

Biogeochemical Coupling of Fe and Tc Speciation in Subsurface Sediments: Implications to Long-Term Tc Immobilization

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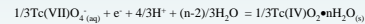
Office of Biological and Environmental Research
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BACKGROUND

⁹⁹Tc is a long-lived ($t^{1/2} = 2.13 \times 10^5$ y) fission product unique to nuclear production and/or reprocessing sites. It exists as an important subsurface contaminant at numerous U.S. DOE sites.

- ORNL/FRC
- Hanford, Paducah, and others

⁹⁹Tc migrates rapidly with vadose zone water and groundwater as the mobile $\text{Tc(VII)}_2\text{O}_7$ anion. It is weakly sorbed under most geochemical conditions. The electrode potential (E°) if the Tc(IV)-Tc(VII) couple ranges between 0.246-0.262 V depending on the crystallinity and hydration (n) of the Tc(IV) oxide:



While the half-cell potential of the Fe(II)/Fe(III) reaction at circumneutral pH is favorable for Tc(VII) reduction over a broad concentration range of reactants, the homogeneous reduction kinetics appear quite slow.

At DOE's Hanford site, four large ⁹⁹Tc groundwater plumes exist and new ones are forming as ⁹⁹Tc released to cribs and leaked from single-shell high-level waste tanks migrates through the vadose zone. Over 40 Ci of $\text{Tc(VII)}_2\text{O}_7$ are forecast to discharge to the Columbia River in future years, making it one of the sites major risk driving contaminants.

Generic scientific questions exist on the redox stability of Tc(VII) in microaerophilic groundwaters and remedial strategies are sought to prevent ⁹⁹Tc migration into sensitive receiving waters such as the Columbia River at Hanford. Techniques under consideration are selective sorbents or reductive barriers allowing capture and removal of mobile Tc(VII) from groundwater.

OBJECTIVES

The overall project has been investigating the reactivity of pertechnetate [Tc(VII)] with Fe(II) forms in model mineral and mineral-microbe systems, and with sediments from the Oak Ridge FRC and the Hanford site. Past project results with Hanford and Oak Ridge sediments have been published in Fredrickson et al., (2004) and Kukkadapu et al., (2006). This poster summarizes a series of model system experiments that investigates whether microbes or biogenic Fe(II) were more important in the reduction of Tc(VII) in an anoxic suspension of ferrihydrite, *Shewanella oneidensis* MR-1, Tc(VII) , and electron donor. Ferrihydrite is used to represent a bioavailable Fe(III) oxide present in small amounts in Oak Ridge and Hanford sediments.

In order to address this overall goal, Tc(VII) reduction rates and redox products were studied in less complex systems where individual abiotic and biotic reactions were isolated for rigorous characterization. The specific objectives of the individual experiments in the series were as follows:

- 1) Identify the rates and products of the reaction of Tc(VII) with aqueous Fe(II) at circumneutral pH values (homogeneous reduction).
- 2) Identify the rates and products of the reaction of Tc(VII) with surface complexed Fe(II) on goethite and hematite in the circumneutral pH range (heterogeneous reduction).
- 3) Identify the rates and products of the reaction of Tc(VII) with MR-1 under anoxic conditions individually with hydrogen and lactate as electron donors (biologic reduction).
- 4) Use insights from the above experiments to determine which of the three above, potentially parallel reactions determine the final speciation of Tc in a mixture of ferrihydrite, respiring MR-1, and Tc(VII) .

METHODS

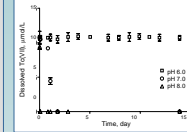
- Under strictly anoxic conditions (i.e., $< 7.5 \times 10^{-9}$ atm O_2), pertechnetate [$\text{Tc(VII)}_2\text{O}_7$] was reacted with aqueous Fe(II) at pH > 6, adsorbed Fe(II) on goethite and hematite, MR-1 (pH 7), and mineral-microbe mixtures (ferrihydrite, MR-1, Tc and electron donor) to gain insights on the reactivities of various Fe(II) -species (and MR-1), and the nature of Tc(IV) products.
- $\text{Tc(IV)}_2\text{O}_7 \cdot n\text{H}_2\text{O}$ was prepared by the reduction of Tc(VII) to Tc(IV) using sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$) inside a controlled atmospheric chamber [Hess et al. (2004), *J. Sol. Chem.* 33, 199].
- Ferrihydrite samples were incubated (MR-1: 1×10^6 cells/mL) under non-growth conditions in presence of Tc(VII) or Tc(IV) with lactate or hydrogen.
- ⁵⁷Fe-Mössbauer spectroscopy, transmission electron microscopy (TEM)-selected area electron diffraction (SAED)-energy dispersive X-ray analysis (EDS), Fe- and Tc-XAS analysis, and wet-chemical extractions were employed to characterize the reduced/biotransformed products.
- Mössbauer measurements were performed with isotopically enriched Fe(III) source containing 96.7% ⁵⁷Fe, the Mössbauer active Fe isotope. This allowed measurements on small amounts of sample (< 10 mg).
- Sputtered gold was employed as standard to interpret electron diffraction patterns.
- Fe and Tc EXAFS and XANES analyses were performed at Advanced Photon Source (APS) sector 20 beam lines, 20-ID and 20-BM. The IFEFFIT and ARTEMIS programs were used for spectral interpretation and fitting.

