Reactive Transport of U and Tc in Subsurface Sediment Systems

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Poster represents post-doctoral research by Tanya Peretyazhko with collaboration from Ravi Kukkadapu(EMSL) on Mössbauer spectroscopy
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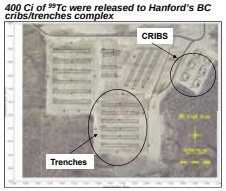
Introduction

This PNNL-SFA project is investigating the reactive transport of U and Tc in Hanford subsurface sediments containing microenvironments or from transition zones. Here we present FY09 research results on the reductive transformation of Tc(VII) in Ringold Formation sediments recovered from a redox transition zone in Hanford's unconfined aquifer in the Columbia River corridor.

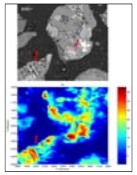
Hanford Science Motivation

400 Ci of ^{99}Tc were released to Hanford's BC cribs/trenches complex



- ^{99}Tc(VII) is a major risk-driving contaminant at Hanford because of high vadose zone inventory, significant mobility, and long half-life.
- ^{99}Tc(VII) is mobile and poorly reactive in the Hanford vadose zone, but localized anoxic, potentially reactive domains exist in groundwater.
- Understanding natural attenuation reactions and processes can provide insights for sustainable remediation.

Important Fundamental Science Issues



Many Fe(II)- and Fe(III)- containing phases exist in Hanford sediment. They are both geogenic, detrital, and biogenic.

- Nature and identity of biogeochemically reactive Fe(II) species.
- Variation in reactive Fe(II) speciation through contiguous zones of variable redox conditions.
- Oxidation rates by different electron acceptors (O_2, Tc(VII)) and influence of Fe(II)/Fe(III) speciation on kinetics.
- Mass transfer processes influencing redox transformations during transport.
- Modeling and scaling heterogeneous redox processes and parameters.

Technetium

Fission

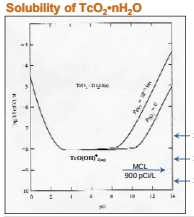
^{235}Uranium → ^{99}Technetium

T1/2 = 7.0 x 10^8 years — 2.1 x 10^5 years

α -emitter — β -emitter

- Fission product of ^{235}Uranium
- ~ 1990 kg produced at Hanford (1943-1987); world-wide inventory ~ 290 MT
- Exists in oxidation states +7 to -1
- Mobile as Tc(VII) as the pertechnetate ion TcO_4^-
- Biological activity high (sulphate analogue)
- Microbial reduction to insoluble Tc(IV)

Solubility of $TcO_2 \cdot nH_2O$



Redox Reactions

$Tc(VII)O_4^- + 4H^+ + 3e^- = Tc(IV)O_2 \cdot nH_2O_{(s)} + (2-n)H_2O$ $E^o = 0.748$ V

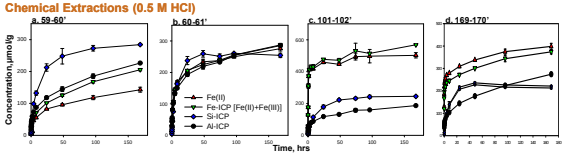
$Tc(VII)O_4^- + 3Fe^{2+} + (n+7)H_2O = Tc(IV)O_2 \cdot nH_2O_{(s)} + 3Fe(OH)_{3(s)} + 5H^+$

- Concentration of Tc(IV) fixed by solubility at reduction point
- Ionic radii and structural similarities suggest coprecipitation with Fe(III) possible.
- Downgradient adsorption of Tc(IV) complexes or another reaction essential to reach MCL (900 pCi/L).
- Adsorption behavior of $TcO(OH)_2^-{}_{(aq)}$ unknown.

Sediment Cores from Hanford's Unconfined Aquifer

- A deep borehole (C6209) that sampled the entire depth sequence of Hanford's Columbia River corridor unconfined aquifer was completed in August 2008 as part of the Hanford IFRC well installation program.
- Intact core samples were collected for microbiologic characterization. Subsamples were removed, handled, and stored under strictly anaerobic conditions for geochemical studies.
- Ringold Formation sediments at and below a redox transition zone at 60' were selected for Tc(VII) reaction studies.
- The aquifer sediments below 60' are variably anoxic, and range significantly in texture and chemistry.
- A multi-level groundwater sampler will be placed over this interval during spring 2009 to characterize the depth discrete redox character of groundwaters over this interval.

