

PHYSICAL METHODS
OF INVESTIGATION

Interaction of Neptunyl with Goethite (α -FeOOH), Maghemite (γ -Fe₂O₃), and Hematite (α -Fe₂O₃) in Water as Probed by X-ray Photoelectron Spectroscopy

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Abstract—The sorption behavior is studied and the physicochemical neptunium species existing on the surface of goethite (α -FeOOH), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃) are determined. Solvent extraction and X-ray photoelectron spectroscopy (XPS) are used to determine the neptunium surface species. The ion and elemental composition of the surface of the minerals and surface neptunyl NpO₂⁺ complexes is determined using these data. Compounds containing neptunium(IV) or neptunium(VI) ions do not appear; rather, neptunyl (Np(V)O₂⁺ group is complexed with surface hydroxide groups of α -FeOOH, γ -Fe₂O₃, and α -Fe₂O₃. Presumably, the oxygen atoms of iron oxides and water and/or carbonate (CO₃²⁻) or nitrate (NO₃⁻) group lie in the equatorial plane of the neptunyl (NpO₂⁺) group.

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The migration behavior of radionuclides is determined by their physicochemical species existing in the environment [1]. The processes occurring at mineral–native water interfaces, such as redox reactions, sorption, and complexing at the mineral surfaces, largely determine the mobility of radionuclides. The major neptunium species in the environment is neptunoyl ion NpO₂⁺, whose low charge is responsible for its chemical inertness. However, redox reactions can occur in the environmental setting to yield Np(IV) or Np(VI)O₂²⁺ [2].

Goethite (α -FeOOH), maghemite (γ -Fe₂O₃), and hematite (α -Fe₂O₃) are abundant minerals having high sorption capacities to heavy-metal ions and radionuclides [3–5].

Here, we use solvent extraction and X-ray photoelectron spectroscopy to study the sorption mechanisms and surface Np(V)O₂⁺ complexes on goethite, maghemite, and hematite. Solvent extraction may be used to separate trace amounts of actinides into their

valence species; however, redox reactions can occur during extraction and induce the redistribution of valence species. X-ray photoelectron spectroscopy is the most adequate method for the determination of the physicochemical states of radionuclides in the environment. Previously, X-ray photoelectron spectroscopy was employed to discover the reduction of chromium(VI) to chromium(III) on the surface of goethite [6], which was explained by the presence of trace iron(II) on this surface, and to study the interaction of uranyl with hydroxylapatite and fluoroapatite in aqueous solutions [7].

EXPERIMENTAL

Synthesis and product identification. A goethite (α -FeOOH) sample was synthesized from Fe(NO₃)₃, using a procedure described in [8], as follows. Chemically pure Fe(NO₃)₃ · 9H₂O (50 g) was dissolved in bidistilled water (825 mL), and 2.5 M KOH (200 mL) was added. The solution was continuously stirred for 24 h at

60°C. Then, a precipitate was washed several times with bidistilled water and acetone and dried at 40°C for 2 days. For sorption experiments, a suspension of α -FeOOH was prepared.

A maghemite (γ -Fe₂O₃) sample was synthesized through Fe(NO₃)₃ hydrolysis using a procedure described in [9] as follows: the salt (100 g) was added to bidistilled water (1 L) and continuously stirred for 18 h. A precipitate was decanted and washed several times with bidistilled water. The product was dried at 40°C.

A hematite (α -Fe₂O₃) sample was synthesized as follows: chemically pure Fe(NO₃)₃ · 9H₂O (10 g) was dissolved in bidistilled water (50 mL), and 30% NaOH was added until pH was 12.5. Then, 30% H₂O₂ (1.5 mL) was added, and the solution was heated to 350°C for 5 days in a hermetically sealed autoclave at 2×10^7 Pa. After cooling, the precipitate was separated from the mother solution and washed several times with bidistilled water.

Powder X-ray diffraction showed the absence of other crystalline phases in the thus-synthesized samples.

Sorption experiments. Aqueous suspensions of the samples synthesized were used in the sorption experiments. The starting neptunium oxidation number (Np(V)O₂⁺) was verified spectrophotometrically. A sorption experiment was carried out at pH 8.1 ± 0.1 in a NaClO₄ solution (0.1 mol/L) and at ²³⁷Np concentration equal to 2×10^{-5} mol/L. Radioactivity in the solution was measured using liquid scintillation spectrometry. The sorption duration was 2 weeks, which was sufficient for the system to acquire a sorption equilibrium.

