THE XPS STUDY OF PHYSICAL AND CHEMICAL FORMS OF NEPTUNIUM GROUP ON THE SURFACE OF MINERALS

by

Anton Yu. TETERIN[1], *Alevtina V. MIKHAILINA*[2], *Konstantin I. MASLAKOV*[1], *Elena V. ZAHAROVA*[2], *and Yury A. TETERIN*[1]*

[1]Russian Research Centre "Kurchatov Institute", Moscow, Russia
[2]A. N. Frumkin Institute of Physical Chemistry and Electrochemistry RAS, Moscow, Russia

The sorption behavior and the physical and chemical forms of neptunium on the surface of minerals of the two chlorate samples, biotite and kaolin, with different contents of Fe(II) was studied. The liquid-liquid extraction and the X-ray photoelectron spectroscopy were employed to identify the valence forms of neptunium. On the basis of the obtained data the quantitative elemental composition of the surface of the studied minerals, as well as the ionic composition of the formed neptunium complexes was determined. It was shown that the Np(IV) and Np(VI) containing compounds did not form, while the complexes $Np(V)O_2$-hydroxyl did form on the surface. The oxygen ions bonded with iron and oxygen belonging to water and/or of carboxyl were suggested to be present in the equatorial plane of the neptunyl group NpO_2.

Key words: neptunyl, oxidation state, migration of radionuclides

INTRODUCTION

Migration behavior of radioactive materials is determined by physical and chemical forms of included radionuclides [1]. The redox reactions, sorption, and formation of complexes on the surface of minerals during the interaction with solutions determine the radionuclide mobility. In the nature neptunium is presented in general as neptunyl ion NpO_2^+. The low charge of this ion determines its relative chemical inertness and high mobility. However, during interaction with minerals some redox reactions resulting in Np(IV) [2] or $Np(VI)O_2^{2+}$ ions formation are possible [3].

Chlorite, biotite, and kaolin are widely spread minerals in the environment with high sorptive power to heavy metals and radionuclides [4, 5]. The present work studied the sorption mechanisms of NpO_2^+ complexes on the surface of the minerals by liquid-liquid extraction and X-ray photoelectron spectroscopy (XPS). The liquid-liquid extraction can be used for separation of the minute amounts of actinides by their valence states; however, redox reactions are possible during the extraction. The XPS is

an effective tool for the study of the surface forms of radionuclides. Previously the XPS studies showed that the interaction of Np(V) ions with granite at the presence of Fe(II)-containing minerals results in Np(IV) formation [2], while the interaction of Np(IV) ions with iron (III) hydroxide and oxides results in Np(V) formation [6, 7].

The alteration of radionuclides' oxidation states on the mineral surface can affect their mobility, which has to be taken into account in the long-term forecasts of radionuclides migration. The studies of neptunium valence forms are especially important since neptunium is one of the most mobile radionuclides in the environment.

EXPERIMENTAL

Sample parameters. The experiments were conducted with the sedimentary rock samples. Their properties are given in tab. 1. The size of the used particles was 0.05 mm to 0.25 mm.

All the studied samples were aluminosilicates. The X-ray diffraction with sensitivity of 2 mass% to 5 mass% showed the absence of other crystalline phases. The studied chlorite samples differed by Fe(II)

---

* Corresponding author; e-mail: teterin@ignph.kiae.ru

2

A. Yu. Teterin, *et al.*: The XPS Study of Physical and Chemical Forms of ...
Nuclear Technology & Radiation Protection: Year 2010, Vol. 25, No. 1, pp. 1-7

Table 1. Parameters of the mineral samples

Mineral	Notation	Chemical formula	Fe(II) content [FeO in mass%]	Surface area [m^2g^{-1}]
Chlorite	I-Cl_3	$MgFe^{2+}[AlSi_3O_{10}(OH)_2]_3Mg,Fe(OH)_2$	6.3	0.55
Chlorite	II-Cl_M	$MgFe^{2+}[AlSi_3O_{10}(OH)_2]_3Mg,Fe(OH)_2$	11.3	0.50
Biotite	III-Bt	$KMg_{2,5}Fe_{0,5}^2AlSiO_3(OH)_{1,75}F_{0,25}$	24.7	0.24
Kaolin	IV-Ka	$Al_2Si_2O_7\,2H_2O$	0.1	11.8

contents, which could be due to the different geological conditions of their formation.

