

Summary of a 2005 NABIR PI Meeting Breakout Session
Monday, April 18, 2005

***What are the major research needs and approaches for
evaluating reoxidation processes?***

Organizers: John Zachara - *Pacific Northwest National
Laboratory*

Jon Lloyd – *University of Manchester, UK*

Invited Presenters: John Coates - *UC Berkeley*

Jack Istok - *Oregon State University*

Abstract

The three hour breakout session will seek input from NABIR investigators and other meeting participants to resolve the central question posed above with emphasis on DOE legacy polyvalent contaminants including but not limited to U, Tc, Cr, and Pu. The session will begin with two brief presentations on abiotic and biotic oxidation mechanisms of reduced contaminants (e.g., U) and major ion metals (e.g., Fe) that will include examples of experimental approaches to assess these processes. Following these, the floor will be opened to any participant who wishes to briefly share experimental or modeling observations, or other perspectives on oxidation that will contribute to the session theme. These presentations and participant contributions will set the context for mediated discussion that will continue through the remainder of the session. The mediators will pose a series of questions for audience response that build upon the central issue of the breakout session. Example questions will include:

- 1.) What do we know about the kinetics, and abiotic and biotic controls on reduced contaminant oxidation?
- 2.) Given NABIR program objectives and our current knowledge state, what are critical additional science information needs to assess the long term stability of reduced contaminants and their potential for and rate of oxidation?
- 3.) What are the most fruitful laboratory and field approaches for investigating contaminant oxidation and do field sites exist to perform comprehensive, integrated studies of oxidation?
- 4.) Should the oxidation process be modeled for field scale prediction, can it be currently, and, if not, what uncertainties preclude this?
- 5.) Can controlled oxidation be exploited to maximize fixation of target contaminants?
- 6.) What are other feasible manipulative strategies to minimize oxidation (e.g., hydrologic, microbiologic, geochemical), and should these be pursued in future NABIR research?

Individual participant responses to each of these will be recorded, organized, and discussed in sequence in order to identify consensus positions if possible, as well as contrasting points of view. The breakout session coordinators will develop a written summary of the proceedings that will be posted on the NABIR web site approximately one month after the PI meeting.

What are the major research needs and approaches for evaluating reoxidation processes?

Introduction and Workshop Format

This three hour breakout session aimed to capture input from NABIR investigators and other meeting participants to resolve the central question posed above, with emphasis on DOE legacy polyvalent contaminants including but not limited to U, Tc, Cr, and Pu.

The central focus of the NABIR program for the last 8 years has been the reductive immobilization of contaminant metals/radionuclides, with emphasis on the reduction of U(VI) to U(IV), Tc(VII) to Tc(IV) and Cr(VI) to Cr(III). Recent NABIR-supported studies have, however, started to address reoxidation, giving a deeper understanding of the full biogeochemical cycle of these elements, informing assessments of the long-term stability of the post-reduction products and potentially offering new stable bioremediation end-points. A number of potential oxidants are been studied, including oxygen, nitrate and in some cases Fe(III).

Several earlier presentations by principal investigators at the NABIR meeting set the scene for this breakout session. John Zachara (PNNL) had discussed the homogeneous and heterogeneous reduction of Tc(VII) by different Fe(II) forms, and the oxidation rates of the various Tc(IV) products formed by reaction with molecular oxygen. Tetsu Tokunaga (LBNL) described a lab-based study that suggested that U(IV) reoxidation was possible after 60 days in column experiments with FRC materials. Here the U(VI) was potentially stabilized by carbonate complexation at neutral/alkali pH (resulting from electron donor oxidation), and Fe(III) was proposed as a possible electron acceptor for U(IV) oxidation. This presentation provoked vigorous debate in the audience. Phil Long (PNNL) then presented results showing the long-term-stability of biogenic U(IV) at the Rifle UMTRA site (>1.5 years).

