



Experiment title: Formation of NpO₂ and Np/PuO₂ nanoparticles under environmental conditions

Experiment number:
20-01-821

Beamline:
BM-20

Date of experiment:
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9

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Report:

²³⁷Np has a very long half-life and contributes significantly to the long-term radiotoxicity of spent fuel. Because of its long half-life, ²³⁷Np will be a major contributor to the radiation inventory of nuclear waste stored in geologic repositories after approximately 100,000 years. The Np has the tendency to show variable oxidation states under different chemical/environmental conditions. The predominance of a given oxidation state is a decisive factor for its fate in a given environmental condition. For example, under aerobic condition Np present as Np(V) (NpO₂⁺), which has a low affinity to chemical reactions, including sorption onto solid surfaces, thus have high mobility in the environment. Under reducing conditions Np(V) may transform to Np(IV) and even form NpO₂ nanoparticles as its neighbors on the Periodic table – Pu and U. The general aim of the proposal was to collect high-energy-resolution fluorescence detected (HERFD) X-ray absorption spectroscopy (HERFD) data at the Np L₃ and M₄ edges and to probe the electronic structure of neptunium nanomaterials, Np oxidation state, Np crystal structure modifications.

We have studied the behavior of Np at solid phase with HERFD at Pu M₄ and L₃ edges to investigate oxidation state and the local environment. First of all, Np(VI), Np(V), and Np(IV) references were synthesized and characterized in order to verify the oxidation states in the samples. Position and the shapes of the reference spectra are quite different (Fig.1), allowing for the difference in the oxidation state and the local environment in other samples.

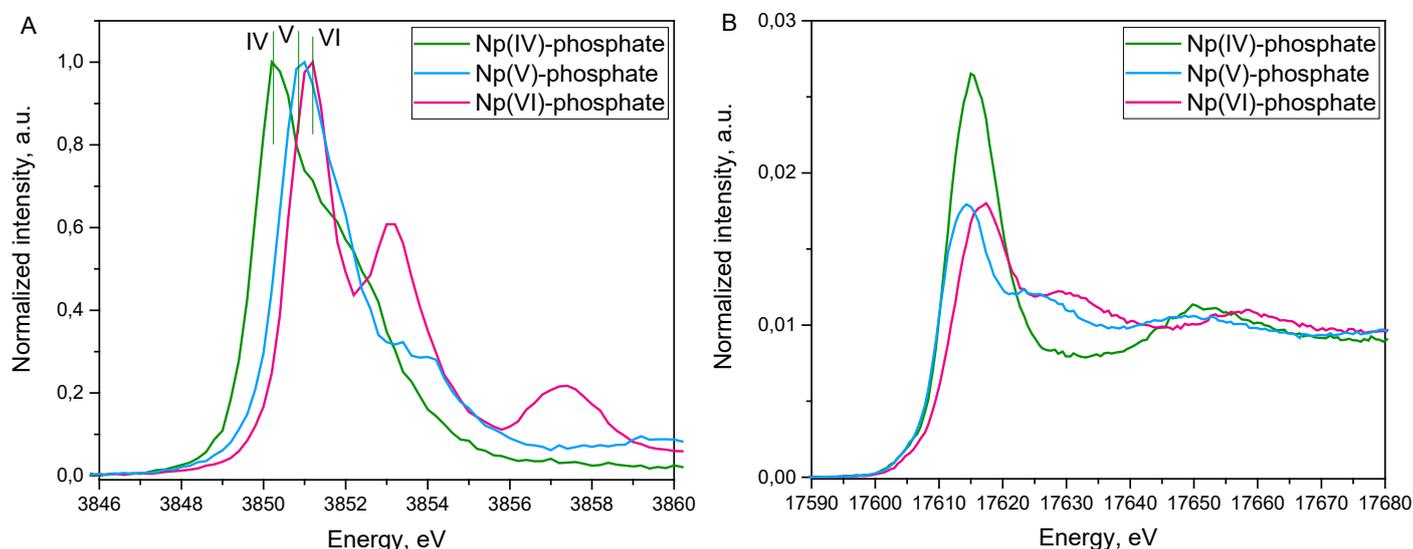


Figure 1. A – Np M₄ and B – Np L₃ HERFD spectra references of Np in different oxidation states.

For the synthesis of NpO_2 NPs procedure similar to PuO_2 that already published by our group^{1,2} was used. Np(IV) hydrolyzed at pH 8 with the formation of the precipitate that was characterized. The two samples were prepared by this method: without aging and with aging in the mother liquid for one day. The spectra of both samples show that the main oxidation state of Np is Np(V) (Fig.2A). The fresh sample has a higher percentage of Np(IV) .