Sorption experiment. The experiments under the aerobic conditions used the aqueous suspensions of the mineral samples with the solid/liquid ratio 1:20. The experiment was done from the solution containing 0.12 M* of $NaNO_3$ at pH 8.0-8.5. Neptunium in the initial solution is presented as the neptunyl ion $[Np(V)O_2^+]$ which was confirmed by the spectrophotometric analysis. Neptunium content was $1\,10^{-3}$ M. The time of the phase contact was 24 hours, which was sufficient for the sorption equilibrium in the system. Three consecutive sorption cycles were conducted with each mineral.

Phase separation was done by centrifugation (about 8000 rotations per minute, 15 minutes). The sorption was evaluated by neptunium contents in the liquid phase. Activity was measured with the liquid-scintillation spectrometry; low-background liquid-scintillation spectrometer SKS-07P-B11 (Russia) with the scintillator OPTIPHASE 'HISAFE' by Perkin-Elmer.

Neptunium content in each 0.1 g sample was about $2\,10^{-6}$ M of ^{237}Np. After the experiment was finished, the solid phase was washed with distilled water to remove the easy-absorbed impurities, then the sample was dried for 24 hours at 30 °C.

Neptunium valence states in liquid and solid phases were determined by liquid-liquid extraction (0.5 M with the solution of 1-(theonyl)-3, 3, 3-trifluoroacetone in toluene) by the technique described in [8].

For the XPS studies the four 0.005 g to 0.01 g mineral samples containing $1-2\,10^{-7}$ M of ^{237}Np were prepared: I – Cl_3 (Chlorite-1), II – Cl_M (Chlorite-2), III– Bt (biotite), IV– Ka (kaolin). The samples were glued with $[—CH_2CH(OCOCH_3)—]_n$ on an 0.15 mm thick aluminium foil substrate ($10\quad10\,mm^2$) as a thin continuous layer. It has to be noted that the use of this technique can result in some extra XPS peaks from the elements included in the substrate. Therefore, a special attention was paid to this during the sample preparation. The glue used in the experiment contained the carboxyl group. Carbon from this group is well identified in the C1s XPS as a peak at 289.1 eV [9]. In the XPS measurements this peak was observed as a low intensity peak.

X-ray photoelectron spectroscopy. XPS spectra of the studied samples were measured with an electrostatic spectrometer MK II VG Scientific using $AlK_{\alpha1,2}$ (hv = 1486.6 eV) radiation under $1.3\,10^{-7}$ Pa at the room temperature. The device resolution, measured as the full width at the half-maximum (FWHM) of the $Au4f_{7/2}$ peak on the standard rectangular gold plate, was 1.2 eV. The binding energies E_b(eV) were measured relatively to the binding energy of the C1s electrons from hydrocarbons absorbed on the sample surface were accepted to be equal to 285.0 eV. For the gold standard the calibration binding energies E_b(C1s) = 284.7 eV and E_b($Au4f_{7/2}$) = 83.8 eV were used. The C1s XPS peak from hydrocarbon on the sample surface was observed to be 1.3 eV wide. The error in the determination of the binding energy and the peak widths did not exceed 0.1 eV (10% of the relative peak intensity) [7].

For all the samples the quantitative elemental and ionic analysis was done. It was based on the fact that the spectral intensity is proportional to the number of certain atoms in the studied sample. The following ratio was used: $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where n_i/n_j is the relative concentration of the studied atoms, S_i/S_j – the relative core-shell spectral intensity, and k_j/k_i – the relative experimental sensitivity coefficient. The following coefficients relative to the C1s were used: 1.00 (C1s), 2.64 (O1s), 12.0 (Fe2p), 8.0 ($Fe2p_{3/2}$), 0.55 (Fe3s), 9.2 (Na1s), 14.0 (Mg1s), 0.80 (Mg2s), 0.48 (Mg2p), 0.74 (Al2p), 1.08 (Si2p), 1.04 (Si2s), 3.32 ($K2p_{3/2}$), 4.49 (K2p), 1.72 (K2s), 4.2 ($Ca2p_{3/2}$), 6.32 (Ca2p), 40.0 ($Np4f_{7/2}$) [10]. Neptunium sensitivity coefficient was drawn by extrapolation of the corresponding values for thorium and uranium [10] and within the measurement error (20%) agrees with k_{ji}($Np4f_{7/2}$) = 49.2 for the $Np4f_{7/2}$ for $Cs_2NpO_2Cl_4$ single crystal, taking into account the corresponding value k_{ji}(Cl2p) = 2.92 for the Cl2p [10]. The Fe3s sensitivity coefficient was drawn by using the data for the Fe2p and photoemission cross-sections [10, 11]. The XPS data from some neptunium compounds were used for the interpretation of the spectra from the samples I-IV (tab. 2).
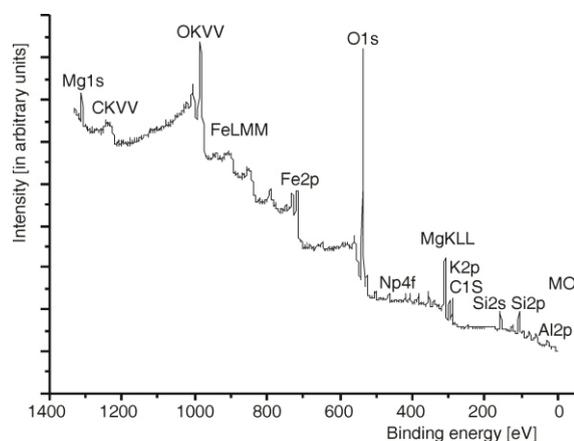
RESULTS AND DISCUSSION