The mother solution after sorption was separated by centrifugation at about 6000 rpm and microfiltration using acetyl cellulose filters with a pore diameter of 0.1 μ m. After the sorption, an aliquot of the mother solution was sampled, and the degree of sorption and the distribution of the redox neptunium species in the mother solution were determined. The neptunium species were determined by solvent extraction using a 0.5 M solution of 2-thenoyltrifluoroacetone in cyclohexane [10]. Three sorption experiments were carried out with each mineral sample, which provided the 30% saturation of the goethite surface (about 1.53×10^{-6} mol ²³⁷Np). After the sorption experiment, the mineral samples were washed with bidistilled water to remove easily adsorbed impurities. Then, the mineral samples were vacuum dried for 30–35 h. As a result, the following three samples were prepared for recording X-ray photoelectron (XPE) spectra: sample **I** was neptunium on goethite (α -FeOOH + Np), sample **II** was neptunium on maghemite (γ -Fe₂O₃ + Np), and sample **III** was neptunium on hematite (α -Fe₂O₃ + Np).

X-ray photoelectron spectroscopy. The X-ray photoelectron spectra of samples **I–III** were recorded on a Scientific MK II VG electrostatic spectrometer using AlK _{α} (1486.6 eV) X-ray radiation in vacuum (10^{-7} Pa) at room temperature. The resolution of the spectrometer measured for the width at half-height of the Au4f_{7/2} line was 1.2 eV. In this work, the binding energies E_b (eV) are given relative to the binding energy of the C1s electrons of hydrocarbons on the surface of the samples, which was set equal to 285.0 eV. The error in electron binding energies was 0.1 eV; the error in relative line intensities was 10% [11]. The samples for XPS spectra were crushed (not ground) powders applied as thick layers to an adhesive band attached to a titanium substrate.

For all samples, quantitative surface analysis was performed on the basis of the fact that the intensities of spectral lines are proportional to the concentration of atoms in the test sample. This analysis was carried out using the relationship $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where n_i/n_j is the concentration ratio of the atoms under consideration, S_i/S_j is the intensity (area) ratio of the core-electron lines for these atoms, and $k_{ji} = k_j/k_i$ is the experimental relative sensitivity factor. The following values were used for the sensitivity factors relative to carbon: 1.00 (C1s), 2.8 (O1s), 8.0 (Fe2p_{3/2}), 0.55 (Fe3s), 9.20 (Na1s), 2.92 (Cl2p), and 40.0 (Np4f_{7/2}) [12]. The sensitivity factor for neptunium was obtained by extrapolation of the values known for thorium and uranium [12]; to the measurement error (20%), the extrapolated value correlated with the value found for Np4f_{7/2} electrons in a Cs₂NpO₂Cl₄ single crystal (k_{ji} (Np4f_{7/2}) = 49.2) with reference to the value for Cl2p electrons (k_{ji} (Cl2p) = 2.92) [12]. The sensitivity factor for Fe3s- electrons was obtained from data for Fe2p electrons and photoeffect cross sections [12, 13]. The assignment of the XPS spectra samples **I – III** was done with reference to the spectral parameters of some neptunium compounds (table).

RESULTS AND DISCUSSION

The determination of the physicochemical radionuclide species in the environment is based on both the conventional parameters of the XPS spectra (the binding energies of core-level electrons and relevant line intensities) and the fine-structure parameters of the valence and inner-level electron spectra. The parameters include the relative intensity of the lines of Fe3d- and Np5f electrons, which weakly participate in the chemical bonding; relative binding energies of the electrons of outer valence molecular orbits (OVMO) and inner valence molecular orbits (IVMO); multiplet splitting ΔE_{ms} (eV) for core-level lines; the fine-structure parameters induced by the dynamic effect; and relative

Neptunium oxidation numbers Np(N) and electron binding energies E_b (eV) for samples I, II, and III and for neptunium compounds [11]

Sample ^a	Np(N)	MO	Fe2 $p_{3/2, 1/2}$ ^b	Fe3 s	Np4 $f_{7/2, 5/2}$	O1 s	C1 s
I α -FeOOH + Np	Np(V)	6.4; 17.6;	711.7 (719.7)	94.1	403.2	530.2	285.0
		22.4; 31.2	725.3 (734.3) (739.2)	101.2	414.9	531.5	286.8
						533.4	288.8
II γ -Fe ₂ O ₃ + Np	Np(V)	7.0; 22.7	712.0 (720.0)	94.0	403.7	530.7	285.0
			725.7 (733.4) (741.3)	101.5	415.5	532.2	286.7
						533.7	288.8
III α -Fe ₂ O ₃ + Np	Np(V)	6.1; 13.1;	711.9 (719.9)	93.8	403.8	531.0	285.0
		26.4; 31.8	725.4 (733.4)	101.3	415.6	533.0	287.0
						534.1	289.2
NpO ₂	Np(IV)				402.5	529.7	284.5
					414.3		
RbNpO ₂ (NO ₃) ₂ ·2H ₂ O	Np(V)	2.9 (Np5 f); 5.4; 27.0			403.6	531.5	285.0
					415.3	533.5	
Cs ₂ NpO ₂ (CH ₃ COO) ₃	Np(V)	2.3 (Np5 f); 4.3; 27.2			403.0	531.5	285.0
					414.6		288.3
Cs ₃ NpO ₂ Cl ₄	Np(V)	2.5 (Np5 f); 4.9; 26.2			403.4	531.6	285.0
					415.2		
Cs ₂ NpO ₂ Cl ₄	Np(VI)	3.3 (Np5 f); 5.3; 25.8			404.6	531.9	285.0
					416.4		
NaNpO ₂ (CH ₃ COO) ₃	Np(VI)	3.4 (Np5 f); 5.9; 24.2; 26.0			405.2	532.0	285.0
					417.0		288.8

