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 $\text{Np}^\text{V}$, whose low charge is responsible for its chemical inertness. However, redox reactions can occur in the environmental setting to yield $\text{Np}^{\text{IV}}$ or $\text{Np}^{\text{VI}}$ ions do not appear; rather, neptunyl (Np(V)O$_2^\text{2+}$) group is complexed with surface hydroxide groups of $\alpha$-FeOOH, $\gamma$-Fe$_2$O$_3$, and $\alpha$-Fe$_2$O$_3$. Presumably, the oxygen atoms of iron oxides and water and/or carbonate (CO$_3^{2-}$) or nitrate (NO$_3^-$) group lie in the equatorial plane of the neptunyl (NpO$_2^\text{2+}$) group.

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**EXPERIMENTAL**

**Synthesis and product identification.** A goethite ($\alpha$-FeOOH) sample was synthesized from Fe(NO$_3$)$_3$, using a procedure described in [8], as follows. Chemically pure Fe(NO$_3$)$_3$·9H$_2$O (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% NaOH was solved in bidistilled water (50 mL), and 30% NaOH was added, and the solution was heated to 40°C.

A precipitate was decanted and washed several times with bidistilled water. The product was dried at 40°C.

A precipitate was washed several times with bidistilled water. The product was dried at 40°C.

A precipitate was decanted and washed several times with bidistilled water. The product was dried at 40°C.

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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 µm. 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-thienoyltrifluoroacetone in cyclohexane [10]. Three sorption experiments were carried out with each min-

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

**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_{av} (eV) for core-level lines; the fine-structure parameters induced by the dynamic effect; and relative...
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Neptunium oxidation numbers Np(N) and electron binding energies E_b (eV) for samples I, II, and III and for neptunium compounds [11]

<table>
<thead>
<tr>
<th>Sample⁹</th>
<th>Np(N)</th>
<th>MO</th>
<th>Fe²p³/₂,½</th>
<th>Fe₃s</th>
<th>Np⁴f⁷/₂,½</th>
<th>O₁s</th>
<th>Cl₁s</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Np(V)</td>
<td>6.4; 17.6; 22.4; 31.2</td>
<td>711.7 (719.7)</td>
<td>94.1</td>
<td>403.2</td>
<td>530.2</td>
<td>285.0</td>
</tr>
<tr>
<td>α-FeOOH + Np</td>
<td></td>
<td></td>
<td>725.3 (734.3) (739.2)</td>
<td>101.2</td>
<td>414.9</td>
<td>531.5</td>
<td>286.8</td>
</tr>
<tr>
<td>II</td>
<td>Np(V)</td>
<td>7.0; 22.7</td>
<td>712.0 (720.0)</td>
<td>94.0</td>
<td>403.7</td>
<td>530.7</td>
<td>285.0</td>
</tr>
<tr>
<td>γ-Fe₂O₃ + Np</td>
<td></td>
<td></td>
<td>725.7 (733.4) (741.3)</td>
<td>101.5</td>
<td>415.5</td>
<td>532.2</td>
<td>286.7</td>
</tr>
<tr>
<td>III</td>
<td>Np(V)</td>
<td>6.1; 13.1; 26.4; 31.8</td>
<td>711.9 (719.9)</td>
<td>93.8</td>
<td>403.8</td>
<td>531.0</td>
<td>285.0</td>
</tr>
<tr>
<td>α-Fe₂O₃ + Np</td>
<td></td>
<td></td>
<td>725.4 (733.4)</td>
<td>101.3</td>
<td>415.6</td>
<td>533.0</td>
<td>287.0</td>
</tr>
<tr>
<td>NpO₂</td>
<td>Np(IV)</td>
<td></td>
<td></td>
<td></td>
<td>402.5</td>
<td>529.7</td>
<td>284.5</td>
</tr>
<tr>
<td>RbNpO₂(NO₃)₂H₂O</td>
<td>Np(V)</td>
<td>2.9 (Np⁵f); 5.4; 27.0</td>
<td></td>
<td>403.6</td>
<td>531.5</td>
<td>285.0</td>
<td></td>
</tr>
<tr>
<td>Cs₂NpO₂(CH₃COO)₃</td>
<td>Np(V)</td>
<td>2.3 (Np⁵f); 4.3; 27.2</td>
<td></td>
<td>403.0</td>
<td>531.5</td>
<td>285.0</td>
<td></td>
</tr>
<tr>
<td>Cs₃NpO₂Cl₄</td>
<td>Np(V)</td>
<td>2.5 (Np⁵f); 4.9; 26.2</td>
<td></td>
<td>403.4</td>
<td>531.6</td>
<td>285.0</td>
<td></td>
</tr>
<tr>
<td>Cs₂NpO₂Cl₄</td>
<td>Np(VI)</td>
<td>3.3 (Np⁵f); 5.3; 25.8</td>
<td></td>
<td>404.6</td>
<td>531.9</td>
<td>285.0</td>
<td></td>
</tr>
<tr>
<td>NaNpO₂(CH₃COO)₃</td>
<td>Np(VI)</td>
<td>3.4 (Np⁵f); 5.9; 24.2; 26.0</td>
<td></td>
<td>405.2</td>
<td>532.0</td>
<td>285.0</td>
<td></td>
</tr>
</tbody>
</table>