The XPS determination of physical and chemical forms of radionuclides is based upon both tradi-

---

* Simbol M denotes molar mass – the mass of one mole of a substance

A. Yu. Teterin, *et al.*: The XPS Study of Physical and Chemical Forms of ...
Nuclear Technology & Radiation Protection: Year 2010, Vol. 25, No. 1, pp. 1-7

3

Table 2. Neptunium oxidation state N(Np), Np4f$_{7/2}$ XPS intensity $I(10^3$ counts per minute) and binding energies E_b(eV) for the samples I-IV and neptunium compounds [12]

Sample	N (Np)	Np5f [eV]	Np4f$_{7/2}$ [eV]	$I(10^3)$ arb. units	Al2p$_{3/2}$ [eV]	Si2p$_{3/2}$ [eV]	Fe2p$_{3/2}$ [eV]	Mg1s, 2s, 2p [eV]	O1s,2s [eV]	C1s [eV]
I-Cl$_3$-(Np)	V		403.2	2.08	74.6		710.7	50.3 89.1 1304.8	531.9 24.2	282.6 285.0
II-Cl$_M$-(Np)	V		403.1	2.84	74.3		710.7	50.3 88.8 1305.2	531.8 24.2	285.0 288.5 290.6
III-Bt-(Np)	V		403.6	4.32	74.3	102.5	710.8	49.8 89.0 1305.2	531.4 23.8	282.1 285.0 287.7
IV-Ka-(Np)	V		403.6	1.22	74.8	103.0		1305.2	532.2 23.7	285.0 288.6
NpO$_2$	IV		402.5						529.7	284.5
RbNpO$_2$ (NO$_3$)$_2$2H$_2$O	V	2.9	403.6						531.5 533.5	285.0
Cs$_3$NpO$_2$Cl$_4$	V	2.5	403.4						531.6	285.0
Cs$_2$NpO$_2$Cl$_4$	V	3.3	404.6						531.9	285.0

tional spectral parameters (binding energies and peak intensities), core and outer levels fine spectral structure parameters like the relative Fe3d and Np5f intensities, relative OVMO and IVMO binding energies, multiplet splitting ΔE_{ms}(eV) of the core levels, dynamic effect related fine spectral structure parameters, and shake-up satellites relative positions ΔE_{sat}(eV) [12]. In the aggregate, these spectral parameters provide the information on the physical and chemical forms of, for example, iron and actinides on the surface of the studied samples. The XPS of the studied samples, beside the peaks related to the included elements, exhibit the Auger MgKLL, FeLMM, OKVV, and CKVV peaks (fig. 1). The survey XPS allows a qualitative conclusion about the elemental composition of the 5 nm surface layer of the studied samples. Thus, the sample III (Np) XPS exhibits the Al2p, Si2s,2p, C1s, K2p, Np4f, O1s, Fe2p, Na1s, and Mg1s peaks (fig. 1). Their intensities with the corresponding photo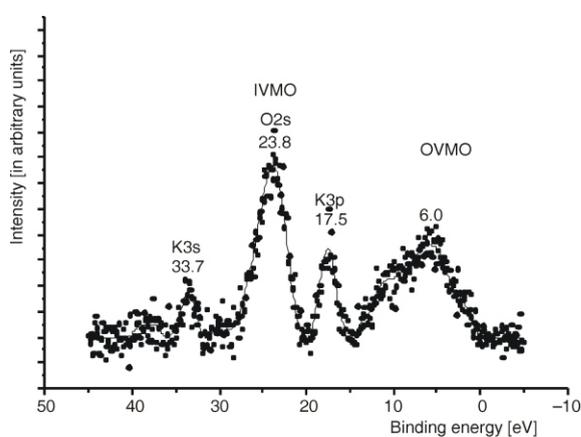emission cross-sections taken into account are proportional to the concentration of the elements. XPS peaks from elements whose concentration is not more than 1 mass%, as a rule, have low intensities.