Invited Presentation Summary

The breakout session began with two invited presentations by John Coates (UC Berkeley) and Jack Istok (Oregon State University). John Coates focused on laboratory studies to demonstrate the concept of permanent immobilization of radionuclides through anaerobic bio-oxidation of Fe(II) with associated sequestration of contaminants in biogenic Fe(III) oxide. Jack Istok presented field evidence for U and Tc bioreduction and reoxidation at the FRC, with U(IV) showing significant oxidation in the field and Tc(IV) showing very little. Following these presentations, the floor was opened to any participant who wished to share experimental or modelling observations, or other perspectives on oxidation that

could contribute to the session theme. Short presentations included those by Baohua Gu (ORNL; impact of humic materials on U(VI) bioreduction and U(IV) oxidation), Lee Krumholz, (University of Oklahoma; U(IV) oxidation during dissimilatory nitrate reduction), Eric Roden (University of Alabama; uranium redox cycling), and Francis Livens (University of Manchester, Tc(IV) biooxidation in organic rich estuarine sediments).

These presentations, with subsequent participant contributions, helped cement the context for mediated discussion that continued through the remainder of the session.

Discussion Summary

The mediators (John Zachara and Jon Lloyd) then posed six questions for audience response that built upon the central issue of the breakout session. Individual responses to each of these were recorded on white boards by the participants, organized, and discussed in sequence in order to identify consensus positions if possible, as well as contrasting points of view. An overview of the responses to these questions is presented below.

1. What do we know about the kinetics, and abiotic and biotic controls on reduced contaminant oxidation?

A growing body of literature, supported in part by the NABIR program, has been examining the oxidation rates of U(IV), Tc(IV), Cr(III), and Pu(III/IV) in reduced sediments of different type. NABIR-support research on these subjects is now beginning to appear in the literature. Cr(III) oxidation is very slow and was not discussed in the breakout session. Uranium(IV) and Tc(IV) are both reactive with molecular oxygen, but measured oxidation rates in sediments show significant variation for reasons that are not understood. Physical location, mineral residence, molecular speciation, and concentrations of Fe(II) all appear to influence the overall rate and extent of U(IV) and Tc(IV) reaction with molecular oxygen. Current scientific understanding is not sufficient to determine whether biostabilized U(IV) or Tc(IV) is more prone to oxidation. U(IV) oxidation also occurs biologically with nitrate as the oxidant, but similar reactions have not been observed for Tc(IV). Intermediate products of dissimilatory nitrate reduction (e.g., nitrite, nitrous oxide, nitric oxide) are also effective, abiotic oxidants of U(IV). In accord with these latter observations, bioreduced U(IV) demonstrated significant oxidative release at the FRC under high-nitrate, microaerophilic conditions, while bioreduced Tc(IV) did not.

Aqueous complexation and the presence of Fe(II) both appear to have significant effects on the oxidation rate. The complexation of U(IV) by soluble humic substances allows the dispersal of reduced U in pore fluid and more ready contact with dissolved molecular oxygen. These factors greatly accelerate U(IV) oxidation. Strong complexation of U(VI) by dissolved carbonate of abiotic or biogenic origin also enhances oxidation by reducing the thermodynamic activity of the oxidation product. Newly evolving data indicates that ferrous iron oxidizes more rapidly than either U(IV) or Tc(IV), and that oxidized Fe in

the form of ferrihydrite or other mineral precipitates may sequester the reduced radionuclides in mineral physical regions and states that are inaccessible to oxidant diffusion and subsequent reaction. Such sequestration limits oxidation, allowing for long term mineralogic stabilization of reduced radionuclides in otherwise oxidized environments. Limited data implies that reduced sulphur forms and particulate organic matter may also stabilize reduced radionuclides.

Solid phase oxidants may play a significant role in remobilizing bioreduced U(IV) and Tc(IV). Mn(III/IV) oxides have been shown to rapidly oxidize bioreduced U and Tc in agitated FRC suspensions. Whether contact between reduced radionuclide microparticles and the Mn oxides can actually occur in an unmixed advective systems such as a column or groundwater system has not been established. Somewhat controversial is the role of Fe(III) oxides in U(IV) and Tc(IV) oxidation. The reduction potentials of Fe(III), U(VI), and Tc(VII) are quite similar at circumneutral pH, with the consequent result that solid phase Fe(III) oxides could conceivably function as oxidants for U(IV) and Tc(IV) under certain conditions of pH and aqueous fluid concentration. Published experimental evidence suggests that such reactions are possible for U(VI).