^a Samples I, II, and III were prepared on an adhesive band; the other samples were prepared on indium.

^b Satellite energies are parenthesized.

energies ΔE_{sat} (eV) of shake-up satellites in the core-electron spectra [14, 15]. These spectroscopic data yield extensive information about the physicochemical states of iron and actinides on the surface of the test samples. The first XPS spectroscopic data on the interaction of the neptunyl group NpO₂⁺ with goethite in aqueous solution were reported in [16].

Spectral region of weakly-bound electrons. The XPS valence bands for samples I–III are observed in the range from 0 to 40 eV; these lines are composed of OVMO electron lines from 0 to 15 eV and IVMO electron lines from 15 to 40 eV (Fig. 1). The lines in the region of the binding energies of the O2 s electrons have relatively large widths at half-height Γ (O2 s), which is equal to 5.7, 4.4, and 6.1 eV for samples I, II, and III, respectively. For the composite O1 s line, the width Γ (O1 s) for these samples is 3.2, 3.2, and 4.0 eV, respectively. This is one argument in favor of the participation of the O2 s atomic orbits (AO) in the formation of the molecular orbits. From the uncertainty relationship $\Delta E \Delta \tau \sim h/2\pi$ (where ΔE is the half-width of the level from which the electron is removed, $\Delta \tau$ is the lifetime

of the resulting hole, and h is the Planck constant), it follows that if the O2 s level were atomic, the width-at-half-height of its O2 s line would be lower than the same width of the O1 s line, which contradicts the experimental data. With reference to literature data for various compounds [14], we may assume that the line in the O2 s electron region is not an atomic one; rather, this line is associated with valence MO electrons.

The valence bands in samples I–III are mainly due to Fe3 d , Fe4 s , Np6 p , Np6 d , Np7 s , Np5 f and O2 s , 2 p electrons of the neighboring iron, neptunium, and oxygen atoms. The OVMO structure is mainly due to the interaction of Fe3 d , Fe4 s , Np6 d , Np7 s , Np5 f , and O2 p electrons; the IVMO structure is mainly due to the interaction of Fe3 d , Fe4 s , Np6 d , and O2 s electrons [14]. Because the electronic configuration of an iron atom is {Ar}3 d^6 4 s^2 (where {Ar} is the argon electronic configuration), because the photoeffect cross section for Fe3 d electrons is far larger than for O2 p electrons [13], and because the neptunium concentration is very low, it should be expected that the line intensity from OVMO electrons is largely due to the Fe3 d^5 electrons of the iron(III) ion (Fig. 1). Unfortunately, it is difficult

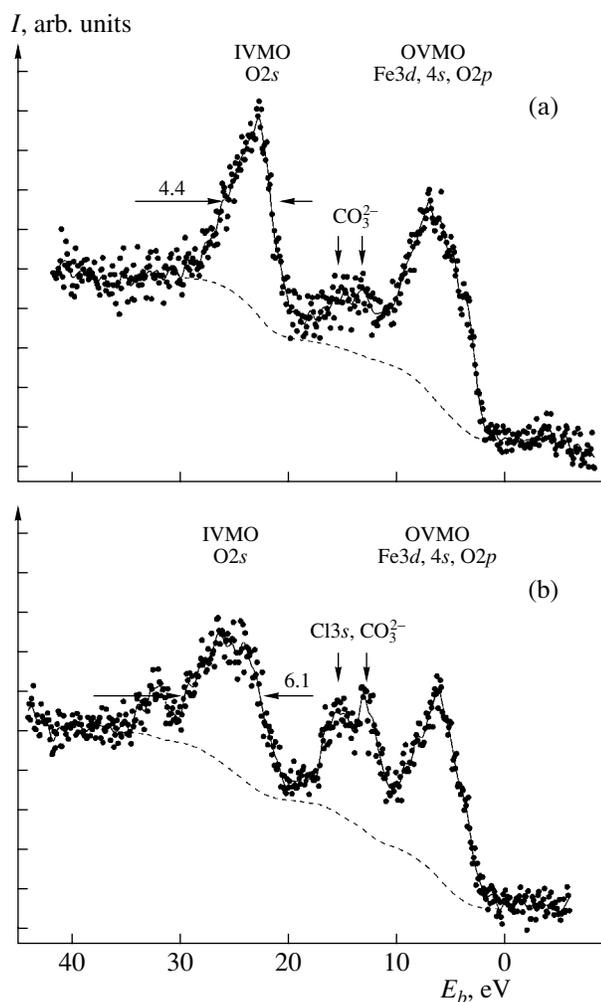


Fig. 1. Low-energy XPS spectra for the interaction products of Np(V)O_2^+ in aqueous solution with (a) maghemite (sample II) and (b) hematite (sample III).