Valence electron spectral range. The valence bands in the XPS from the studied samples (sample I, II, III, IV) are observed in the binding energy range 0-40 eV. It consists of the OVMO (0- ~13 eV) and IVMO (~13-40 eV) related lines (fig. 2). The lines in the O2s binding energy range are relatively wide Γ(O2s) = 2.8 eV, 3.1 eV, 2.7 eV, and 2.9 eV for the samples I, II, III, and IV, respectively, while Γ(O1s) = 1.4 eV for these samples. This peak can interfere only with the Ca2p one, which has low intensity (see tab. 2). This O2s widening confirms that the O2s atomic orbitals (AO) in the considered complex compounds participate in the IVMO formation.

Indeed, the uncertainty ratio $E \cdot \tau \sim h/2$, where E is the FWHM of a level from which an electron was removed, τ – the lifetime of a hole on this level, and h the Plank's constant, shows that if the O2s level was atomic, Γ(O2s) would be less than Γ(O1s), which con-

Figure 1. Survey XPS from sample III-Bt (biotite with Np)

Figure 2. Valence electron XPS from sample III-Bt (biotite with Np)

4

A. Yu. Teterin, *et al.*: The XPS Study of Physical and Chemical Forms of ...
Nuclear Technology & Radiation Protection: Year 2010, Vol. 25, No. 1, pp. 1-7

tradicts the experimental data. Taking into account the data for various compounds [12, 13], one can suggest that the line in the O2s binding energy range is IVMO-related, not atomic.

The valence bands in the XPS from samples I-IV are generally formed from the Mg3s, Al3s,3p, Si3s,3p, K3s,3p,4s, Fe3d,4s, Np6p,6d,7s,5f, and O2s,2p electrons. The OVMO structure forms mostly from the interaction of the Mg3s, Al3s,3p, Si3p, K4s, Fe3d,4s, Np6p,6d,7s,5f, and O2p electrons, while the IVMO structure – from the interaction of the Si3s, K3s,3p, Fe3d, Np6p, and O2s electrons [12, 13]. Since iron electronic configuration is $\{Ar\}3d^64s^2$, where $\{Ar\}$ – argon electronic configuration, the Fe3d photoemission cross-section is much higher than the O2p one [11] and neptunium concentration is very low, the OVMO intensity is expected to be formed mostly by the Fe3d electrons (fig. 2). Unfortunately, these spectra do not provide a correct quantitative relative Fe3d intensity. The low intensity structure at 12 eV to 16 eV can be attributed to the MOs of carboxyl group CO_3^{2-}, although on the basis of the C1s spectrum it is expected to be low intensity [6]. The K3p and K3s peaks are observed at 17.5 eV and 33.7 eV in the XPS from sample III (fig. 2).

A sharp peak attributed to the Np5f electrons weakly participating in the chemical bond is expected at E_b 2.5 eV in the low binding energy XPS from neptunyl-mineral interaction products (samples I-IV) (see tab. 2). The intensity of this peak is proportional to the number of the Np5f electrons and characterizes neptunium oxidation state in compounds. Unfortunately, this peak is hard to separate in spectra from the studied samples because of low neptunium concentration (fig. 2).

Core electron XPS range. During the sample preparation carbohydrates can absorb on the surface. In this work the surface was not cleaned in order to avoid surface destruction, although there are techniques to do this. The C1s XPS from the studied samples consist of the basic peak at $E_b = 285.0$ eV (saturated hydrocarbons) used for the binding energy calibration, the peak at 286.9 eV attributed to the $-CH_2-O-$ groups, the peak at 289 eV attributed to the carboxyl group CO_3^{2-} (fig. 3a, tab. 2). A weak peak at 282.1 eV attributed to the $Np5p_{1/2}$ electrons involved in the dynamic effect is also observed (fig. 3a). Dynamic effect is a phenomenon resulting in an extra two-hole final state ($Np5p^65d^85f^{n+1}$) in addition to the basic one-hole final state due to the gigantic Coster-Kronig electronic transition during the photoemission from the Np5p level [12]. This can complicate the Np5p XPS structure in the binding energy range of 275-285 eV. The XPS from the sample III at 293.6 and 296.4 eV exhibits an intense doublet attributed to the K2p spin-orbit interaction with $E_{sl} = 2.8$ eV.