Chemical Extractions (0.5 M HCl)



I. 59-60'	[Fe(II)]<[Fe-ICP]<[Al-ICP]<[Si-ICP]
II. 60-61', 128-129', 155-156'	[Fe(II)]=[Fe-ICP]=[Al-ICP]=[Si-ICP]
III. 101-102', 169-170'	[Fe(II)]=[Fe-ICP]>[Si-ICP]>[Al-ICP]

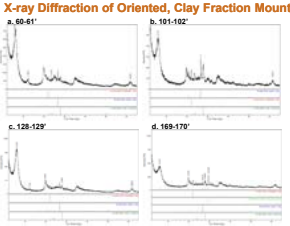
- Weak acid extraction was used to quantify reactive Fe(II).
- Si and Al were also monitored to assess phyllosilicate dissolution.
- A readily extractable Fe(II) pool was present in all sediments.
- Three dominant patterns of Fe(II) release were noted (I, II, III).
- The quantity of extractable Fe(II) was dependent on extraction time.
- Pattern II was representative of Fe(II) smectite and Pattern III of a discrete phase Fe(II).

Sediment Properties

Sample	Clay Fraction %	XRD (Clay Fraction)	IC*(%)	OC**(%)	Tot Fe (%)	Tot Fe (mmol/g)
59-60	4.64	Dioctahedral smectite; traces of chlorite, illite, kaolinite and quartz	< 0.02	< 0.05	3.76	0.671
60-61	8.00	Dioctahedral smectite; traces of illite, kaolinite, quartz, and feldspar	< 0.02	0.08	3.80	0.679
101-102	10.54	Dioctahedral smectite; traces of chlorite, illite, quartz, and feldspar	0.42	0.05	4.83	0.862
128-129	14.82	Dioctahedral smectite; traces of illite, kaolinite, quartz, and feldspar	< 0.02	0.21	5.63	1.00
155-156	13.20	Dioctahedral smectite; traces of illite, kaolinite, chlorite, quartz, and feldspar	< 0.02	1.33	4.29	0.766
169-170	15.06	Dioctahedral smectite; traces of calcite, quartz, and feldspar	2.65	0.30	7.96	1.42

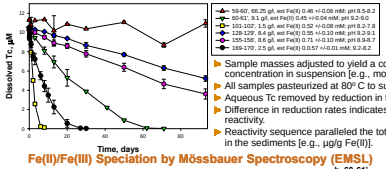
*IC = inorganic carbon; **OC = organic carbon

X-ray Diffraction of Oriented, Clay Fraction Mounts



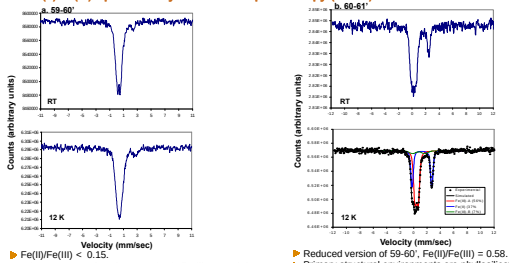
- Mineralogy of the clay-sized fraction of all sediments very similar.
- All 14-15 Å peaks expand cleanly to 17-19 Å when glycol saturated, implying presence of smectite.
- Chlorite, quartz, and feldspars are also observed, with calcite at 169-170'.
- No crystalline Fe(III) oxides or discrete Fe(II) phases evident.

