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Experiment Report Form

ESRF	**Experiment title:** Technetium interaction with redox-sensitive minerals	**Experiment number**: EV 376
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Report:

Technetium-99 (Tc^{99}) is a fission product of U^{235} and Pu^{239} that possesses environmental concern because of its long half-life ($2.14\cdot10^5$ years) and the high mobility of the anion pertechnetate ($Tc(VII)O_4^-$).[1]
However, Tc migration can be mitigated when Tc(VII) is reduced to Tc(IV). This scavenging step is carried out by reducing agents, such as as S(-II), Sn(II) and Fe(II).[2]

During the measurement campaign we analysed three solids able to reduce aqueous Tc(VII): i) green rust (a Fe(II) and Fe(III) mixed hydroxide), ii) Sn(II) sorbed on alumina nanoparticles, and iii) S(-II) sorbed on alumina nanoparticles. Samples prepared under different pH and Tc loading conditions were evaluated with the aim of determining the oxidation state and the molecular environment of Tc in the solid. This information is crucial for safety assessment within nuclear waste management.

X-ray absorption spectroscopy was used to measure the samples at ESRF. The Tc K-Edge (21,044 eV) spectra were collected in fluorescence mode. Likewise, Sn K-edge (29,200 eV) spectra were collected for the Sn-containing samples. The samples were cooled down with a He-Ne cryostat at 15 K while the measurements were performed. In total, 16 samples were measured at the Tc K-edge, and 7 samples at the Sn K-Edge.

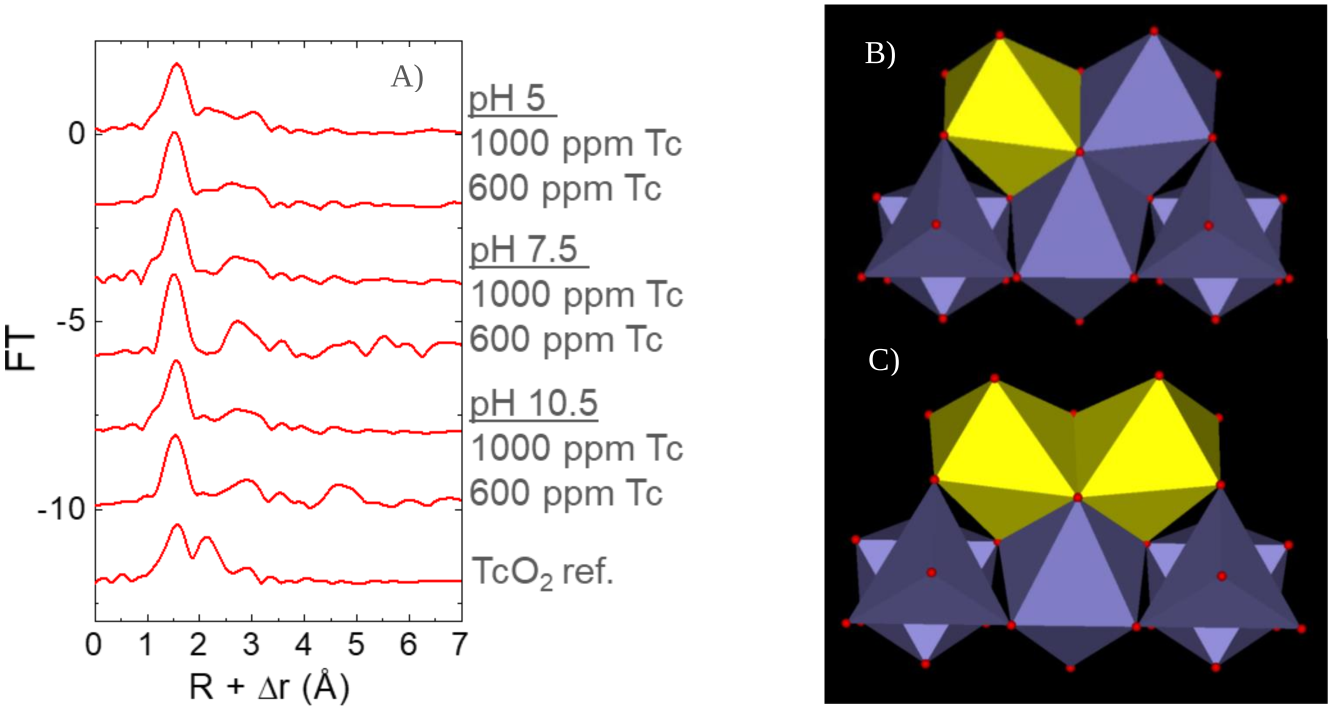

Figure 1. A) Fourier transforms (FT) of the Tc K-edge EXAFS spectra of Tc retained on green rust for different Tc loadings and pH values. Tc(IV) molecular environments that theoretically fit the two components responsible of the Tc EXAFS spectra: B) Tc(IV) edge&corner sharing surface complexation on ferrrihydrite and C) Tc(IV)-Tc(IV) chains edge&corner sharing surface complexation on an iron oxide model.

The XANES spectra of all measured samples show that Tc is present as Tc(IV) (results not shown), which supports Tc reductive immobilization as the main Tc retention mechanism. However, the molecular environement of Tc with the various solids is very diverse, leading to different EXAFS spectra.

For sake of brevety, this report focus on the results obtained for green rust containing Tc (Figure 1).

It is observed that the obtained EXAFS spectra of Tc in contact with green rust have different shape depending on the pH and Tc loading (Figure 1A). The experimental EXAFS can not be solely explained by the presence of TcO_2, however, the presence of a feature at around 2.1 Å indicates the existance of Tc-Tc interaction. Preliminary fits of the EXAFS spectra suggest the presence of two main components. Those components can be theoretically well reproduced by two Tc(IV) surface complexes on an iron oxide model (based on tethraedra and octahedra iron goemetries): A Tc(IV) edge&corner sharing (ECS) complex (Figure 1B), and a Tc(IV) dimeric edge&corner sharing (DES) complex (Figure 1C). Note that also other structural arrangements could be possible for the ECS and DES complex if the measured distances would meet 2xFe @3.09 Å, 2xFe @ 3.52 Å and 1xTc @ 2.55 Å, 1xFe @ 3.08 Å, 2xFe @ 3.52 Å, respectively. The structures here reported differ of those recently proposed for a Fe(II)-Al(III) layered double hydroxide: Tc(IV) monodentate surface complexation on and incorporation in hematite.[3]

Up to date, only one work reported few XAS data on the interaction of Tc with green rust, unfortunately no interpretation of the molecular structure of Tc(IV) in the solid was performed.[4] Thus, this ongoing work is of great relevance as we will be able to provide new insights on forming Tc speciaies at a molecular level.

References

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