

# Np M<sub>5</sub>-edge HR-XANES and L<sub>3</sub>-edge EXAFS spectroscopy on illite samples with 20 - 140 ppm Np

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A deep geological disposal with a multi-barrier system is proposed, to safely isolate the high-level radioactive waste from the biosphere. Clays are considered as potential host rock and as potential backfill material. This study is focused on understanding the interaction between illite, a clay mineral present in several clay host rocks, and Np-237, a radionuclide presenting a considerable fraction in high-level waste. Np is a redox-sensitive element with pentavalent Np being stable in oxidizing to redox-neutral environment and tetravalent Np prevailing under reducing conditions. To understand the mechanism of Np retention, it is necessary to understand the sorption but also the migration behaviour.

This investigation probes the redox-species and the atomic environment of Np sorbed onto illite for samples from batch sorption and diffusion experiments applying different spectroscopic and microscopic techniques (Np M<sub>5</sub>-edge high-energy resolution X-ray absorption near edge structure (HR-XANES) [1], Np L<sub>3</sub>-edge extended X-ray absorption fine structure (EXAFS), Fe K-edge XANES, and Mössbauer spectroscopy as well as scanning electron (SEM), transmission electron (TEM), and fluorescence microscopy).[2]

This is the first Np M<sub>5</sub>-edge HR-XANES study where it was possible to record conclusively spectra at very low Np loadings of  $(18 \pm 6)$  ppm due to an optimised set-up and sample preparation. It was conducted at the CAT-ACT beamline for catalysis and actinide science at the Karlsruhe research accelerator (KARA) at KIT, Karlsruhe [3]. Np L<sub>3</sub>-edge XANES and Np M<sub>5</sub>-edge HR-XANES spectra strongly suggest the presence of Np(IV) and Np(V) in both the dispersed illite sorption samples kept under anaerobic conditions but also in segments taken from the diffusion experiments carried out under an aerobic atmosphere. These results are corroborated by the results of solvent extraction according to the method of Bertrand and Chopin (1982) [4]. EXAFS analyses of illite sorption samples prepared at pH 9 confirm the presence of solely sorbed mononuclear Np species and a Np-O-Fe coordination at  $(3.44 \pm 0.02)$  Å. Fe K-edge XANES and Mössbauer spectroscopy found Fe(III) and Fe(II) in the structure of illite. Results obtained by SEM, TEM, and fluorescence microscopy studies exclude the presence of amorphous Fe phases and microorganisms as possible reductants. The observation of a partial reduction of Np(V) and the finding that Np is coordinated to Fe-OH groups points to a partial reduction through electron transfer from structural Fe(II) in the illite.

The present study demonstrates that by the complementary application of advanced spectroscopic methods, mechanistic insight into complex geochemical actinide reactions can be achieved at even low concentrations.

*Acknowledgements: The authors are grateful for SEM (Dr. Dieter Schild, KIT-INE), TEM measurements (Dr. Oliver Dieste, Joint Research Center Karlsruhe, Germany) and Mössbauer spectroscopy (Prof. Dr. Zara Cherkezova-Zheleva, Institute of Catalysis, Bulgarian Academy of Sciences). The authors would like to thank Dr. Jörg Göttlicher (KIT, Institute for Photon Science and Synchrotron Radiation) for the help with Fe-XAS experiments and Sabrina Gfrerer (KIT, Institute for Applied Microbiology) for the help with the fluorescence microscopy. We thank the Institute for Beam Physics and Technology (IBPT), KIT for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).*

## References

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