

Spectroscopic identification of Np(V) sorption complexes on birnessite

KATHARINA MÜLLER*¹, BÉNÉDICTE SIMON^{1,2}, FRANK BOK¹, ANDRÉ ROSSBERG¹

- ¹ Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Dresden, Germany
 - ² National Graduate School of Chemistry, Paris, France
- (*correspondence: k.mueller@hzdr.de)

Mn oxide minerals are ubiquitous in soils and sediments and participate in a variety of chemical reactions that affect groundwater and bulk soil composition. Even at tracer concentrations they play a decisive role in regulating the mobility of contaminants due to their high sorption and redox capacity and scavenging capability [1]. Due to its long half-life and its toxicity, Np-237 is considered as a major contaminant of the ecosystem in the long-term safety assessment of nuclear waste repositories. The pentavalent state is environmentally most relevant [2].

In this work, Np(V) sorption on amorphous birnessite (Bs) is investigated using a combination of ATR FT-IR and EXAFS spectroscopy on a molecular level with thermodynamic modelling of batch sorption studies.

For the first time, in-situ Np(V) sorption is comparatively studied on the oxyhydroxides of Fe and Mn by ATR FT-IR spectroscopy under a variety of environmentally relevant sorption conditions, e.g. micromolar Np concentrations, low acidic to neutral pH, moderate ionic strength [3]. From the results, the formation of single inner-sphere complexes can be derived. In addition, time resolved spectra provide kinetic information on the surface reactions. Complementary EXAFS measurements evidence mononuclear bidentate edge-sharing Np(V) complexes on the Bs surface.

- [1] Post, J. E. (1999) *Proc. Natl. Acad. Sci. U. S. A.* **96**, 3447-3454.
- [2] Kaszuba, J. P. et al. (1999) *Environ. Sci. Technol.* **33**, 4427-4433.
- [3] Müller, K. et al. (2015) *Environ. Sci. Technol.* **49**, 2560-2567.