The O1s XPS (sample III) consists of a symmetric widened peak $\Gamma(O1s) = 2.4$ eV at $E_b = 531.4$ eV (fig. 3b). After the peak width calibration by the $\Gamma(C1s) = 1.3$ eV, $\Gamma(O1s)$ becomes 1.4 eV. A 1.0 eV
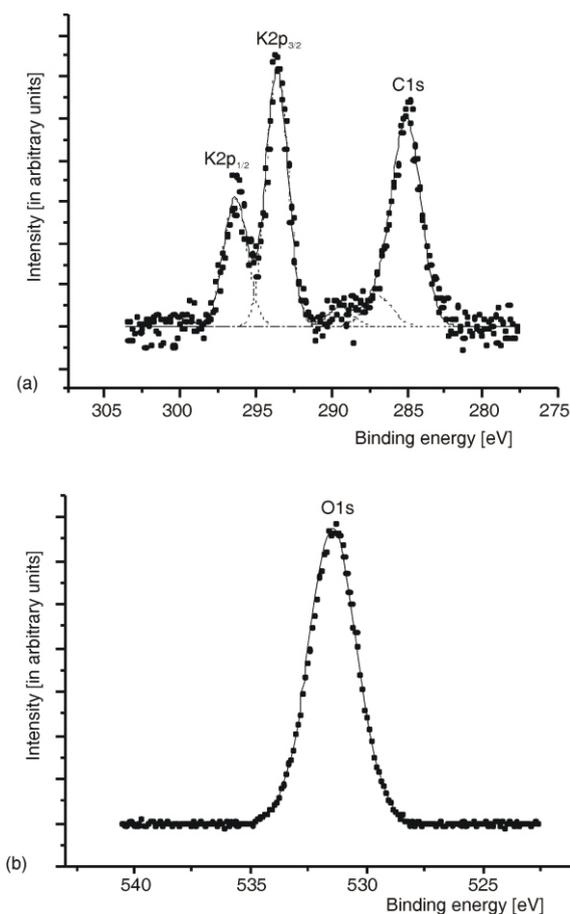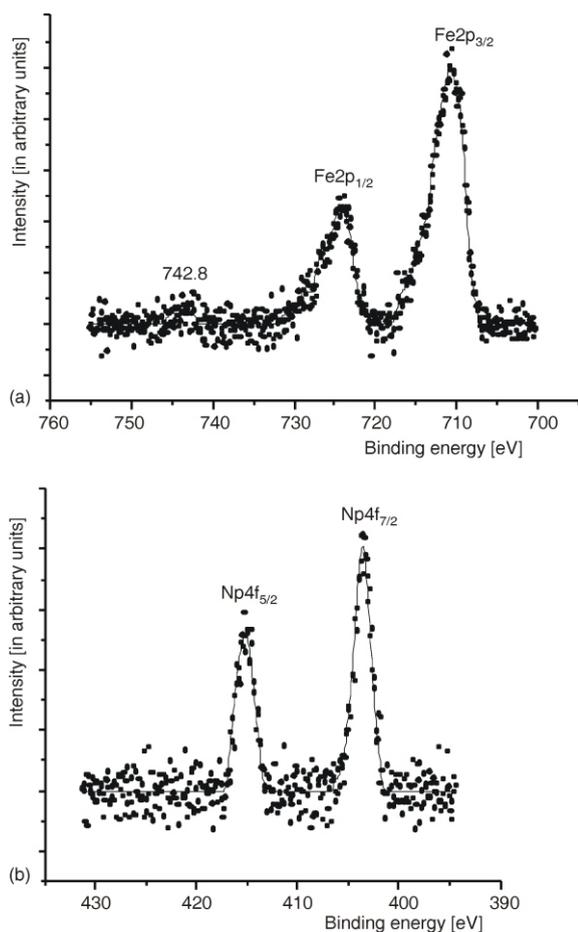

Figure 3. XPS from sample III-Bt (biotite with Np): (a) – C1s and K2p, (b) – O1s

widening can be attributed to the non-uniform sample charging depending on the sample preparation quality. This XPS FWHM calibration is experimentally well grounded on many examples [13]. The basic O1s peak at 531.4 eV can be attributed to hydroxyl groups (tab. 2). The similar O1s peak shape is observed in all the studied samples. Despite the surface contamination, the core electron peaks are observed to be relatively intense.

