

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Comparative investigation of the neptunium complexation onto gibbsite by means of FT-IR and EXAFS spectroscopy	Experiment number: 20-01-715
Beamline: BM20	Date of experiment: from: 21. July 2012 to: 24. July 2012	Date of report: 21.01.2013
Shifts: 9	Local contact(s): André Rossberg	<i>Received at ESRF:</i>

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Report:

The molecular reactions of actinides at the solid-water interface play an important role in the retardation of radionuclide migration in the environment. In recent years, the sorption behavior of neptunium (Np) onto synthetic and naturally occurring minerals was insufficiently studied. The majority of these studies provide macroscopic results presenting sorption capacities of the substrates and the effect of selective parameters on the sorption behaviour. However, for a better understanding of the sorption mechanisms, structural information on a molecular level of the type of surface complex is still needed.

Recently, comprehensive studies using ATR FT-IR spectroscopy have been carried out to investigate *in situ* the formation of neptunyl(V) surface complexes on aluminium hydroxide, namely gibbsite. This substrate serves as model for more complex mineral systems, e.g. clay minerals. To characterize the surface complex on amorphous and crystalline gibbsite in more detail, a multiplicity of online monitored experiments were performed in the presence and absence of atmospheric carbonate in order to illustrate the impact of carbonate ions on the sorption processes. In the absence of carbonate, only one inner-sphere complex is formed on amorphous and crystalline gibbsite. In the presence of carbonate and dependent on the crystal structure, different surface species (inner-sphere and ternary) were derived from the spectra.

The formation of different bound species as a function of carbonate concentration has been reported from other metal oxide surfaces, in particular for iron minerals investigated by batch experiments, ATR FT-IR and EXAFS spectroscopy [1-4]. Because the FT-IR spectroscopic data obtained do not provide clear evidence for the formation of ternary NpO_2^+ -carbonate complexes, further structural information is required.

A series of batch sorption samples of Np(V) onto amorphous and crystalline $\text{Al}(\text{OH})_3$ was prepared in presence and absence of atmospheric carbonate, showing different degree of Np(V) loading. These samples were expected to reflect the different stages of the sorption processes in analogy to the IR spectra recorded *in situ*.

Results.

Due to very low Np concentrations and contamination with Zr, which adsorption edge is close to the one of Np, an interpretation and analysis of the EXAFS results are difficult. But first fits strengthen the suggestion of formation of different inner-sphere surface complexes of Np(V) onto gibbsite dependent on the absence or presents of carbonate. No influence of the cristallinity of the gibbsite sample can be observed with EXAFS spectroscopy. The formation of ternary Np(V)-carbonato complexes on gibbsite can be proposed from the IR and EXAFS results. Further IR as well as EXAFS experiments needs to be done to verify these findings.

References

1. Müller, K., et al., *Sorption of Np(V) onto TiO₂, SiO₂, and ZnO: an in situ ATR FT-IR spectroscopic study*. Environmental Science & Technology, 2009. **43**(20): p. 7665-7670.
2. Combes, J.M., et al., *EXAFS spectroscopic study of neptunium(V) sorption at the alpha-FeOOH water interface*. Environmental Science & Technology, 1992. **26**(2): p. 376-382.
3. Arai, Y., et al., *In situ spectroscopic evidence for neptunium(V)-carbonate inner-sphere and outer-sphere ternary surface complexes on hematite surfaces*. Environmental Science & Technology, 2007. **41**(11): p. 3940-3944.
4. Wu, T., S. Amayri, and T. Reich, *Neptunium(V) sorption onto gibbsite*. Radiochimica Acta, 2009. **97**(2): p. 99-103.