Structure and Chemical Properties of Iron-Containing Mineral Microparticulates Isolated from Hanford Site Sediments

D.R. Baer, E. S. Ilton, K. M. Krupka, J. Liu, J. C .Myers,* R. L. Penn,* A. Pepin,* and J. M. Zachara
Pacific Northwest National Laboratory, Richland, Washington, U.S.A.
*University of Minnesota, Minneapolis, Minnesota, U.S.A.

Pacific Northwest NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Introduction & Objectives

The nature of reactive surfaces, the accessibility of reactive sites, and the structures of surface and interface layers differ for different minerals present in sediments and soils, both due to their composition and their history. Their properties can change significantly because of trace element composition and in response to surface structure alterations, phase changes, and passive layer formation as mineral particles respond to and react with their local environment. The objective of our research is to obtain fundamental information about the reactivity of natural materials that occur on the Hanford site. One objective is to understand how local mineralogy and geochemically mediated transformations alter reactivity, electron availability, and mobility of naturally occurring Fe-oxide microparticles relative to their impact on the redox behavior and mobility of U and Tc in subsurface geologic systems.

"The [Hanford] sediments invariably contain a magnetic, Fe-rich mineral fraction (at ≤2 mass %) that contains magnetite, ilmenite, Fe(II)/Fe(III) phyllosilicates, and Fe(III) oxides. This potentially reactive fraction has not been well studied and is expected to show considerable variation between the Hanford and Ringold formations and specific vadose zone samples from within them." Zachara et al. www.vadosezonejournal.org · Vol. 6, No. 4, November 2007

Overview and Approach

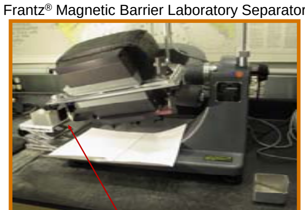
Results of four activities are reported:

- **Use separation methods to isolate the mineral phases from Hanford sediments – initial focus on highly magnetic particles**
- **Characterize isolated phases (including microscopy, diffraction, and surface measurements)**
- **Use probe molecules to measure the reactivity of isolated components**
- **Test the ability to measure reaction products on individual natural particles**

Separation and Characterization of Magnetic Minerals from Hanford Sediments

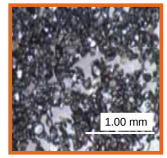
Density and magnetic separation were used to enrich magnetic phases from sediments from the Hanford site. Nearly pure magnetite crystallites were isolated and fractions enriched in iron containing micas were produced.

Frantz® Magnetic Barrier Laboratory Separator



Stronger (top) and Weaker (bottom) Paramagnetic Fractions

Highly Magnetic Component



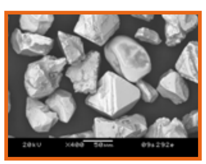
X-ray Diffraction: Magnetite

0.3 Amp Paramagnetic Fraction

X-ray Diffraction: Mixed phases, enriched in Fe containing components (see table below)

XRD Observed Phases B8814 Hanford Sand Bulk and Separated Components by wt%	Plagioclase Feldspar	Orthoclase Feldspar	Biotite & Muscovite	Quartz	Chlorite	Magnetite	Amphibole (Hornblende)
Bulk*	30.0	7.4	4.5	43.0	1.0	0.1	2.0
Magnetic Fraction 0.3A	47.0	9.5	25.0 (~13 biotite)	10.0	4.3	0.0	5.0
Magnetic Fraction 0.5A	30.0	4.9	29.0 (~ 12 biotite)	12.0	11.0	0.0	13.0
Highly magnetic panned						99.0	

*From: RPP-7884 Field Investigation Report for Waste Management Area S-SX

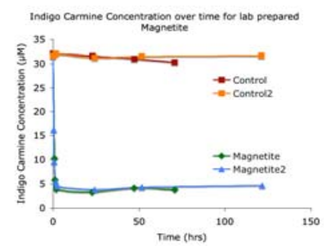


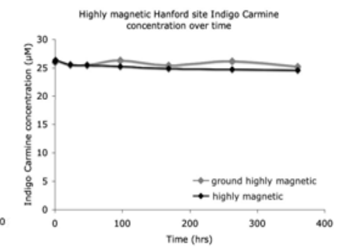
Fe Oxide (EDS indicates no Ti or other identifiable metals)

A highly magnetic phase was identified as nearly 100% magnetite by XRD, consistent with SEM/EDS measurements on mounted particles. This phase makes up about 0.15 wt% of the sediment. Fe 2p photoelectron peaks indicate the presence of both Fe^{+2} and Fe^{+3}, consistent with magnetite. However, the measurements also suggest the presence of a ~ 1.5 nm surface layer composed of Ca and Si containing phases.

