

  ROBL-CRG	Experiment title: Structural characterization of Tc(IV) sorption complexes on nanocrystalline iron phases in 0.1 M NaCl solution	Experiment number: 20-01-712
Beamline: BM 20	Date of experiment: from: 23.07. 2011 to: 27.07.2011	Date of report: 12.03.2012
Shifts: 12	Local contact(s): Dr. SCHEINOST, Andreas	<i>Received at ROBL:</i>
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Report:

For the safety assessment for nuclear waste disposal, it is necessary to predict the chemical behaviour of ⁹⁹Technetium (Tc-99) under relevant geochemical conditions. Hence, the Tc redox behaviour needs to be understood. In the present study, we focus on the redox transformation of Tc(VII)/Tc(IV) in the presence of iron minerals. The pH, E_h, and Tc concentration were measured, and Tc sorbed on the solids analyzed by XANES and EXAFS.

Magnetite (Fe₃O₄), mackinawite (FeS), siderite (FeCO₃), goethite (α-FeOOH), and hematite (Fe₂O₃) were synthesized following [1], and the products confirmed by XRD. Small aliquots of Tc-99 stock solution were added to the Fe mineral suspensions to obtain 2×10⁻⁵ M initial TcO₄⁻ concentration (0.1 M NaCl). Samples were kept in an Ar glove box for several weeks at KIT-INE. Hydrogen ion concentration (pH_c), redox potential (E_h) and Tc concentration after ultrafiltration (10 kD) was determined. The solid phases were then separated by centrifugation and frozen in liquid nitrogen to avoid the oxidation state change during the transport and measurement. XANES and EXAFS spectra of the solids were acquired in fluorescence mode at the Tc-K edge (21,044 eV) at the Rossendorf Beamline (ROBL).

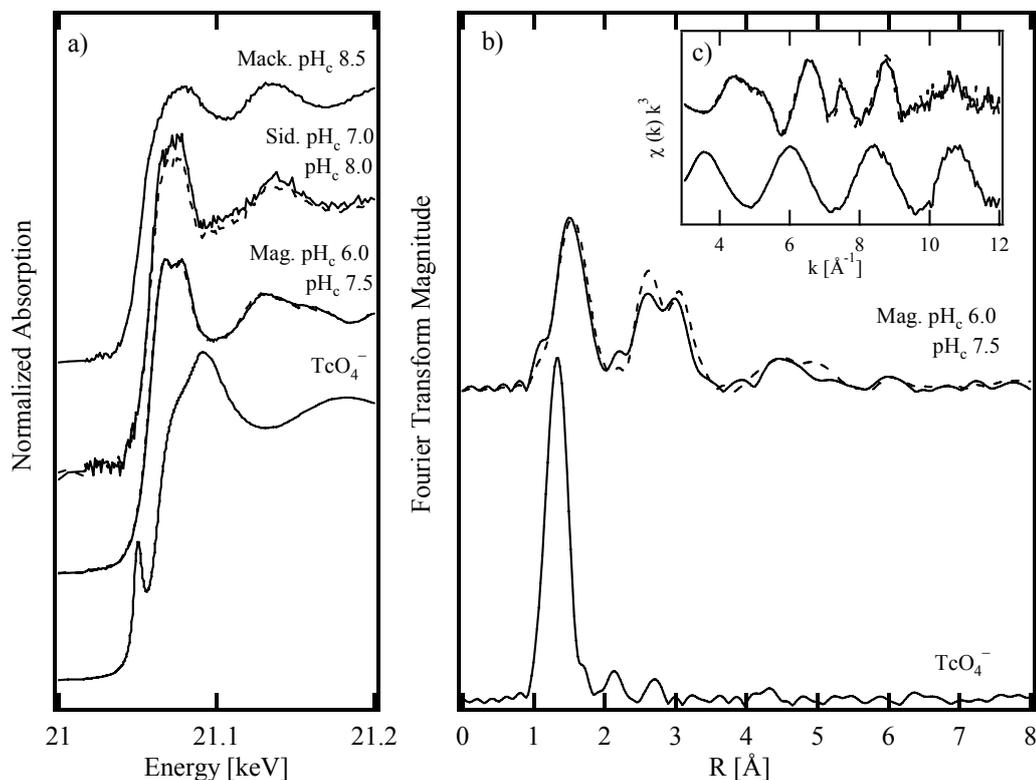


Fig. 1:
 (a) Tc-K edge XANES spectra,
 (b) EXAFS Fourier transforms and
 (c) corresponding EXAFS spectra for the two magnetite samples and TcO₄⁻ [2].

In the samples with goethite and hematite, no signal for Tc-99 was obtained in XAS measurement, indicating no reduction of initial TcO₄⁻. On the other hand, XANES spectra for magnetite, mackinawite, and siderite suspensions under neutral pH_c condition, indicate a Tc oxidation state of +IV. (Figure 1a). The k³-weighted EXAFS spectrum and Fourier Transforms for magnetite samples at pH_c 6.0 and 7.5 are presented in Fig. 1b. The EXAFS spectra of both magnetite samples are very similar, with a strong FT peak at about 1.5 Å followed by a double peak centered at 3 Å (values not corrected for phase shift). The first peak represents backscattering of the coordinating oxygen atoms. The shell fit provided a coordination number (CN) of 6 and a distance of 2.02±0.01 Å, in line with an octahedral oxygen coordination of Tc(IV). The corresponding coordination numbers could be fixed to a magnetite-like environment, i.e. 6 Fe neighbors in edge-sharing linkage and 6 Fe neighbors in corner-sharing linkage, suggesting Tc-for-Fe substitution in magnetite. For siderite samples, the signal intensity was not enough to fit any results, and for mackinawite samples, the signal intensity was also very weak. The observed oxidation state distribution of Tc is in good agreement with the thermodynamical predictions and corresponding E_h-pH diagram.

References

- [1] Kirsch, R. et al., Environ. Sci. Technol. **45**,7267 (2011).
- [2] Saeki, M. et al., Inorg. Chem. 2012, submitted.