2. Given NABIR program objectives and our current knowledge state, what are critical additional science information needs to assess the long term stability of reduced contaminants and their potential for and rate of oxidation?

Participants in the breakout session responded to this question by recommending the following as critical science needs.

- Local chemical speciation, spatial location, and mineralogic residence of the radionuclides/metals/oxides including the solid phases.
- Ligand effects on reduction potentials [especially with respect to U(IV)] and electron transfer in minerals.
- The biogeochemical implications and effects of local pH change near the organism-mineral interface caused by metal [Fe(III) and Mn(IV)] reduction.
- The biosynthesis, identity, and function of intracellular and extracellular microbial antioxidants and their potential role in stabilizing reduced radionuclides.
- Relative susceptibility of biogenic versus abiotic reduced phases to oxidation and causes for differences if observed.
- The conditions and importance of bacterial oxidation (model organisms, genetic markers, environmental factors).

- Flow and transport controls on the abiotic and bacterial oxidation of reduced radionuclide phases

3. What are the most fruitful laboratory and field approaches for investigating contaminant oxidation?

Participants recommended the following approaches and needed new capabilities for investigating contaminant oxidation.

- Laboratory “model system” studies that are designed with target field environments in mind, that utilize relevant solids and microorganisms, and that operate over realistic ranges of contaminant, nutrient and electron donor, oxidant, microorganism concentrations.
- Laboratory column studies to investigate abiotic and bacterial oxidation where suitably reduced sediments with immobilized radionuclides are contacted with target oxidants (e.g., O₂, NO₃) under advective conditions.
- Meso-scale characterization of intact field sediments or cores and reactive transport experiments in larger, laboratory physical models to bridge results of smaller scale laboratory experiments with field observations.
- Parallel field and laboratory studies with multidisciplinary teaming (microbiology, geochemistry, hydrology, and geophysics).
- Using biogeochemical transport codes to link the laboratory and field and to identify hydrologic, geochemical, and microbiological process contributions at different scales.
- Upscaling investigations to address heterogeneity effects on lab/field experimental results.
- More field-scale geophysics, perhaps “potential” based methods for redox zones. Field-scale monitoring.
- Capabilities are needed for higher frequency field sampling, as are specialised measurements to discern microbiological community changes and associated biogeochemical responses.

4. Should the oxidation process be modelled for field scale prediction, can it be currently, and, if not, what uncertainties preclude this?

Participants had the following ideas regarding biogeochemical modelling of radionuclide oxidation.

- Yes, need to sort out kinetic versus thermodynamic controls in experiments to allow formulation and application of appropriate biogeochemical models.
- Yes, the oxidation process should be modelled to describe inground stability, but oxidation mechanisms, rates, and controlling variables need first be identified and parameterized in laboratory experiments.
- The oxidation process needs to be modelled at the field scale, but the model may require pore-scale detail to handle the effects of FeS grain coatings and sequestration of incompletely oxidized radionuclides by Fe-oxide precipitates.
- The biogeochemical process of bio-immobilization and oxidation involves various nonequilibrium reactions and processes that are difficult to model. A model should explicitly include mass transfer limitations and chemical heterogeneity.
- The science of the NABIR program that involves coupled microbiologic, hydrologic, and geochemical processes is sufficiently complex that models are essential to interpret both laboratory and field observations.
- Various types of models and modelling could be useful to the program given its scientific focus. These could range between deterministic pore-scale models that deal with local/millimeter scale physical, chemical, mineralogic, and biologic detail to stochastic field scale models that address the complex effects of physical heterogeneity at increasing spatial scales.
- Consider and identify appropriate scales for different processes (e.g., microbiological, geochemical, and hydrologic) and develop models and sensitivity calculations around them.
- The complete biogeochemical system should be modelled, not just the components and reactions that initially appear practical (i.e., all species and reactions should be included).
- It may be reasonable to assume oxidation is “instantaneous” relative to the field-time scale for the assessment of the effectiveness of bioremediation.

