

Biogeochemistry of Fe and Tc Reduction and Oxidation in FRC Sediment

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Natural and Accelerated Bioremediation Research (NABIR) Program

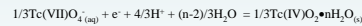
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BACKGROUND

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 Tc(VI)O_4^- anion. It is weakly sorbed under most geochemical conditions. The electrode potential (E^0) of 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 Tc(VI)O_4^- are forecast to discharge to the Columbia River in future years, making it one of the sites major risk driving contaminants.

Remedial strategies are critically sought to prevent ⁹⁹Tc migration into sensitive receiving waters such as the Columbia River at Hanford. Techniques under consideration include getters or highly selective sorbents, or the placement of reductive barriers allowing capture and removal of mobile Tc(VII) from groundwater.

OBJECTIVES

- To rigorously characterize the distribution of Fe(II) and Fe(III) in FRC sediment.
- To identify changes to Fe(II)/Fe(III) distribution and concentration resulting from DIRB activity.
- To determine the dependence of Tc(VII) reduction rate on biogenic Fe(II) and its forms.
- To establish tendency of Tc(IV) and biogenic Fe(II) to oxidize and their effects on Tc immobilization.

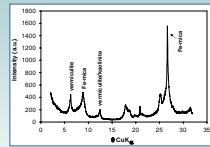
METHODS

The mineralogical and chemical properties of the pristine, bioreduced, and chemically extracted FRC sediments were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), X-ray microscopy (XRM), at the PNC-CAT beamline at APS, Mössbauer spectroscopy, and scanning and transmission electron microscopy with lattice fringe imaging. Chemical extraction included dithionite-citrate-bicarbonate (DCB), acid ammonium oxalate (AAO), and hydroxylamine hydrochloride (HAH).

The FRC sediment was incubated under anoxic conditions with the facultative dissimilatory metal-reducing bacterium *Sewanella putrefaciens*, strain CN32 in defined aqueous solutions/media with bicarbonate and PIPES buffers for time periods exceeding 75 d. Lactate was used as the electron donor. Aqueous and sorbed Fe(II) (ferrozine assay and 0.5 N HCl extraction) and Mn(II) (ICP-MS and 10 mM CuSO_4 extraction), and pH were monitored to define the reduction progress and extent. The bioreduced materials were characterized using the above-mentioned techniques.

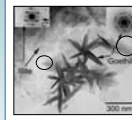
Bioreduced (pasteurized) sediment or chemically extracted/reduced sediment spiked with Fe(II) was washed with a PIPES buffer/electrolyte solution, and spiked with NaTc(VII)O_4 to yield a concentration of 20 μM . The Tc(VII) -spiked samples were agitated and equilibrated at 25°C and sampled over time to assess the Tc(VII) reduction rate. Selected sediment samples containing 20 μM of reduced Tc(IV) were subjected to oxidation by: 1.) successive headspace replacements of air, and 2.) open system equilibration with air. Removed aqueous samples were filtered (< 2 μm) and counted to determine the Tc(VII) concentration. Thin sections of the bioreduced/chemically reduced Tc(VII) reacted/oxidized sediments were analyzed by backscattered electron microscopy and X-ray microspectroscopy.

PRISTINE FRC SEDIMENT



➤ X-ray diffraction demonstrates the presence of vermiculite, Fe-mica, and kaolinite in the phyllosilicate fraction.

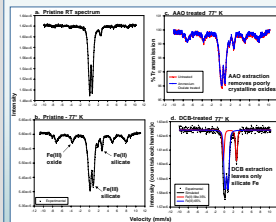
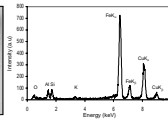
TEM



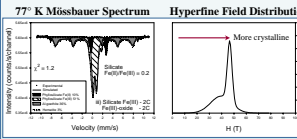
➤ Fe(III) oxides exist in the FRC background sediment as 200-300 nm aggregates of small acicular crystallites (left).

➤ Analyses of many individual goethite crystallites showed limited Al substitution (right).

EDS pattern



➤ Mössbauer spectra measured on chemically extracted sediments indicated the presence of three Fe phases: small particle size Fe(II) oxide, and silicate Fe(II) and Fe(III) .



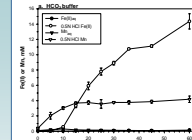
➤ The 77 K Mössbauer spectrum was modeled with a component additivity approach using the RECOIL program.

➤ Most of the Fe was associated with phyllosilicates (61%, vermiculite/illite), and 36% of the Fe was associated with the low-Al goethite shown above.

➤ The hyperfine field distribution for the goethite (right) indicated that it exhibited a range in particle size and/or crystallinity; possibly indicating the presence of two sediment sources.

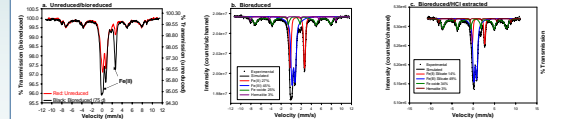
BIOREDUCE FRC SEDIMENT

Anoxic Incubation of FRC Sediment with *S. putrefaciens*



➤ Mn(III/IV) oxides were reduced to completion before Fe(III) reduction commenced. All of the biogenic Fe(II) was sorbed by the sediment. Buffer type had negligible effect.

