electrons and the Np oxidation state. Since the Np concentration in the sample is low, this line is very weak. The weak Na2*p* line is observed at 32.2 eV. In the spectra of samples II and III, the shoulder at the low-energy side of the band at 5 eV is more clearly resolved. The O2*s* band in the spectrum of sample II is slightly broadened (Fig. 1b) as compared to that in spectra of samples I and III.

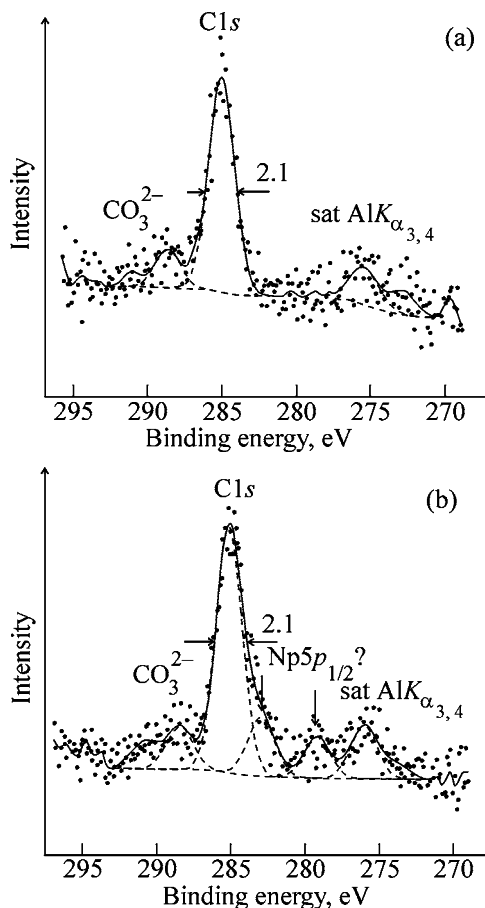


Fig. 2. C1s spectra of samples (a) I and (b) II.

Spectra of inner electrons. Oxygen-containing hydrocarbon molecules and water molecules can be sorbed on the sample surface in the course of their preparation. To avoid destruction of the surface layer, we did not clean the sample surface. The C1s spectrum of sample I (α -FeOOH) consists of the main line at $E_b = 285.0$ eV (saturated hydrocarbons) used as internal reference, line of carbon of the carbonate group CO_3^{2-} at $E_b = 288.6$ eV, and $\text{AlK}_{\alpha_{3,4}}$ satellites with $E_b = 275.4$ eV (Fig. 2a). The lines of AlK_{α_3} and AlK_{α_4} satellites are located, respectively, at a distance of 9.8 (7.33%) and 11.9 eV (3.66%) from the main line in the low-energy region (the relative intensities are given in percents in parentheses [15]). The spectrum of sample II (α -FeOOH + NpO_2^+) contains two weak additional lines at $E_b = 279.1$ and 282.8 eV, which can be partially due to the $\text{Np}5p_{1/2}$ electrons and the dynamic effect (Fig. 2b). In this case the dynamic effect is caused by the fact that additional two-hole state ($\text{Np}5p^6 5d^8 5f^{n+1}$) appears along with the main single-hole state ($\text{Np}5p^6 5d^{10} 5f^n$) due to super-Coster-Kronig electronic transition after photo-

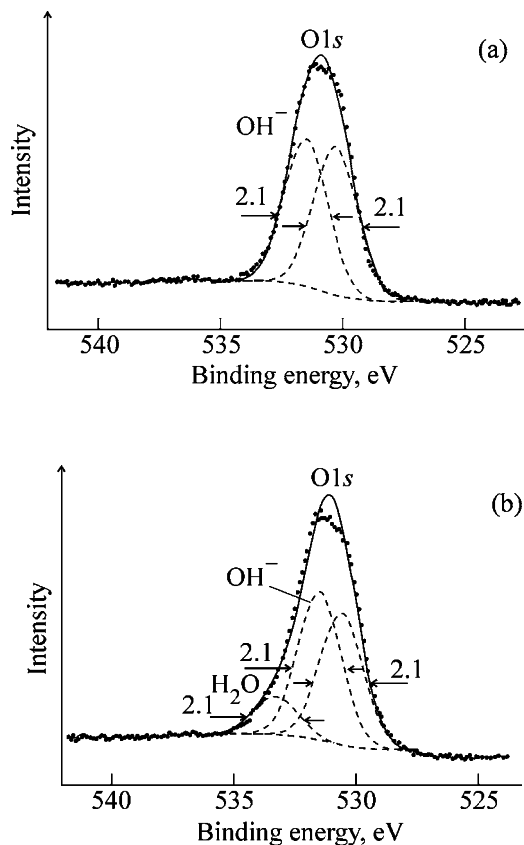


Fig. 3. O1s XPS spectra of samples (a) I and (b) II.

emission of the $\text{Np}5p_{1/2}$ electrons [10]. A complex fine structure of the $\text{Np}5p$ spectrum, in particular, in the range from 275 to 285 eV can appear due to this effect.

