Rates and Mechanisms of Heterogeneous Pertechnetate Reduction by Mixed-Valent Iron Oxides

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Pacific Northwest NATIONAL LABORATORY

Introduction and Objective

This project is focused on developing a molecular-scale understanding of biogeochemical electron transfer reactions affecting the stability of U and Tc in Hanford-specific microenvironments. It is part of the Biogeochemical Electron Transfer (BET) theme of the PNNL Science Focus Area (SFA). Sediments at the Hanford Site contain significant total Fe, of which a large percentage exists in the reactive ferrous state. The Fe(II) component in part arises in the form of magnetites crystallized within the basaltic source material that are present in the sediments both as subhedral to euhedral micron-sized free crystal grains and as mineral components of basaltic lithic fragments. These magnetites naturally contain variable amounts of impurities in the form of isostructural alio- and isovalent metal substitutions. Ti is a dominant constituent, and the resulting metal oxide can therefore be described with the titanomagnetite formula $Fe_{3-x}Ti_xO_4$, which falls between endmember magnetite (x = 0) and ulvöspinel (x = 1). In the absence of surface passivation, Fe(II)-bearing minerals such as these have been shown to be redox-active polyvalent metal reductants. At Hanford, it has been speculated that grain interfaces of such minerals are reducing microenvironments, especially if oxygen is scavenged by associated oxygen-consuming mineral reactions or by microbial activity. In the present study, the objective is to determine the role of electron equivalent availability for Tc(VII) reduction in terms of the reactive Fe(II) component(s) supplied by the mineral phases.

Titanomagnetite Minerals

Titanomagnetites have the feature that substitution of Ti(IV) into the metal sublattice is charge compensated by a proportional increase in the Fe(II) content. This built-in natural 'tunability' of the Fe(II)/Fe(III) ratio in principle adjusts the reducing capacity of the solid, and is therefore central to its redox reactivity with respect to contaminant reduction. This project has been focused on developing a molecular-level understanding of rate controlling factors in the heterogeneous reduction of pertechnetate by such phases, including surface oxidation, passivation, and Fe(II) resupply towards improved predictability of the reducing potential in Hanford-specific microenvironments. Using EMSL facilities we developed successful procedures to synthesize compositionally controlled $Fe_{3-x}Ti_xO_4$ (i) bulk powders; (ii) nanoparticles to provide a high surface area pristine material compatible with complementary batch studies; and (iii) thin films to provide crystallographically oriented well-defined surfaces for detailed characterization.

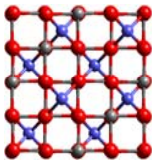
Magnetite (x = 0.0)

$Fe^{3+}_{Tet}(Fe^{2+}, Fe^{3+})_{Oct}O_4$

(substitution & reduction)

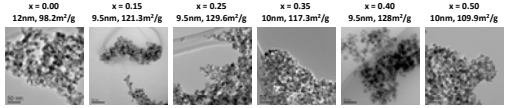
$Fe^{2+}_{Tet}(Fe^{2+}, Ti^{4+})_{Oct}O_4$

Ulvöspinel (x = 1.0)



Titanomagnetite Characterization

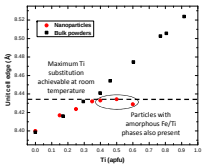
Transmission Electron Microscopy



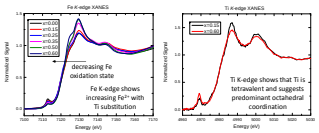
Acid Digestion

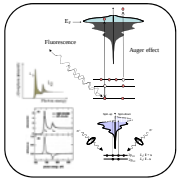
$Fe_{3-x}Ti_xO_4$ x	Ferrozine Fe(II) mM/g solid	ICP-MS Fe(III) mM/g solid	Ti(IV) mM/g solid	Composition
0.00	4.23	8.20	0.00	$Fe^{II}_{1.00}Fe^{III}_{1.60}O_4$
0.15	4.44	6.33	0.55	$Fe^{II}_{1.15}Fe^{III}_{1.40}Ti_{0.15}O_4$
0.25	4.63	5.91	0.97	$Fe^{II}_{1.25}Fe^{III}_{1.15}Ti_{0.25}O_4$
0.35	4.76	5.02	1.38	$Fe^{II}_{1.27}Fe^{III}_{1.10}Ti_{0.35}O_4$
0.40	4.79	4.99	1.58	$Fe^{II}_{1.27}Fe^{III}_{1.13}Ti_{0.40}O_4$
0.50	5.30	4.39	2.06	$Fe^{II}_{1.31}Fe^{III}_{1.19}Ti_{0.50}O_4$
0.60	4.90	3.34	2.24	$Fe^{II}_{1.38}Fe^{III}_{0.94}Ti_{0.60}O_4$

In Situ MicroXRD



Fe and Ti K-Edge XANES





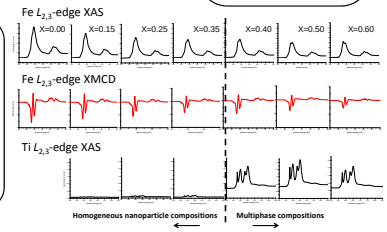
X-Ray Magnetic Circular Dichroism

Transitions: core levels to spin-split valence band
ELEMENT SPECIFIC

Differences at L_3 and L_2 edges
SPIN & ORBITAL MOMENTS

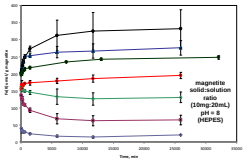
Soft x-ray region is dominated by Auger decay
TEY measurements are **SURFACE SENSITIVE**

Transitions depend on local atomic environment
DISTINGUISH METALS & OXIDES
SITE SPECIFIC...