to adequately quantify the relative intensity of this line and the number of weakly bound Fe3d electrons on the basis of such spectra. The low-intensity structure observed at 12–16 eV may be associated with the MO electrons of the carbonato group CO_3^{2-} and the nitrate group NO_3^- and with the Cl3s electrons [14]. At 31.2 eV, the Na2p line is observed in the spectra of samples I and III.

The Np5f line is expected to appear at $E_b \sim 2.5$ eV in the low-energy electron spectra of the products of the reaction of the minerals with the neptunyl group (samples I–III): the Np5f electrons weakly participate in the chemical bonding; the area of this line is proportional to the number of these electrons and characterizes the neptunium oxidation number in the compounds (table). Unfortunately, it is difficult to resolve this line from the

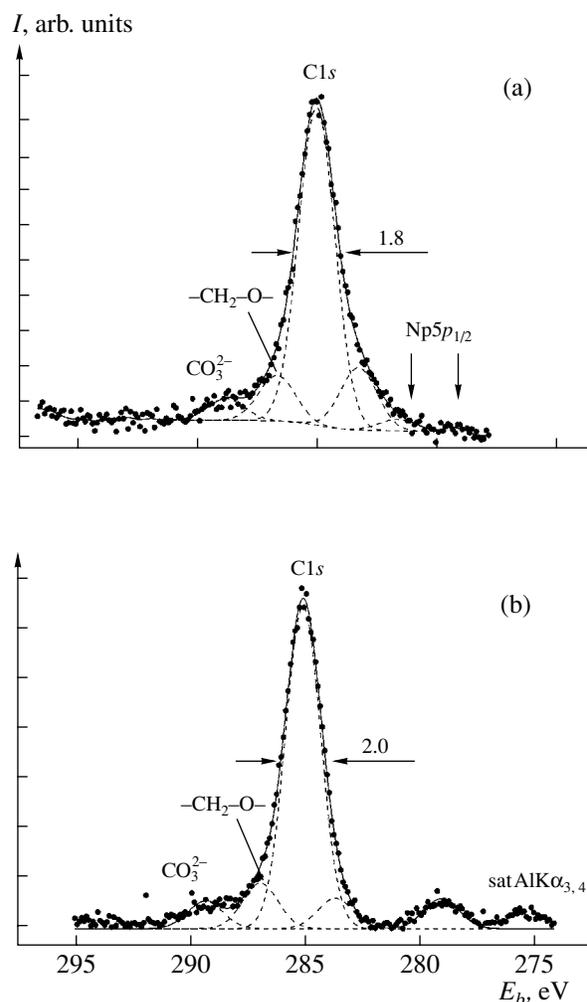


Fig. 2. C1s spectra for the interaction products of Np(V)O_2^+ in aqueous solution with (a) maghemite (sample II) and (b) hematite (sample III).

spectrum because of the low neptunium concentration in the test samples.

Core-electron spectral region. Hydrocarbon molecules, which can bear oxygen atoms, and water molecules can be adsorbed on samples while they are prepared. There are surface cleansing methods, but they were not employed in this work in order to conserve the surface layer of the samples. The C1s electron spectra of the test samples consist of the main line at $E_b = 285.0$ eV (from saturated hydrocarbons), against which the energy calibration of the spectra was carried out; a line at 287 eV, which is associated with $-\text{CH}_2-\text{O}$ groups; a line at 289 eV, which is associated with the carbonate carbon; and a line at 275.4 eV, which is associated with the $\text{AlK}_{\alpha3,4}$ satellites (Fig. 2, table). The $\text{AlK}_{\alpha3}$ and $\text{AlK}_{\alpha4}$ satellite lines lie at 9.8 eV (7.33%) and 11.9 eV (3.66%) on the low-binding-energy side from the main

line; the figures in the parentheses indicate the percentage relative intensities of the lines [17]. In all cases, low-intensity extra lines are observed at 279 and 283 eV; these extra lines may be partially assigned to the structure associated with the Np5p_{1/2} electrons and induced by a dynamic effect (Fig. 2). The dynamic effect is a phenomenon as a result of which a two-hole final state (Np5p⁶5d⁸5f^{*n*} + 1) appears, in addition to the one-hole final state (Np5p⁵5d¹⁰5f^{*n*}), after the photoemission of a core-level Np5p electron because of giant Coster–Kronig electron transitions, which involve the inner and outer electron shells [11]. A complex fine structure may appear in the Np5p electron spectrum, in particular, in the range of the electron binding energies from 275 to 285 eV. In the spectrum of sample **I** at 293.2 and 296.1 eV, there is a low-intensity doublet due to the spin–orbit coupling of the potassium 2p electrons with $\Delta E_{sl} = 2.9$ eV.