The O1s spectrum of sample I contains slightly broadened [$\Gamma(\text{O}1s) = 2.6$ eV] line at $E_b = 530.9$ eV. This line can be separated in two components with similar intensities (Fig. 3a). The line at $E_b = 530.3$ and 531.5 eV may be assigned to the oxide oxygen and the oxygen of the hydroxy group of goethite (the corresponding bands for α -FeOOH are located at 530.1 and 531.8 eV [15]). The surface oxygen speciation changes after treatment of goethite with an aqueous solution of NpO_2NO_3 (Fig. 3b). New line assignable, in particular, to water molecules appears at $E_b = 533.1$ eV. The similar additional line with substantially lower intensity is observed in the spectrum of sample III in which the Pu content is lower than the detection limit (formula of III will be given below). The content of two main oxygen ions in samples I and III is similar, whereas in sample II the oxide oxygen content is lower [formulas (I)–(III)]. The decrease in the in-

tensity of the line at $E_b = 530.5$ eV can be, e.g., due to formation of neptunyl(V) surface complexes.

Although the sample surface is contaminated with hydrocarbons, the lines of inner electrons of surface species are relatively strong. Mathematical treatment of the Fe2*p* spectrum shows that it has a complex structure and cannot be properly separated into the components [16]. This can be due to the fact that the Fe2*p* spectrum is complicated by both multiplet splitting caused by the presence of unpaired Fe3*d*⁵ electrons in the ground state and shake-up satellites arising from additional excitation of MO electrons in the course of photoemission of the Fe2*p* electrons [14, 15].

The binding energy of Fe2*p*_{3/2} electrons in sample I ($E_b = 771.6$ eV) is slightly higher than that in α -FeOOH (771.0 eV) [15]. The spin-orbital interaction calculated from this spectrum ($\Delta E_{so} = 13.5$ eV) is similar to that in metallic iron ($\Delta E_{so} = 13.2$ eV) [17]. Satellites at $\Delta E_{sat1} = 8.2$ and $\Delta E_{sat2} = 18.3$ eV are observed from the high-energy side of the main bands (Fig. 4a, see table). In the spectra of samples II and III, the Fe2*p*_{3/2} line is shifted, respectively, by $\Delta E_b = 0.3$ and 0.4 eV toward the higher energies, probably due to oxidation of surface iron under the action of the solutions. The fine structure of the spectra slightly changes (Fig. 4b, see table).

The Fe3*s* spectrum of α -FeOOH (sample I) has a complex fine structure. The doublet observed in the spectrum of these electrons originates from the multiplet splitting. The value of the splitting ($\Delta E_{ms} = 7.4$ eV) is proportional to the multiplicity ($2S + 1$), where S is the total spin of the ion, or to the number of unpaired Fe3*d*⁵ electrons [14, 15]. The ratio of the intensities of the doublet components should be $I_1/I_2 = (S + 1)/S$, i.e., 7/5, which agrees with the experimental value (7/5). The shape of the experimental spectrum is, however, more complex. Since $E_b(\text{Fe}3s) \sim 2E_b(\text{Fe}3p)$, additional final state can be formed along with the ground state after emission of the Fe3*s* electron (dynamic effect [14, 15, 18]). The following final states of a Fe(III) ion are possible: Fe3*s*¹3*p*⁶3*d*⁵ (single-hole ground state) and Fe3*s*²3*p*⁴3*d*⁶ (additional two-hole state). As a result, the spectrum is strongly complicated and hence the determination error of the multiplet splitting increases. In this work we separated this spectrum into the components to illustrate its possible structure (Fig. 5a). Since the dynamic effect has a resonance origin, the structure of the spectrum caused by this effect depends, as previously shown for barium compounds [17], on the type of ligands and their arrangement in