⁹ Samples I, II, and III were prepared on an adhesive band; the other samples were prepared on indium.

Satellite energies are parenthesized.

energies ΔEₕ (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 O₂s electrons have relatively large widths at half-height Γ(O₂s), which is equal to 5.7, 4.4, and 6.1 eV for samples I, II, and III, respectively. For the composite O₁s line, the width Γ(O₁s) for these samples is 3.2, 3.2, and 4.0 eV, respectively. This is one argument in favor of the participation of the O₂s atomic orbitals (AO) in the formation of the molecular orbitals. From the uncertainty relationship ΔΕΔτ ≈ h/2π (where ΔΕ is the half-width of the level from which the electron is removed, Δτ is the lifetime of the resulting hole, and h is the Planck constant), it follows that if the O₂s level were atomic, the width-at-half-height of its O₂s line would be lower than the same width of the O₁s line, which contradicts the experimental data. With reference to literature data for various compounds [14], we may assume that the line in the O₂s 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 Fe³d, Fe⁴s, Np⁶p, Np⁶d, Np⁷s, Np⁵f and O₂s,2p electrons of the neighboring iron, neptunium, and oxygen atoms. The OVMO structure is mainly due to the interaction of Fe³d, Fe⁴s, Np⁶d, Np⁷s, Np⁵f, and O₂p electrons; the IVMO structure is mainly due to the interaction of Fe³d, Fe⁴s, Np⁶d, and O₂s electrons [14]. Because the electronic configuration of an iron atom is {Ar}₃d⁶s² (where {Ar} is the argon electronic configuration), because the photoeffect cross section for Fe³d electrons is far larger than for O₂p 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 Fe³d electrons of the iron(III) ion (Fig. 1). Unfortunately, it is difficult
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 and the nitrato group 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 $E_b \approx 2.5$ 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 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 AlKα3,4 satellites (Fig. 2, table). The AlKα3 and AlKα4 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_{3/2} 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 \((Np5p^5d^55f^0 + 1)\) appears, in addition to the one-hole final state \((Np5p^5d^05f^6)\), 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 \(\Delta E_{sd} = 2.9\) eV.

The O1s electron spectrum (sample I) is a slightly broadened line with \(I(O1s) = 3.2\) 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 \(\alpha\)-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 ClO_4^−, NO_3^−, 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 Fe3d^5 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 \(\alpha\)-FeOOH in [17] (711.0 eV). The spin–orbit coupling found from this spectrum is \(\Delta E_{sd} = 13.6\) eV, which is comparable with the value found for metallic iron \((\Delta E_{sd} = 13.2\) eV) [19]. On the high-binding-energy side from the main lines, there are characteristic satellites at \(\Delta E_{sd} = 8\) 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 \((\Delta E_{ms})\) is 6.9, 7.5, and 7.5 eV for samples I, II, and III, respectively (table). This \(\Delta E_{ms}\) value is proportional to the multiplicity \((2S + 1)\), where \(S\) is the full ion spin, or to the number of unpaired Fe3d^5 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 \(E_g(Fe3s) = 2E_g(Fe3p)\) holds, there is a certain probability of the appearance of an...
additional final state, in addition to the ground state, after the photoemission of the Fe\(\text{3s}\) electron (the dynamic effect [15, 17, 20]). The following final states of the iron(III) ion may appear as a result: Fe\(\text{3}\)s\(^1\)p\(^6\)d\(^5\) (the one-hole ground state) and Fe\(\text{3}\)s\(^2\)p\(^4\)d\(^6\) (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 Fe\(\text{3s}\) 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 of the Fe\(\text{3s}\) electron spectrum may be due to the Si\(\text{2p}\) line (\(\Delta E_{\text{el}} = 102.3\) 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 Si\(\text{2p}\) line may be taken into account when determining the overall intensity of the Fe\(\text{3s}\) spectra. From the structure of these spectra in the ionic approximation, it may be inferred that iron(III) exists on the surface.