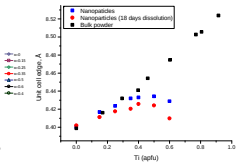


Titanomagnetite Reactivity

Aqueous Fe(II) Release

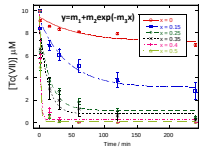


Structural Fe(II) Remaining

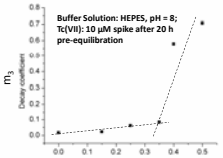


Fe(II) release depends on Ti content: Low Ti = Fe(II) reabsorption over time
High Ti = Fe(II) release over time

Pertechnetate Reduction



X	Mass mg	Dissolved Fe(II) µ mol	Fe(II) in solid µ mol	Consumed Tc(VII) µ mol
0	1.355	0.031	6.565	0.091
0.15	1.300	0.130	5.500	0.215
0.25	1.304	0.199	5.065	0.288
0.35	1.274	0.221	6.363	0.294
0.50	1.274	0.323	6.669	0.300



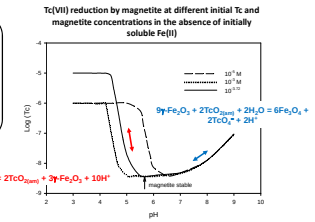
Tc(VII) is reduced by released Fe(II) and structural Fe(II)
Reduction is substantially faster above x=0.35

Thermodynamic Analysis

Magnetite-Maghemite Interconversion

$Fe_3O_4 + 2H^+ = \gamma\text{-}Fe_2O_3 + 2Fe^{2+} + H_2O$

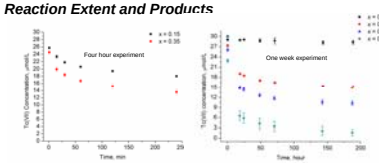
Topotactic transformation of magnetite (Fe_3O_4) to maghemite (γ-Fe_2O_3) in acidic solution entails transport of electrons from the bulk to the surface where surface oxygen protonation reactions lead to release of Fe(II) into solution. Simultaneously, cationic vacancies migrate in the reverse direction and maintain charge balance in the solid.



$6Fe^{2+}_{(aq)} + 2TcO_4^- + 5H_2O = 2TcO_{2(aq)} + 3\gamma\text{-}Fe_2O_3 + 10H^+$

Conceptual Model Development

Reaction Extent and Products

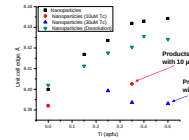


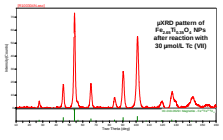
Higher Fe(II) content yields more Tc(VII) reduction for both 10mM and 30mM Tc(VII).

Longer term experiments with higher Tc(VII) concentration show that a portion of Fe(II) in the solid appears inaccessible to Tc(VII)

1.3 mg $Fe_{3-x}Ti_xO_4$ NPs reacted with 30 µmol/L Tc(VII) in 30 mL of HEPES buffer solution for 4 h (left) and 1 week (right).

X	SA m²	Dissolved Fe(II) µ mol	Fe(II) in solid µ mol	Consumed Tc(VII) µ mol
0	0.138	0.031	6.565	0.091
0.15	0.158	0.130	5.499	0.646
0.35	0.152	0.225	6.513	0.691
0.50	0.204	0.330	7.254	0.810

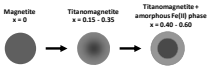




Cell parameter decreases after reduction experiments, which indicates reaction between Tc(VII) and structural Fe(II)

Summary and Conclusions

The collective measurements point to a picture of condition-sensitive dynamic exchange of reducing equivalents between bulk lattice Fe(II), more accessible surface-associated Fe(II), and solubilized Fe(II) that is dictated by the chemical potential of Fe(II) built into the solid, a property that depends in turn on the nature and content of aliovalent metal substitution impurities. Contaminant reduction kinetics therefore appear to be strongly dependent on the availability and relative proportions of these Fe(II) pools.



Structure-Reactivity Model

Future Research

Reduction rates observed for Tc in combination with molecular modeling will be used to develop analytic kinetic expressions for a reactive interface moving to the solid interior. Metal oxides produced from this project will be used as electron accepting or donating substrates for reactivity studies with key redox biomolecules (with Liang Shi) and Pu compounds (with Andy Felmy) under study in the BET theme of the PNNL SFA, as well as comprising test substrates for colonization and surface transformation studies for key redox horizons downwell at the Hanford IFRC site (with Jim Fredrickson).

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