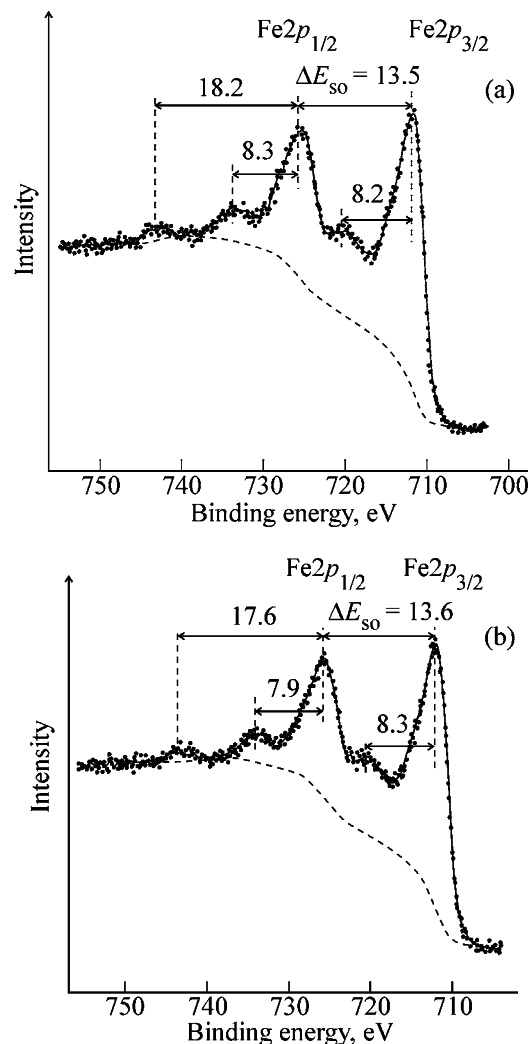


Fig. 4. Fe2*p* XPS spectra of samples (a) I and (b) II.

the coordination sphere of iron. Nevertheless, the multiplet splitting and the number of unpaired electrons can be calculated with a definite error from the Fe3*s* spectrum. The multiplet splitting for samples II and III is $\Delta E_{ms} = 7.0$ eV (Fig. 5b, see table). The different structure of the spectra of samples I and II can be due to coordination of neptunyl group to surface iron atoms of goethite (Fig. 5). It should be noted that the structure of these spectra in the ionic approximation shows that the oxidation state of surface iron is 3.

The doublet of relatively narrow lines in the Np4*f* spectrum is caused by the spin-orbital splitting with $\Delta E_{so} = 11.6$ eV (Fig. 6). The binding energy $E_b(\text{Np}4f_{7/2}) = 403.6$ eV is closest to that in the Np(V) compounds Cs₃NpO₂Cl₄ (403.4 eV) and RbNpO₂(NO₃)₂·2H₂O (403.6 eV). The Na1*s* band was observed at $E_b(\text{Na}1s) = 1073.1$ eV (sample II),

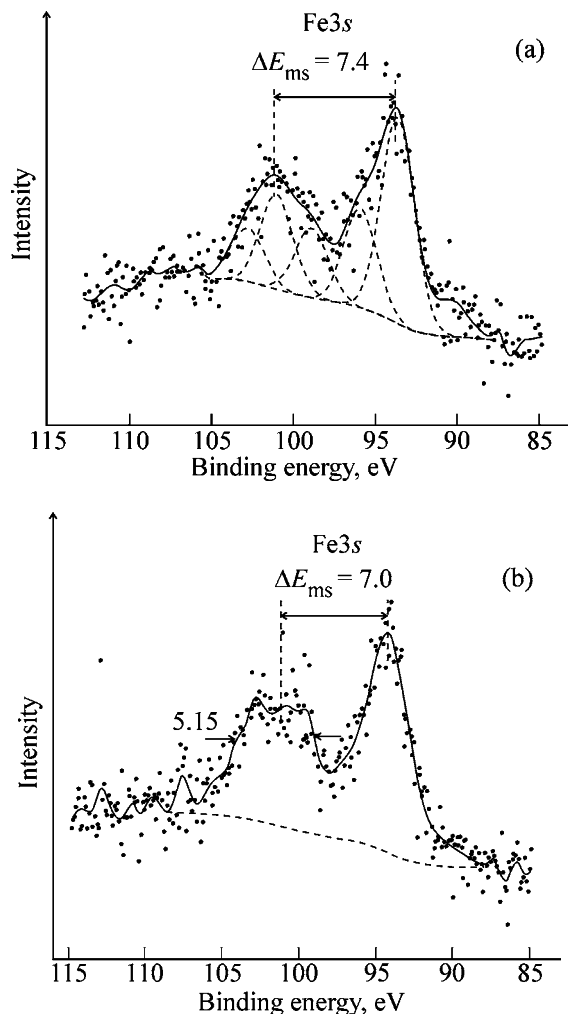


Fig. 5. Fe3s XPS spectra of samples (a) I and (b) II.