The O1s electron spectrum (sample **I**) is a slightly broadened line with $\Gamma(O1s) = 3.2$ eV at $E_b = 531$ eV. This line may be separated into three components. The line at 530.2 eV may be assigned to the oxide oxygen, the line at 531.5 eV to the hydroxide oxygen of goethite, and the line at 533.4 eV to the water oxygen (table). These binding energies agree with the respective values for α -FeOOH (530.1 and 531.8 eV) [17]. The O1s electron spectrum from the surface of sample **II** also consists of three lines, which are observed at 530.7, 532.2, and 533.7 eV (table, Fig. 3). The first line may be assigned to the oxide oxygen, the second to the surface oxygens, and the third to water molecules. The O1s spectrum of sample **III** differs substantially from the spectra of samples **I** and **II** (Fig. 3). In sample **III**, there are a relatively weak line from the iron oxide oxygen at 531.0 eV and a very strong line at 533.0 eV; the latter should be assigned to the oxygens of ClO₄⁻, NO₃⁻, and other impurities (Fig. 3). The line from the water oxygen appears at 534.1 eV.

In spite of the contamination of the surface with hydrocarbons, their inner-level electron lines are relatively intense. From the results of processing Fe2p electron spectra, it follows that they have a very complex fine structure and they cannot be adequately separated into components [18]: in the Fe2p electron spectrum, there is a high probability of the appearance of both multiplet splitting, which is associated with the existence of unpaired Fe3d⁵ electrons in the ground state, and shake-up satellites, which appear as a result of extra electron excitation in the process of Fe2p electron photoemission [15, 17].

The Fe2p_{3/2} electron binding energy in sample **I** ($E_b = 711.7$ eV) is slightly higher than the value measured for α -FeOOH in [17] (711.0 eV). The spin–orbit coupling found from this spectrum is $\Delta E_{sl} = 13.6$ eV, which is compa-

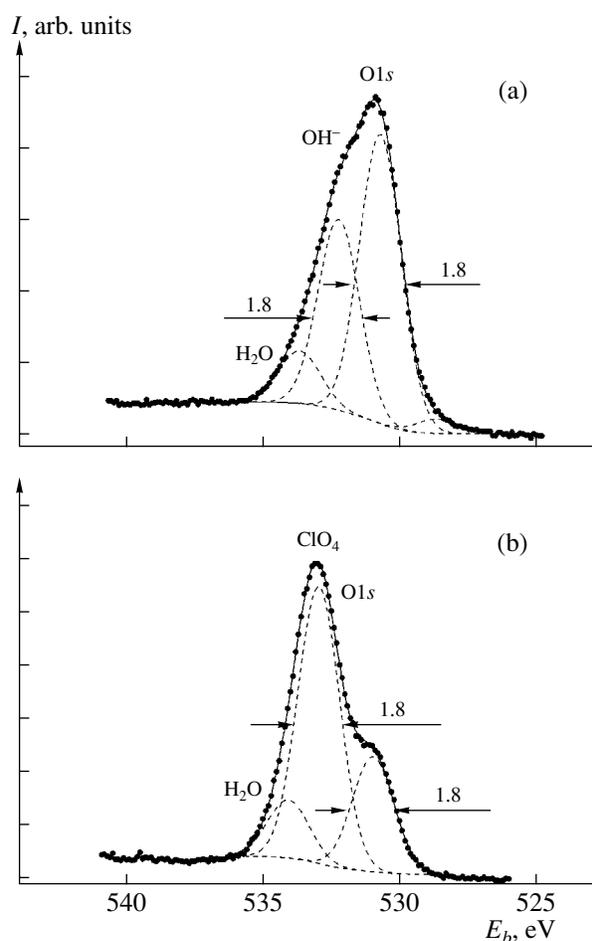


Fig. 3. O1s spectra for the interaction products of Np(V) O₂⁺ in aqueous solution with (a) maghemite (sample **II**) and (b) hematite (sample **III**).

table with the value found for metallic iron ($\Delta E_{sl} = 13.2$ eV) [19]. On the high-binding-energy side from the main lines, there are characteristic satellites at $\Delta E_{sat} = 8$ eV (Fig. 4, table). Regarding the spectra of samples **II** and **III**, the satellites in sample **III** are slightly diffuse.