The mathematic processing of the Fe2p XPS cannot provide a correct deconvolution into separate components because of a very complicated structure [14]. This Fe2p complex structure can be explained by the multiplet splitting due to the uncoupled Fe3d electrons in the ground state and the shake up satellites due to the extra electronic excitations within the valence band during the Fe2p photoemission [12-15].

Since iron valence electronic configuration is $Fe3d^64s^2$, the Fe(II) ion electronic configuration is $Fe3d^6$. If this ion is located, for example, in the octahedral oxygen environment, it does not have uncoupled electrons in the ground state. In this case the Fe3s and Fe2p XPS must consist of relatively sharp peaks. In case of the Fe(III) ion, the electronic configuration is $Fe3d^5$, and due to the high spin state the Fe3s and Fe2p

Figure 4. XPS from sample III-Bt (biotite with Np): (a) – Fe2p, (b) – Np4f

XPS exhibit the complex structure attributed to the multiplet splitting and many-body perturbation. In particular, the Fe2p XPS from various iron compounds exhibit the typical shake up satellites [6, 7], which are less pronounced in the XPS from the studied samples (fig. 4a). The Fe3s XPS peak has low intensity. It does not allow a correct conclusion on iron oxidation state. The Fe2p XPS allows a conclusion that iron oxidation state in the studied materials is close to Fe(II) – fig. 4(a). The $Fe2p_{3/2}$ binding energy for the sample III $E_b = 710.8$ eV is a bit lower than the corresponding value 711.0 eV for -FeOOH [15]. The spin-orbit splitting of $E_{sl} = 13.5$ eV is comparable to $E_{sl} = 13.2$ eV for metallic iron [16]. The observed peaks of the doublet are found to be widened and asymmetric compared to those from metallic iron. The similar picture was observed in the XPS from other studied samples. For the sample III it was also found that $E_b(K2p_{3/2}) = 293.6$ eV, and for the sample IV – $E_b(Ca2p_{3/2}) = 347.9$ eV and $E_b(Na1s) = 1073.1$ eV.
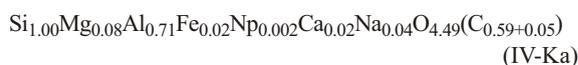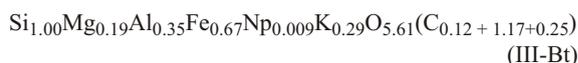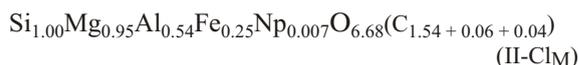
The Np4f XPS from the studied samples consist of doublets of relatively sharp spin-orbit split ($E_{sl} = 11.7$ eV) peaks (fig. 4b). Neptunium oxidation state in compounds can be determined on the basis of both core

electron binding energies and the Np5f and Np4f spectral structures [12]. The relative Np5f intensity is proportional to the number of the Np5f electrons in neptunium ion.

Unfortunately, the Np5f intensity is too low to be evaluated correctly. In the Np4f XPS the distance basic peak -shake up satellite (E_{sat}) correlates with neptunium oxidation state. Thus, for Np(V), and Np(IV) the values for E_{sat} it are 6.8 eV, 9.4 eV, and 3.5 eV, while their relative intensities are 17%, 12%, and 20% of the basic peak intensity, respectively [12]. The Np4f shake up satellites are not observed because of low neptunium concentration, *i. e.* low Np4f intensity. It can be explained by the fact that neptunium in the studied compounds does not form big clusters and the shake-up satellites in the XPS from Np(V) compounds are the least intense – fig. 4(b). The binding energies $E_b(Np4f_{7/2})$, 403.2 eV, 403.1 eV, 403.6 eV, and 403.6 eV for the studied samples I, II, III, and IV are close to 403.4 eV and 403.6 eV for $Cs_3NpO_2Cl_4$ and $RbNpO_2(NO_3)_2$ $2H_2O$ containing Np(V) ions (tab. 2).

The Np4f XPS from all studied samples did not show the NO_3-related N1s peak at 407.3 eV – figs. 1 and 4(b). It confirms the fact that the neptunyl groups NpO_2^+ present on the surface are not in the form of nitrates or other salts, but form complexes with oxygen bonded to iron and hydroxyl groups in the equatorial planes.