Probe Molecule Reactions with Natural and Synthetic Magnetite

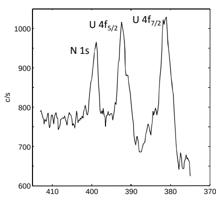
Synthetic magnetite is highly reactive with Indigo Carmine as a redox probe molecule. Isolated natural magnetite from one Hanford sediment appears nonreactive both as extracted and when fresh surface is exposed by grinding.





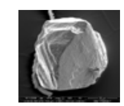
U sorption on Individual Natural Magnetite Crystals

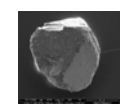
Small amounts of some types of isolated phases limit the types of reaction studies that can be conducted. A set of experiments looking at U(VI) sorption on the natural magnetite crystals demonstrates that XPS can be used to study sorption reactions on individual grains approximately 100 µm in size.



Binding Energy (eV)

U sorbed on individual ~100 µm magnetite particles as measured by XPS after exposure to a 25 µM U(VI) solution at pH5. Particles were analyzed using a 50 µm diameter focused x-ray spot (Phi Quantum 2000).





Conclusions

- Magnetic characterization of a 200 Area composite sediment sample (B8814) indicates that roughly 25% of the sample is ferromagnetic or paramagnetic.
- A highly magnetic component isolated by both density and magnetic properties is nearly pure magnetite with a crystallite size of ~ 100 µm as identified by XRD.
- The natural magnetite is much less reactive to indigo carmine (a redox probe molecules) than artificial magnetite.
- XPS can be used to measure U (and possibly Tc) sorption on individual grains.
- Much of the magnetic material is comprised of phyllosilicate grains and granite or basalt clasts that contain several mineral phases. Separates rich in Fe containing mica and other components can be separated.

Acknowledgments

Dr. Andrew Grosz at the U.S. Geological Survey (Reston, VA) is gratefully acknowledged for use of his laboratory and technical guidance on magnetic separation of sediment samples. Mark Engelhard is acknowledged for collecting the XPS data. This research was supported by the Environmental Remediation Science Program (ERSP), Office of Biological and Environmental Research (BER), U.S. Department of Energy (DOE). A portion of the research was performed using EMSL, a national scientific user facility sponsored by DOE-BER and located at Pacific Northwest National Laboratory (PNNL). PNNL is operated for DOE by Battelle under contract DE-AC06-76RLO 1830.

- Results will be presented from studies of the reaction properties of naturally occurring Fe containing particles with Tc and organic redox indicators. Various fractions of Fe-containing minerals have been separated using particle size, density and magnetic susceptibility techniques from select sediment samples from the U.S. Department of Energy's Hanford Site in Washington State. The mineralogy, composition [especially Fe(II/III), Mn(III/IV) and Ti], and surface chemistry and structure of the Fe containing microparticle fractions have been characterized by a variety of methods including optical microscopy, micro-focus x-ray diffraction, scanning and transmission electron microscopy, and x-ray photoelectron spectroscopy. Experiments are being completed to evaluate the relative electron-mediated reactivity of these different Fe-oxide fractions, in with respect to redox changes resulting from contact dissolved pertechnetate [Tc(VII)] and organic probe molecules (e.g. carbon tetrachloride or benzoquinone). Results of the relative reactivity experiments will be presented and evaluated in the context of the mineral characterization information determined for the different Fe-oxide microparticle fractions used for testing. Impacts of surface precipitation and surface passivation on particle reactivity and the time dependence of reactivity relative to electron-transfer reactions will also be discussed.