The Fe3s spectra have a quite complex fine structure instead of a single, relatively narrow line (Fig. 5). Multiplet splitting appears in these spectra with a high probability and in its simplest form (as a doublet); the multiplet splitting value (ΔE_{ms}) is 6.9, 7.5, and 7.5 eV for samples **I**, **II**, and **III**, respectively (table). This ΔE_{ms} value is proportional to the multiplicity ($2S + 1$), where S is the full ion spin, or to the number of unpaired Fe3d⁵ electrons [15, 17]. The intensity ratio of the doublet should be equal to $I_1/I_2 = (S + 1)/S$, i.e., 7/5, in agreement with the experimental value, which is equal to 7/5. Actually, this spectrum has a more complex structure. Inasmuch as the constraint $E_b(Fe3s) \approx 2E_b(Fe3p)$ holds, there is a certain probability of the appearance of an

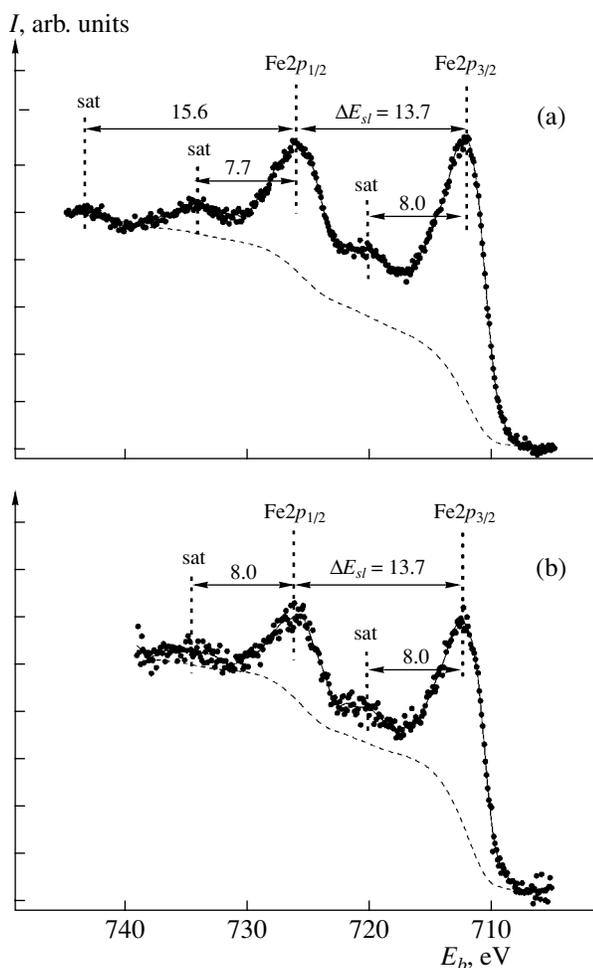


Fig. 4. Fe2p spectra for the interaction products of Np(V)O₂⁺ in aqueous solution with (a) maghemite (sample II) and (b) hematite (sample III).

additional final state, in addition to the ground state, after the photoemission of the Fe3s electron (the dynamic effect [15, 17, 20]). The following final states of the iron(III) ion may appear as a result: Fe3s¹3p⁶3d⁵ (the one-hole ground state) and Fe3s²3p⁴3d⁶ (an additional two-hole state). The spectrum becomes appreciably more complex, which in turn increases the measurement error for the multiplet splitting. Because the dynamic effect has a resonance nature, the spectral structure it induces may be affected by the nature and arrangement of the ligand atoms around the iron atom, as shown for barium compounds [20]. In spite of this, the multiplet splitting and the number of unpaired electrons may be found with a certain error from the Fe3s spectrum. The different spectral structures of samples I–III may arise from some alteration in the environment of surface iron ions induced by complexing of the neptunyl group with minerals (Fig. 5). Some increase in the intensity of the high-energy component