Quantitative analysis results. An error in areas under the core XPS peaks during the quantitative elemental and ionic analysis of the studied samples I, II, III, and IV grew up because of the extra structure due to the multiplet splitting and secondary electronic processes (many-body perturbation and dynamic effect). Since the many-body perturbation results in shake up satellites at the higher binding energy side of the basic peaks, their intensities can be partially taken into account in the analysis. The dynamic effect related intensity changes can be hardly taken into account, but the influence of this effect on the studied XPS spectra is not too high. All these effects can lead to an extra error in the quantitative elemental and ionic analysis exceeding 10%. In this approximation the surface (~5 nm) elemental composition of the studied samples related to silicon was found to be:

$$Si_{1.00}Mg_{1.05}Al_{0.66}Fe_{0.16}Np_{0.006}O_{6.61}(C_{0.36 + 1.40}) \quad (I\text{-}Cl_3)$$

$$Si_{1.00}Mg_{0.95}Al_{0.54}Fe_{0.25}Np_{0.007}O_{6.68}(C_{1.54 + 0.06 + 0.04})$$
$$(II\text{-}Cl_M)$$

$$Si_{1.00}Mg_{0.19}Al_{0.35}Fe_{0.67}Np_{0.009}K_{0.29}O_{5.61}(C_{0.12 + 1.17 + 0.25})$$
$$(III\text{-}Bt)$$

$$Si_{1.00}Mg_{0.08}Al_{0.71}Fe_{0.02}Np_{0.002}Ca_{0.02}Na_{0.04}O_{4.49}(C_{0.59 + 0.05})$$
$$(IV\text{-}Ka)$$

The concentrations of carbon in different chemical states are given in parenthesis (see tab. 2). The observed oxygen excess in the studied samples can be

6

A. Yu. Teterin, *et al.*: The XPS Study of Physical and Chemical Forms of ...
Nuclear Technology & Radiation Protection: Year 2010, Vol. 25, No. 1, pp. 1-7

partially explained by the absorbed hydroxyl groups on the surface. In ref. [6] we showed that at neptunium concentration of 1 Np ion per 1000 ions [0.1 at.% of Np(V)] the XPS method can reliably determine Np oxidation state. It is possible to suggest that neptunyl ions interact with minerals via oxygen ions bound with iron and hydroxyl groups in the equatorial plane of NpO_2^+, while the rest of vacant places can be occupied by water and/or carboxyl groups CO_3^{2-}. Indeed, the XPS elemental analysis shows that neptunium concentration on the surface grows together with iron concentration.

The impurity groups which can participate in complex formation with neptunium ions were present on the surface of all the studied samples. Physical absorption of neptunyl ions on the surface of the studied samples can be excluded. Despite the presence of many types of functional groups on the sample surfaces, the Np4f XPS (the Np4f doublet consists of sharp peaks) allows a conclusion that neptunium is present in the form of Np(V) ions. Other valence forms of neptunium like Np(IV) and Np(VI) were absent on the surface of the studied samples. The absence of neptunium involving redox reactions on the surface of the studied samples was confirmed by the liquid-liquid extraction study.

CONCLUSIONS

The XPS study of interaction of NpO_2^+ ions in aqueous solution with minerals: two chlorite samples (Cl_3 and Cl_M), biotite (Bt) and kaolin (Ka) was carried out. It determined the elemental and ionic compositions of the surfaces of the studied samples, as well as neptunium physical and chemical states on the surface.

It was established that NpO_2^+–mineral (chlorite, biotite, kaolin) interaction in aqueous solution does not result in formation of the Np(IV) and Np(VI) containing compounds, while $Np(V)O_2^+$ compounds with oxygen bonded with iron and oxygen belonging to water and/or of carboxyl in the equatorial plane, do form.

ACKNOWLEDGEMENT

REFERENCES

[1] Sapozhnikov, Yu. A., Aliev, R. A., Kalmykov, S. N., Radioactivity of Environment (Theory and Practice) (in Russian), BINOM Laboratory of Knowledge, Moscow, 2006

[2] Romer, J., Kienzler, B., Schild, D., p *Proceedings*, 6th EC FP – FUNMIG IP Annual Workshop, Saclay, France, November 28th to December 1st, 2005, pp. 135-139

[3] Choppin, G. R., Wong, P. J., The Chemistry of Actinide Behavior in Marine Systems, *Aquatic Geochemistry, 4* (1998), 1, pp. 77-101

[4] Suzer, S., Erten, H. N., Photoelectron Spectroscopy: A Tool in Sorption Studies, *Tr. J. of Chemistry, 21* (1997), 4, pp. 409-414

[5] Lombardy, K. C., Guimaraes, J. L., Mangrich, A. S., Mattoso, N., Abbate, M., Schreiner, W. H., Wypych, F., Structural and Morphological Characterization of the PP-0559 Kaolinite from the Brazilian Amazon Region, *J. Braz. Chem. Soc., 13* (2002), 2, pp. 270-275