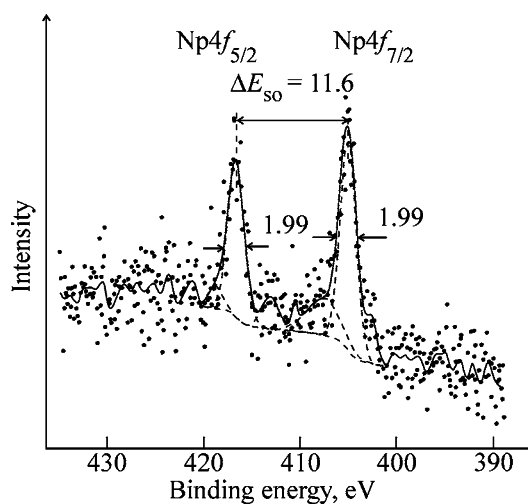
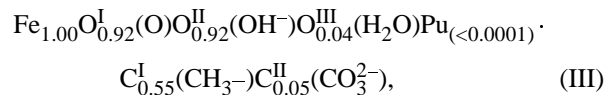
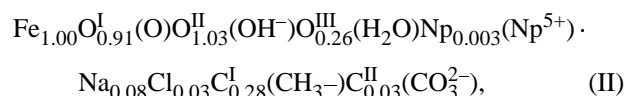
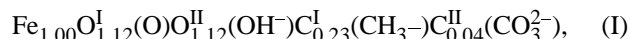


Fig. 6. Np4f XPS spectrum of the interaction products of goethite with NpO₂NO₃ (sample II).

whereas the intensity of the band of the Cl2p electrons of the perchlorate anion ClO₄⁻ and the band of the N1s electrons of the nitrate group NO₃⁻ was beyond the spectrometer sensitivity (1 at. %). A weak band at $E_b(\text{Cl}2p_{3/2}) = 199.6$ eV (sample II) can be assigned to Cl2p electrons of NaCl [formula (II)]. The binding energy and the spin-orbital splitting of the Pu4f_{7/2} electrons in the spectrum of Cs₂PuO₂Cl₄ single crystal are $E_b(\text{Pu}4f_{7/2}) = 428.7$ and $\Delta E_{so}(\text{Pu}4f_{7/2}) = 12.5$ eV, respectively. However, in the spectrum of sample III this doublet is not observed owing to insufficient sensitivity of the spectrometer. Based on these data, we estimated the upper concentration level of Pu on the surface of sample III [formula (III)].

Quantitative analysis. We performed the quantitative elemental and ionic analysis of samples I–III. The determination error of the peak areas for the inner metal electrons was high because of fine structure of these bands caused by both multiplet splitting and secondary electronic processes (multielectron excitation and dynamic effect). Since the shake-up satellites observed on the high-energy side of the main lines are caused by multielectron excitation, the intensity of these satellites can be partially taken into account in the course of the analysis (Fig. 4). The decrease in the intensity of the main lines due to the dynamic effect is difficult to estimate. However, this effect is insignificant in the spectra of the examined samples. The total error of the elemental and ionic analysis can exceed 10%. Since it is difficult to subtract the background of the secondary scattered electron from the Fe2p spectrum owing to its complex structure [16], we used the Fe3s lines for the quantitative analysis. In this approximation we found that the sample surface (~5 nm) had the following composition (per iron atom):



where O^I(O), O^{II}(OH⁻), and O^{III}(H₂O) are the oxygen atoms of oxides, hydroxy groups, and water.

The oxygen excess in samples I and II can be partially due to adsorption of oxygen-containing molecules and the high determination error mentioned above. The oxidation state of Np can be reliably determined by XPS even if its concentration is 0.1 at. % Np (sample II) (Fig. 6). We suggest that the surface

neptunyl(V) complex contains hydroxy groups of goethite in the equatorial plane. The other coordination sites of the neptunyl(V) ion are occupied by water molecules and/or carbonate group CO_3^{2-} .

Thus, interaction of a Np(V)O_2^+ solution with goethite ($\alpha\text{-FeOOH}$) was studied by XPS for the first time. The physicochemical state of Np on the surface was determined. No Np(IV) and Np(VI) compounds were found. Neptunyl(V) is chemisorbed on the goethite surface to form complexes in which the equatorial plane is occupied by the oxygen atoms of goethite surface groups, water, or/and carbonate anion CO_3^{2-} .

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