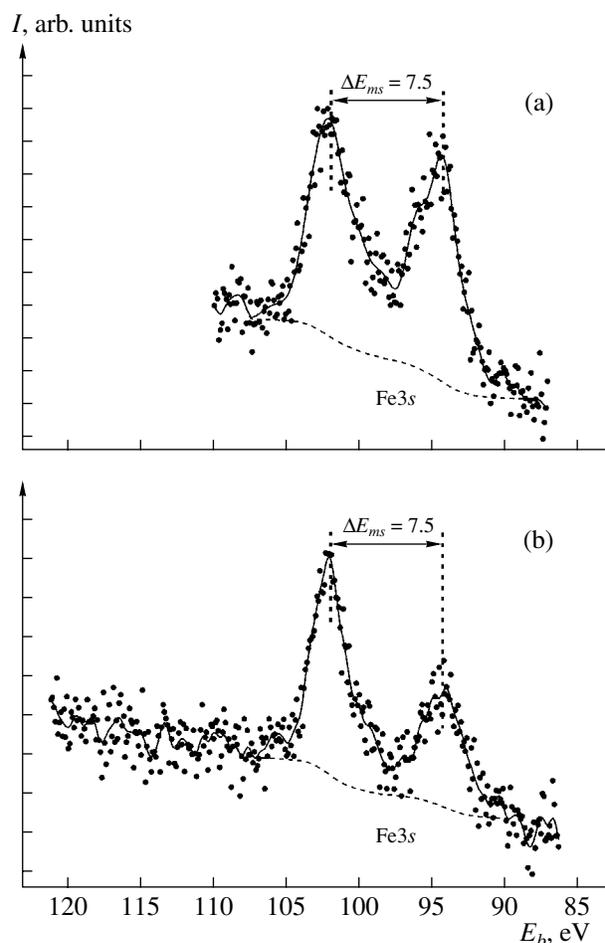


Fig. 5. Fe3s spectra for the interaction products of Np(V)O₂⁺ in aqueous solution with (a) maghemite (sample II) and (b) hematite (sample III).

of the Fe3s electron spectrum may be due to the Si2p line (ΔE_b = 102.3 eV) from silicon contained in the adhesive band, which was used in this work as a substrate. Because the intensity ratio for these two lines is 7/5, the extra contribution to the intensity of the low-energy component from the Si2p line may be taken into account when determining the overall intensity of the Fe3s spectra. From the structure of these spectra in the ionic approximation, it may be inferred that iron(III) exists on the surface.

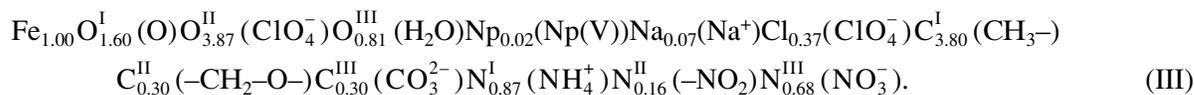
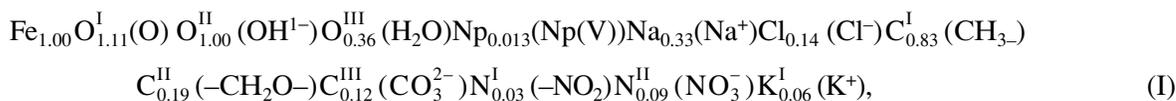
The Np4f spectra consist of doublets of relatively narrow lines, which are due to the spin–orbit splitting with an average value of ΔE_{sl} = 11.7 eV (Fig. 6). The binding energies E_b(Np4f_{7/2}), equal to 403.2, 403.7, and 403.8 eV for samples I, II, and III, respectively, are the closest to the respective values (403.4 and 403.6 eV) observed in neptunium(V) compounds Cs₃NpO₂Cl₄ and RbNpO₂(NO₃)₂ · 2H₂O (table).

All Np4*f* spectra display N1*s* peaks. The lines at 407.8 eV in sample **I**, at 407.6 eV in sample **II**, and 407.3 eV in sample **III** are due to the NO₃⁻ group. The lines at 404.8 eV in sample **I** and 404.5 eV in sample **III** are presumably assigned to the NO₂⁻ group. The line at 402.3 eV in sample **III** is due to the NH₄⁺ group.

The Na1*s* line is observed at 1072.2 eV in sample **I** and 1072.8 eV in sample **III**. A low-intensity Cl2*p* line, presumably from NaCl, appears at $E_b(\text{Cl}2p_{3/2}) = 199.4$ eV in sample **I**. The Cl2*p*_{3/2} line at 208.6 eV from the perchlorato group ClO₄⁻ is observed in the spectrum of sample **III**.

Quantitative analysis. In the quantitative elemental and ion analysis of samples **I–III**, the uncertainties in the measurement of line areas in the core-electron spectra of the metals are increased due to the fact that the spectra have an extra structure associated with both

multiplet splitting and secondary electron processes (multielectron excitation and the dynamic effect). Because multielectron excitation generates shake-up satellites on the high-binding-energy side of the main lines, their intensity may partially be included into the analysis (Fig. 4). It is difficult to account for the dynamic effect on the decrease in the intensity of the main lines, but in the spectra in question, it is not high. An extra error higher than 10% in the elemental and ion analysis may appear as a result. The subtraction of the secondary (scattered) electron background is difficult because of the complexity of the Fe2*p* spectrum [18], and here, we used the Fe3*s* lines for the quantitative analysis. A possible contribution of the Si2*p* line into the intensity of the high-energy component of the Fe3*s* spectrum was taken into account. It was found using this approximation that the surface (~5-nm) layer of the test samples has the following composition per iron atom:



Here, O^I(O), O^{II}(OH⁻), O^{III}(H₂O), and O_{3.87}^{II}(ClO₄⁻) are the oxygens of the oxide, hydroxide, water, and perchlorato group. The observed excess of oxide oxygen in samples **I** and **II** may be partially due to adsorbate oxygen-containing molecules and to a relatively high measurement error, which was noted previously. We showed in [16] that in cases where there is about one neptunium ion per 1000 atoms (≈ 0.1 at. % Np(V)) in the sample, XPS spectroscopy determines the neptunium oxidation number adequately. We may assume that the neptunyl ion interacts with minerals via hydroxide groups or oxygen atoms that lie in the equatorial plane of the NpO₂⁺ ion; water molecules and/or carbonato group CO₃²⁻ and nitrate group NO₃⁻ may occupy the other sites in the equatorial plane. Foreign groups, which can complex with neptunyl ions, exist on the surface of all test samples. The physisorption of neptunyl compounds on the samples also cannot be ruled out. In spite of the fact that the mineral surfaces bear many foreign functional groups, the Np4*f* spectra imply that the only surface neptunium species is the neptunium(V) ion: the Np4*f* doublet appears in the

spectra as a single and fairly narrow line. There are no other neptunium surface species (neptunium (IV) and neptunium (VI)) in the test samples. The nonoccurrence of surface redox reactions involving neptunium was verified by solvent extraction.

CONCLUSIONS

We have carried out the first XPS spectroscopic study of the interaction of Np(V)O₂⁺ in aqueous solution with goethite, maghemite, and hematite. As a result, we have determined the elemental and ion composition of the surface of these minerals and the physicochemical surface neptunium species.

The reaction of the neptunyl group with goethite, maghemite, and hematite in aqueous solution does not produce neptunium(IV) or neptunium(VI) compounds. Rather, new neptunyl compounds with Np(V)O₂⁺ are formed; the oxide oxygen atoms of goethite, maghemite, and hematite and the oxygen atoms of water molecules and/or carbonato group CO₃²⁻ and

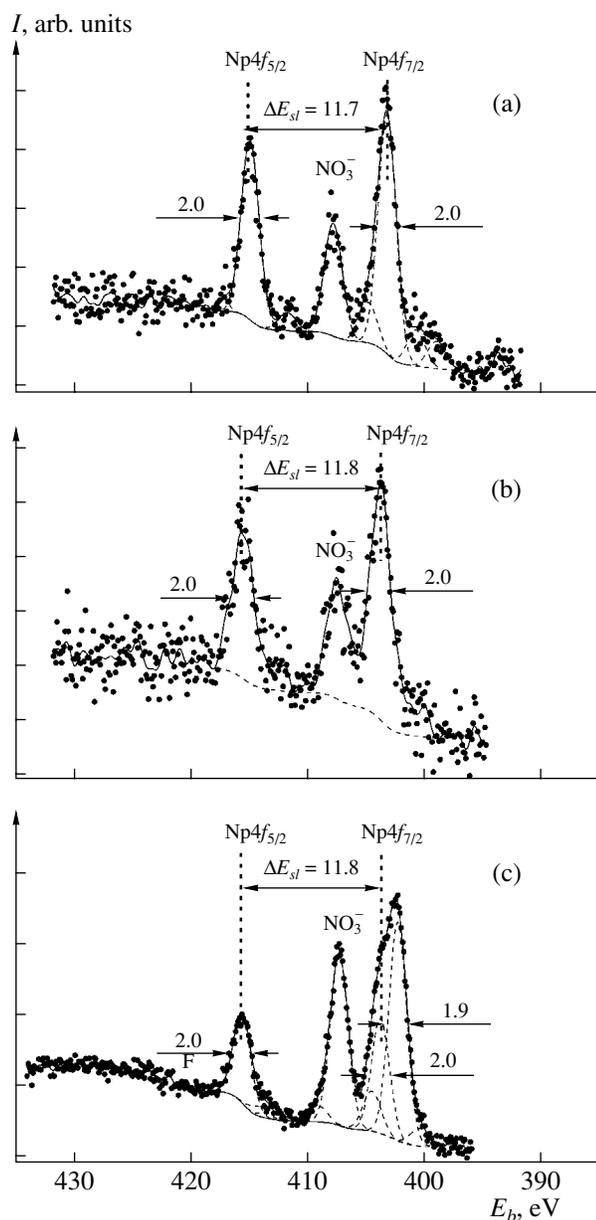


Fig. 6. Np4f spectra for the interaction products of Np(V)O₂⁺ in aqueous solution with (a) goethite (sample I), (b) maghemite (sample II), and (c) hematite (sample III).

nitrate group NO₃⁻ may lie in the equatorial plane of these compounds.

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