[6] Teterin, Yu. A., Kalmykov, S. N., Novikov, A. P., Sapozhnikov, Yu. A., Vukchevich, L., Teterin, A. Yu, Maslakov, K. I., Utkin, I. O., Hasanova, I. B., Shcherbina, N. S., X-Ray Photoelectron Spectroscopy Study of Interation of Np^{5+} with Goethite -FeOOH, *Nuclear Technology & Radiation Protection, 20* (2005), 1, pp. 38-44

[7] Teterin, A. Yu., Maslakov, K. I., Teterin, Yu. A., Kalmykov, S. N., Ivanov, K. E., Vukchevich, L., Hasanova, A. B., Shcherbina, N. S., Interaction of Neptunyl with Goethite (-FeOOH), Maghemite (-Fe$_2$O$_3$), and Hematite (-Fe$_2$O$_3$) in Water as Probed by X-Ray Photoelectron Spectroscopy, *Russian Journal of Inorganic Chemistry, 51* (2006), 12, pp. 1937-1944

[8] Morgenstern, A., Choppin, G. R., Kinetics of the Oxidation of Pu(IV) by Manganese Dioxide, *Radiochim. Acta, 90* (2002), 2, pp. 69-74

[9] Veleshko, A. N., Veleshko, I. E., Teterin, A. Yu., Maslakov, K. I., Vukčević, L., Teterin, Yu. A., Ivanov, K. E., The X-Ray Photoelectron Spectroscopy Study of Uranyl – Chitosan Interaction, *Nuclear Technology & Radiation Protection, 23* (2008), 2, pp. 43-50

[10] Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy (Eds. D. Briggs, M. P. Seah), John Wiley & Sons, Chichester, USA, 1983

[11] Scofield, H., Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV, *J. Electr. Spectr. Relat. Phenom., 8* (1976), pp. 129-137

[12] Teterin, Yu. A., Teterin, A. Yu., The Structure of X-Ray Photoelectron Spectra of Light Actinide Compounds, *Russian Chemical Reviews, 73* (2004), 6, pp. 541-580

[13] Teterin, Yu. A., Teterin, A. Yu., Structure of X-Ray Photoelectron Spectra of Lanthanide Compounds, *Russian Chemical Reviews, 71* (2002), 5, pp. 347-381

[14] Scrocco, M., Satellite Structure in the X-Ray Photoelectron Spectra of Fe(III) Halides: Evidence of Multielectron Excitation and Multiplet Structure, *Phys. Rev. B, 23* (1981), pp. 4381-4390

[15] Nefedov, V. I., X-Ray Photoelectron Spectroscopy of Chemical Compounds (In Russian), Khimiya, Moscow, 1984

[16] Fuggle, J. C., Core-Level Binding Energies in Metals, *J. Electr. Spectr. Relat. Phenom., 21* (1980), pp. 275-281

A. Yu. Teterin, *et al.*: The XPS Study of Physical and Chemical Forms of ...
Nuclear Technology & Radiation Protection: Year 2010, Vol. 25, No. 1, pp. 1-7

7

**Антон Ј. ТЕТЕРИН, Алевтина В. МИХАИЛИНА,
Константин И. МАСЛАКОВ, Јелена В. ЗАХАРОВА, Јуриј А. ТЕТЕРИН**

ПРОУЧАВАЊЕ ФИЗИЧКИХ И ХЕМИЈСКИХ ОБЛИКА НЕПТУНИЈУМОВЕ ГРУПЕ НА ПОВРШИНИ МИНЕРАЛА РЕНДГЕН-ИНДУКОВАНОМ ФОТОЕЛЕКТРОНСКОМ СПЕКТРОСКОПИЈОМ

Посматрано је сорпционо понашање физичких и хемијских облика нептунијума на површини два узорка хлоридних минерала, биотита и каолина, који имају различите садржаје Fe(II). За идентификацију валентних форми нептунијума коришћене су методе течно-течне екстракције и рендген-индуковане фотоелектронске спектроскопије. На основу добијених података извршена је квалитативна идентификација елемената који улазе у састав површина посматраних минерала, као и одређивање јонског састава формираних нептунијумових комплекса. Показано је да се не формирају једињења која садрже Np(IV) и Np(VI), док се на површинама формирају $Np(V)O_2^+$-хидроксил комплекси. Сугерисано је да су у екваторијалној равни нептунил групе NpO_2^+ присутни јони кисеоника везани са гвожђем и кисеоником који припада молекулу воде и/или карбоксилној групи.

Кључне речи: нептунил, оксидационо стање, миграција радионуклида