To stabilize Np(IV) in the NpO_2 colloids, another sample was prepared by mixing Np(V) solution with Fe(II) at neutral pH. The spectrum shows the higher percentage of Np(IV) in this case while Np(V) is still visible.

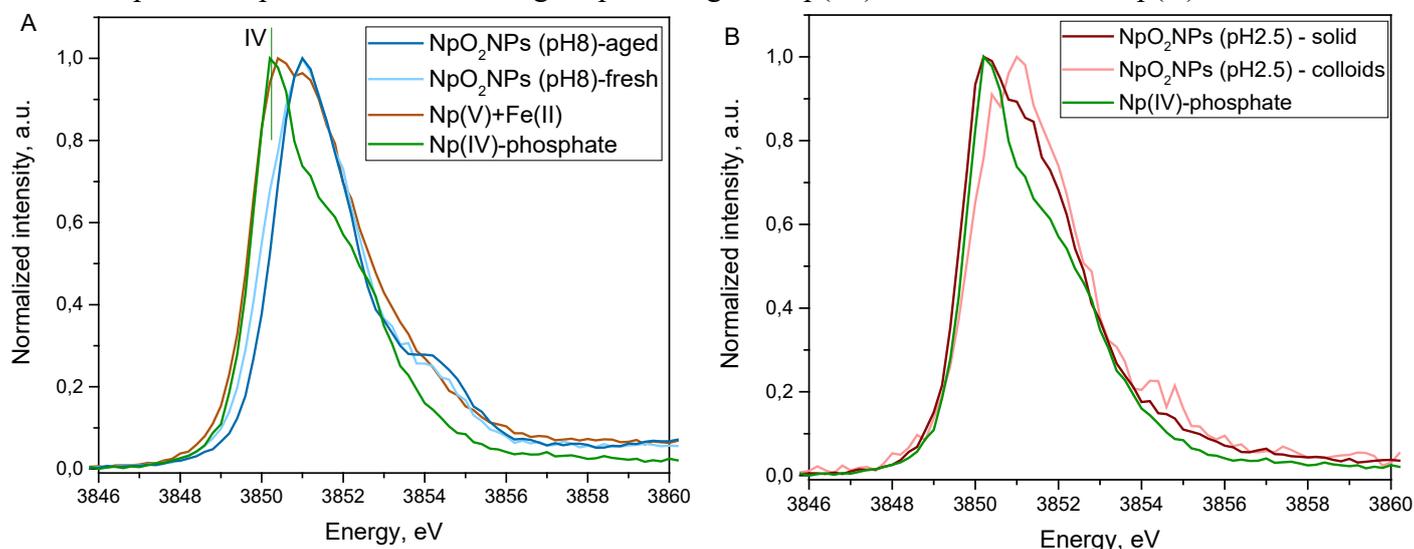


Figure 2. Np M_4 HERFD spectra of NpO_2 NPs prepared A – at pH 8 and B – at pH 2.5.

The stable colloid suspension of NpO_2 NPs was prepared from Np(IV) solution at pH 2.5. The spectra of both – colloids and solid part from them were measured during the beamtime. It is clearly seen the spectrum of solid from these colloids demonstrate the highest content of Np(IV) in the series of NpO_2 NPs samples. The colloids at pH 2.5 contained both Np(V) and Np(IV) which is caused by oxidative dissolution of NpO_2 NPs at low pH values.

These findings have been used in the preparation of the manuscript.

Literature

- (1) Gerber, E.; Romanchuk, A. Y.; Pidchenko, I.; Amidani, L.; Rossberg, A.; Hennig, C.; Vaughan, G. B. M.; Trigub, A.; Egorova, T.; Bauters, S.; Kalmykov, S. N.; Kvashnina, K. O. The Missing Pieces of the PuO_2 Nanoparticle Puzzle. *Nanoscale* **2020**, *12* (35), 18039–18048. <https://doi.org/10.1039/d0nr03767b>.
- (2) Kvashnina, K.; Romanchuk, A.; Pidchenko, I.; Gerber, E.; Trigub, A.; Rossberg, A.; Weiss, S.; Popa, K.; Walter, O.; Caciuffo, R.; Scheinost, A.; Butorin, S.; Kalmykov, S. A Novel Meta-Stable Pentavalent Plutonium Solid Phase on the Pathway from Aqueous Pu(VI) to PuO_2 Nanoparticles. *Angew. Chem. Int. Ed.* **2019**, *58*, 17558–17562. <https://doi.org/10.1002/anie.201911637>.