IS Tc(VII) REACTIVE WITH AQUEOUS Fe(II) ?

Wet Chemical Reaction Kinetics

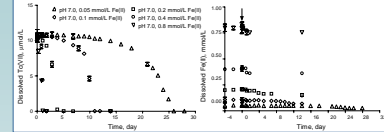
Reduction of soluble Tc(VII) by aqueous Fe(II) in pH 6-8 solutions was investigated under strictly anoxic conditions using an oxygen trap.

Effect of pH on Tc(VII):Fe(II) Rxn



Complete and rapid reduction of Tc(VII) to Tc(IV) occurred at pH 7 and pH 8 samples. No significant reduction occurred at pH 6.

Effect of Fe(II) Concentration on Rxn with Tc(VII) at pH=7

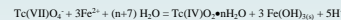


The reduction rate increased with Fe(II) concentration. Tc(VII) reduction was a combination of homogeneous and heterogeneous reaction, and the latter was more rapid. The homogeneous reduction rate correlated with the concentration of Fe(OH)_2^+ and $\text{Fe(OH)}_2^{\text{aq}}$.

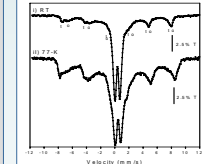
Solution analysis indicated that excess Fe(II) associated with the solid phase redox product.

Nature of the Redox Products

The redox products were ferrihydrite, chemically homogeneous coprecipitates with 13-15% Tc(IV) . The Fe:Tc ratio of ~5.9-6.5 was higher than expected given the idealized redox reaction:



Mössbauer (pH 8)



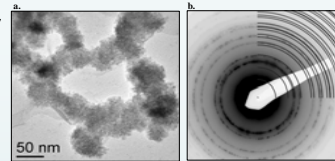
Mössbauer spectra revealed presence of ferrihydrite (central doublet) and magnetite (sextets, indicated by τ (tetrahedral sites) and σ (octahedral sites)). Spectra of the pH 7 and pH 8 samples were similar to each other.

The apparent Mössbauer parameters of the central doublet were in agreement with ferrihydrite, small particle goethite (<5-nm), and magnetite (<5-nm).

The persistent doublet at 77-K was not due to magnetite.

Similar Mössbauer spectra were reported [Jolivet et al. (1992), *Clays Clay Miner.* 40, 531] for a Fe(II) -induced transformation product of ferrihydrite with a) nascent spinel structure, b) poor long range order, and c) tetrahedral site vacancies.

TEM-SAED

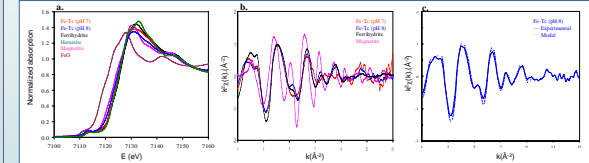


TEM of the pH 7 and 8 coprecipitates were similar, consisting of 30-50 nm particle aggregates (a). The individual aggregates were comprised of tightly packed 5-10 nm crystallites that exhibited distinct lattice fringes.

The precipitates exhibited homogeneous Tc spatial distributions (>100 nm to <5 nm).

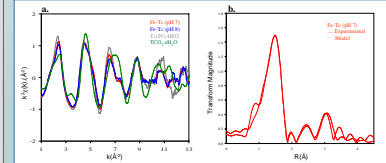
SAED measurements indicated the presence of poorly crystalline (~75%) and crystalline (~25%) phases. The ring pattern of the crystalline materials (b) was similar to magnetite.

Fe-XANES and -EXAFS



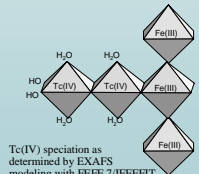
a.) Fe-XANES measurements of the pH 7 and pH 8 coprecipitates were similar, and each contained Fe(II) and Fe(III) . The pre-edge feature at 7113 eV indicated some tetrahedral Fe(II) (magnetite) was present. b.) EXAFS measurements showed that the bonding environment was different from pure magnetite or ferrihydrite, and c.) XANES and EXAFS spectra were well fit as a mixture of Fe(II) -rich ferrihydrite with minor magnetite.

Tc-EXAFS



Tc-XANES (not shown) indicated only Tc(IV) was present.