The Np\(\text{4f}\) spectra consist of doublets of relatively narrow lines, which are due to the spin–orbit splitting with an average value of \(\Delta E_{\text{el}} = 11.7\) eV (Fig. 6). The binding energies \(E_{\text{b}}(\text{Np}\text{4f}_{7/2})\), 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 Cs\(_3\)NpO\(_2\)Cl\(_4\) and RbNpO\(_2\)(NO\(_3\))\(_2\) \cdot 2H\(_2\)O (table).
All Np4f spectra display N1s 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 NH3 group.

The Na1s line is observed at 1072.2 eV in sample I and 1072.8 eV in sample III. A low-intensity Cl2p line, presumably from NaCl, appears at 199.4 eV in sample I. The Cl2p3/2 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 Fe2p spectrum [18], and here, we used the Fe3s lines for the quantitative analysis. A possible contribution of the Si2p line into the intensity of the high-energy component of the Fe3s 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:

\[
\begin{align*}
\text{Fe}_{1.00} & \text{O}_{1.11}^\text{I}(\text{O})^\text{II} \text{O}_{0.09}^\text{III} (\text{OH}^-) \text{O}_{0.07}^\text{III} (\text{H}_2\text{O}) \text{Np}_{0.013} \text{(Np(V))N}_{0.33} \text{(Na)Cl}_{0.14} \text{(Cl}) \text{C}_{0.83} (\text{CH}_3) \\
\text{C}_{0.19} (\text{CH}_2\text{O}^–) & \text{O}_{1.12} (\text{CO}_3^{2–}) \text{N}_{0.03} (\text{NO}_2) \text{N}_{0.09} (\text{NO}_3) \text{K}_{0.06} (\text{K}^+) \\
\text{Fe}_{1.00} & \text{O}_{0.71} (\text{O})^\text{III} \text{O}_{0.20} (\text{H}_2\text{O}) \text{Np}_{0.008} \text{(Np(V))C}_{0.56} (\text{CH}_3) \text{C}_{0.09} (\text{CH}_2\text{O}^–) \text{C}_{0.04} (\text{CO}_3^{2–}) \text{N}_{0.06} (\text{NO}_3), \\
\text{Fe}_{1.06} & \text{O}_{1.60} (\text{O})^\text{III} \text{O}_{3.87} (\text{ClO}_4^-) \text{O}_{0.81} (\text{H}_2\text{O}) \text{Np}_{0.02} (\text{Np(V))N}_{0.07} \text{(Na)Cl}_{0.37} (\text{ClO}_4^-) \text{Cl}_{3.80} (\text{CH}_3) \\
\text{C}_{0.30} (\text{CH}_2\text{O}^–) & \text{C}_{0.30} (\text{CO}_3^{2–}) \text{N}_{0.37} (\text{NH}_4^+) \text{N}_{0.16} (\text{NO}_2) \text{N}_{0.68} (\text{NO}_3). 
\end{align*}
\]

Here, O\textbf{I}(\text{O}), O\textbf{II}(\text{OH}^-), O\textbf{III}(\text{H}_2\text{O}), and O\textbf{III}(\text{ClO}_4^-) are the oxides 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 CO3^{2–} and nitrat 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 Np4f spectra imply that the only surface neptunium species is the neptunium(V) ion: the Np4f 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 CO3^{2–} and
nitrato group NO$_3^-$ may lie in the equatorial plane of these compounds.

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