Tc Reduction

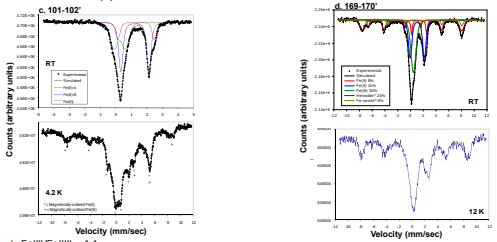


- Sample masses adjusted to yield a common extractable Fe(II) concentration in suspension [e.g., mol/L Fe(II)].
- All samples pasteurized at 80° C to suppress microbial activity.
- Aqueous Tc removed by reduction in five of six sediments.
- Difference in reduction rates indicates significant difference in Fe(II) reactivity.
- Reactivity sequence paralleled the total extractable Fe(II) concentration in the sediments [e.g., µg/g Fe(II)].

Fe(II)/Fe(III) Speciation by Mössbauer Spectroscopy (EMSL)

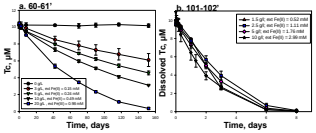


- Fe(II)/Fe(III) < 0.15.
- Primary structural environment is phyllosilicate Fe(III).
- No evidence for Fe(III) oxides .
- Reduced version of 59-60', Fe(II)/Fe(III) = 0.58.
- Primary structural environments are phyllosilicate Fe(II) and Fe(III) most likely associated with smectite.



- Fe(II)/Fe(III) = 1.1.
- Complex and unusual Mossbauer spectra.
- One ferric phase that may be phyllosilicate Fe(III), no Fe(III) oxides.
- Two Fe(II) phases, with magnetic ordering at low T.
- Discrete Fe(II) phase that is not siderite or GR, and phyllosilicate Fe(II)?
- Fe(II)/Fe(III) = 0.64.
- Magnetically ordered phase at RT = crystalline Fe(III) oxides.
- Phyllosilicate Fe(III) at 0.75 mm/sec (green).
- Two ferrous forms, phyllosilicate Fe(II) (blue) and adsorbed Fe(II) (red) absent Scherer effect .

Variable Mass Tc Reduction



- Kinetic experiments were performed to asses reaction order with respect to Fe(II) for two of the sediments, 60-61' and 101-102'.
- The experiments were performed with $Tc(VII)_{aq} \approx 10$ µM, and variable sediment masses to yield a concentration range in reactive, extractable Fe(II).
- Sediment 60-61' showed rate dependence on $[Fe(II)_{ext}]$ while sediment 101-102' did not.
- All experimental conditions presented at least a 10-fold excess in extractable Fe(II) over Tc(VII).
- The redox properties and/or accessibility of Fe(II) in the two sediments was different.
- Perhaps structural phyllosilicate Fe(II) in 60-61' was physically limited in its contact potential with aqueous oxidants.

Preliminary Conclusions

- Subsurface sediments from locally anoxic zones in the Ringold Formation of Hanford's unconfined aquifer can reduce Tc(VII) to Tc(IV), lowering aqueous concentrations by factors of 1000 or more.
- Reaction half-lives ranged from 2 d to over 70 d.
- Reduction rates normalized to sediment extractable Fe(II) concentration showed high variability, indicating a controlling role of Fe(II) speciation.
- A dominant mineral phase in the clay-size fraction of all reactive sediments was Fe(II)-containing smectite. The presence of a specific sediment with this as the primary Fe(II) repository (60-61') allowed the reactivity of this phase to be assessed. Intrinsic reduction rates for smectite varied by 100x across a local redox interface (59-60' as compared to 60-61').
- Reduction rates decreased in the following order: separate Fe(II) phase + Fe(II)-smectite (101-102') > Fe(II)-sorbed Fe(III) oxide + Fe(II) smectite (169-170') >> Fe(II) smectite (60-61').
- Unclear relationships between Fe(II) distribution and microbiologic activity (microbial ecology of samples described by Konopka in Hanford IFRC plenary session).

Future Research

- Molecular speciation of Tc(IV) phase and its dependence on reduction rate, and Fe(II) reactant speciation (APS beam-run in April).
- Further Mössbauer characterization, quantification, and modeling of reactive sediment Fe(II) phases.
- Flow-through reactor oxygen consumption studies with the various sediments.
- Tc(IV) oxidation rates in different sediments, and dependence on molecular and Fe(II) speciation using flow-through reactors.
- Molecular nature, physicochemical environment, and mineral residence of oxidation resistant Tc(IV).

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