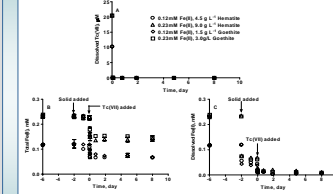
a.) Tc-EXAFS of the pH 7 and pH 8 coprecipitates were similar, but different from $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. b.) A structural model was developed for ferrihydrite, into which various structural motifs of Tc(IV) were embedded. The model that gave the best fit to the experimental data is shown to the right.



Tc(IV) speciation as determined by EXAFS modeling with FEFF 7/IFEFFIT was most consistent with a Tc(IV) octahedral dimer complexed in edge-sharing mode to an octahedral surface or structural defect site in ferrihydrite.

IS ADSORBED Fe(II) MORE REACTIVE TOWARDS Tc(VII) THAN AQUEOUS Fe(II) ?

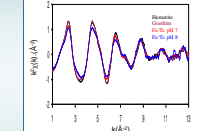
Chemical Data



The reaction of Tc(VII) with Fe(II) adsorbed on goethite and hematite was investigated at pH 7.

The heterogeneous reduction rate is almost instantaneous. Other experiments show the reaction slows at lower pH. Excess Fe(II) is sorbed during the surface redox reaction.

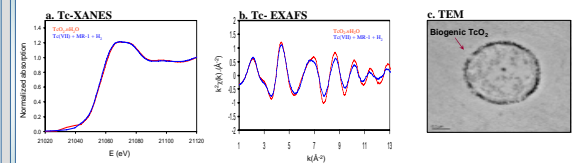
Tc-EXAFS



The Tc(IV) product on the surfaces of goethite and hematite was identical to the pH 7 and 8 coprecipitates obtained by the reaction of Tc(VII) with aqueous Fe(II) .

WHAT IS THE FUNCTIONAL REDUCTANT IN MINERAL-MICROBE MIXTURES [Fe(II) OR DMRB]?

Biotic Reduction of Tc(VII) by MR-1



Reduction of Tc(VII) was investigated with MR-1 in the presence of electron donor (H_2 and lactate). The reduction rate is much slower with lactate as electron donor.

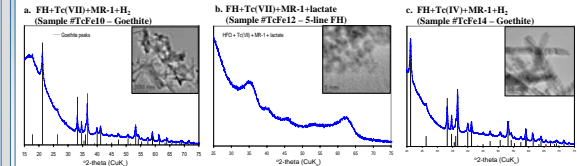
Tc-XANES and -EXAFS (a and b) of the biogenic Tc(IV) were identical to abiotic $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.

Biogenic $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ precipitates within the periplasm and on the surfaces of MR-1(c).

MINERAL-MICROBE MIXTURE

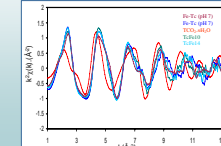
Hypothesis: Tc(IV) in a $\text{Fe(III)-Oxide/DMRB}$ Mixture = Biogenic $\text{TcO}_2 \cdot n\text{H}_2\text{O}$?

XRD and TEM



Mixtures containing ferrihydrite (FH), Tc(VII) or Tc(IV) , and electron donor (lactate or hydrogen) were incubated with MR-1 to yield different biotransformation products (5-line FH and goethite). Chemical data indicated that the samples contained ~1% Tc and 5-10% of sorbed Fe(II) .

Tc-EXAFS



The biogenic Tc(IV) product was similar in all the products. The EXAFS spectra were significantly different from $\text{TcO}_2 \cdot n\text{H}_2\text{O}$. The product was same as that observed for the reaction of Tc(VII) with aqueous Fe(II) (left panels), Tc(VII) with adsorbed Fe(II) on the surfaces of goethite and hematite (above), and a Tc(IV) -ferrihydrite coprecipitate. A heterogeneous reduction mechanism is implied.

CONCLUSIONS

- Aqueous Fe(II) was reactive with Tc(VII) at pH > 6.0. The joint homogeneous/heterogeneous precipitate was poorly ordered and chemically homogeneous. Spectroscopy indicated that the solid was Fe(II) ferrihydrite (with some minor magnetite) containing surface- or vacancy-bound $\text{Tc(IV)}_2\text{O}_7$ octahedral dimers.
- Adsorbed Fe(II) on goethite and hematite rapidly reduced Tc(VII) to Tc(IV) . Excess Fe(II) was sorbed during the redox reaction to create a Fe(II) -enriched ferrihydrite surface phase. The Fe:Tc surface product was same as that resulting from the reaction of Tc(VII) with aqueous Fe(II) .
- The Tc(IV) -product in the MR-1 and Tc(VII) reaction mixture was $\text{TcO}_2 \cdot n\text{H}_2\text{O}$.
- The Tc -product in the mineral-microbe mixtures was the same as that observed for the reaction of Tc(VII) with aqueous and sorbed Fe(II) . This and absence of $\text{TcO}_2 \cdot n\text{H}_2\text{O}$ features in the Tc-EXAFS spectra implied that biogenic Fe(II) (most likely surface complexed) but not MR-1 was the functional Tc(IV) reductant.