Mössbauer Spectra

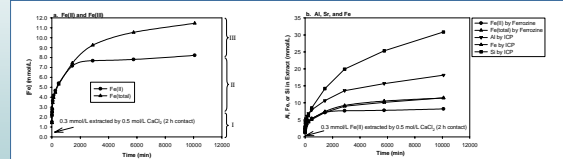


➤ Bioreduction enhanced the Fe(II)-silicate signal and decreased that associated with crystalline Fe(III) oxide. The spectral contribution of the Fe(II) signal was decreased by 11% and Fe(III) silicate by 7% (b). Ammonium oxalate Fe(II) was also removed.

➤ Rapid, weak acid extraction removed 50% of the Fe(II) signal indicating that it was not a silicate (c). This phase was not extractable in CaCl_2 . The identification of this Fe(II) phase has proven difficult. Obvious choices have been discounted.

➤ Mössbauer spectra of the acid extracted residue (c) indicated bacterial reduction of some phyllosilicate Fe(II) [-3% of Fe_{TOT}]. This Fe(II) was not weak-acid soluble.

Weak Acid (0.5 N HCl) Extraction of Biogenic Fe(II)



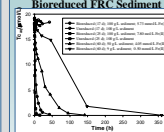
➤ Weak acid extraction (0.5 N HCl, 2 h) is often used to determine biogenic Fe(II) .

➤ We have observed that Fe(II) release from reduced FRC sediment is a complex function of time.

➤ Three intervals of Fe(II) release can be identified: I) exchangeable and surface precipitated biogenic Fe(II) extracted in 2 h; II) biogenic, phyllosilicate Fe(II) that dissolves in 2-25 h, and III) phyllosilicate Fe(II) and Fe(III) that dissolves from 25-166 h.

Tc(VII) REDUCTION

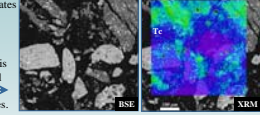
Tc(VII) Reduction in 75 d Bioreduced FRC Sediment



➤ Tc(VII) reduction rate correlates with biogenic Fe(II) concentration.

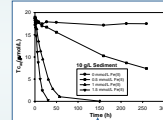
➤ Precipitated Tc(IV) (green) is disseminated in fine-grained saprolite aggregates where biogenic Fe(II) resides.

XMP Image



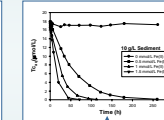
Fe(II) was Spiked into Chemically Treated FRC Sediment in PIPES Buffer to Study the Reactivity of Different Fe(II) Forms

Hydroxylamine Treatment to Remove Mn(III/IV) Oxides



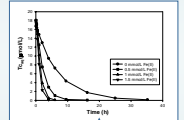
➤ Spiked Fe(II) formed surface complexes on residual Fe(III) oxide (goethite) and exchange complexes on high Fe(III) vermiculite. This was the weakest reductant.

DCB/HCl Treatment to Remove Mn and Fe Oxides and Sorbed Fe(II)



➤ Spiked Fe(II) formed exchange complexes on Fe(II)/Fe(III) vermiculite. This was a moderate reductant. Phyllosilicate Fe(II) was unreactive with Tc(VII) .

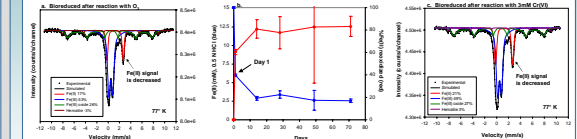
DCB Treatment to Remove Mn and Fe Oxides



➤ Spiked Fe(II) was augmented with residual sorbed Fe(II) from the DCB extraction. The residual Fe(II) from the DCB extraction existed as an unidentified precipitate that was the strongest reductant.

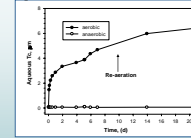
Fe(II) and Tc(IV) OXIDATION

Abiotic Oxidation of Biogenic Fe(II)

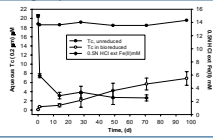


➤ Biogenic Fe(II) was rapidly reactive with both O_2 and Cr(VI) , both oxidants converted approximately 80% of the biogenic Fe(II) to Fe(III) . The resulting Fe(III) increased the intensity of the central doublet, consistent with the formation of ferrihydrite.

Episodic Oxidation



Open System Oxidation



➤ 20 μM of Tc(VII) was reduced to Tc(IV) by reaction with biogenic Fe(II) in 75 d bioreduced sediment. Approximately 30% was reoxidized after 2 headspace replacements with air.

➤ 20 μM of Tc(IV) oxidizes slowly in a 75 d bioreduced sediment that is bathed in oxygenated electrolyte. Fe(II) is oxidized at a rate that is more than 10x higher.

CONCLUSIONS

- The dominant Fe forms in pristine FRC sediment are phyllosilicate Fe(II) (10%) and Fe(III) (51%), and crystalline Fe(III) oxide (Al-goethite, 36%).
- DIRB reduce approximately 15-20% of the Fe(III) ; 4% of this is silicate Fe(III) and the remainder is primarily crystalline Fe(III) oxide.
- Biogenic Fe(II) resulting from Fe(III) oxide reduction is strongly sorbed as a hydroxide-like precipitate.
- The sorbed Fe(II) phase, and not silicate Fe(II) , is a moderate-strong reductant of Tc(VII) . Reduction rate qualitatively correlates with Fe(II) .
- Tc(IV) reacts with O_2 , albeit at much slower rates than the Tc(VII)-Fe(II) reaction.