5. Can controlled oxidation be exploited to maximize fixation of target contaminants? How best to evaluate?

Participant views on the use of controlled oxidation to facilitate long term contaminant fixation were mixed. Their responses were as follows.

- Mechanistic modelling of oxidation (if achieved) could be used to advantage here if data were available on the influence of oxidation rate and associated geochemical conditions on contaminant fixation.
- An alternative concept could be to “control oxidation” at rates that maintain contaminant release to concentrations below the MCL. Laboratory and field data would be required that document feasibility and that demonstrate suitable and required levels of control.
- Ferrous iron could be injected into the bioreduced system with immobilized radionuclides to facilitate immobilization, by Fe(III) oxide precipitation, upon system oxidation. Technical challenges, however, could outweigh benefits.
- Controlled oxidation could be an effective strategy to limit long-term remobilization. It may, however, be challenging for bulk deployment, and more work is required to determine if the degree of control required can be obtained in a real world system.

6. What are other feasible manipulative strategies to minimize oxidation (e.g., hydrologic, microbiological, geochemical), and should these be pursued in future NABIR research?

Participants recommended several manipulation strategies to minimize oxidation. These included the following responses.

- Inject ferrous iron [Fe(II)] into the bioreduced zone to function as an antioxidant and to armor reduced radionuclide microprecipitates against oxidation.
- Stimulate sulphate reduction at the latter stages of biostimulation to enrich system with sulfides and to scavenge potential oxidants.
- Consider controlled geometry of the biostimulation zone with subsequent permeability and hydrologic management to control oxidant intrusion.
- Control/manipulate system biogeochemistry to optimize for formation of specific, desired radionuclide phases and species.

Conclusions and Recommendations

NABIR and other research has clearly shown that U(IV) and Tc(IV) are both susceptible to reaction with molecular oxygen and other select oxidants when the redox potential becomes oxidizing. These reactions, including biologic ones for uranium, can lead to the remobilization of sparingly soluble reduced radionuclides that compromises bioremediation. Discussion in the breakout session indicated that far less is known about

the oxidation process, than is known about reduction. Research understanding is insufficient to predict oxidation rate and extent in even the most studied environments (e.g., the FRC). Critical controlling variables have not yet been identified, and the relative importance of abiotic versus bacterial oxidation remains undetermined. Highly variable results have been obtained by multiple research groups because of the use of different experimental approaches and the effects of variables that are poorly understood, and therefore, uncontrolled.

The potential for oxidation is possibly the most critical research issue for bioremediation. Both laboratory and field research has shown that the reduction of U(VI) and Tc(VII) under conditions of biostimulation occurs rapidly and to sufficient extent to meet remedial objectives. While important details require resolution, there is little doubt that bio-immobilization may be accomplished under most circumstances. The key remaining issue is the long term stability of the reduced radionuclides and their rate and extent of release as oxidizing conditions inevitably return. Participants believed that multiple techniques as well as laboratory and field systems require use to understand the complexities of the oxidation process. The most fruitful experimental and modelling approaches require demonstration, because relatively little research has been performed on reduced radionuclide oxidation. All agreed that models of different types and scales are needed and require parameterization to aid in experimental interpretation, and to extrapolate results to field systems and/or different conditions. Furthermore, there was belief on the part of certain participants that the oxidation process could be controlled and/or manipulated by various approaches to minimize long-term radionuclide release.

The following are overall recommendations for additional research on abiotic and bacterial oxidation processes:

- Strive to understand the primary factors controlling reduced radionuclide oxidation and release in sediments from the microscopic to macroscopic scales.
- Seek a mechanistic understanding of the involved biogeochemical processes and reactions by integrating molecular speciation measurements with kinetic rate studies of different types.
- Identify suitable environmentally relevant model microorganisms for laboratory studies on radionuclide oxidation, including characterization of key genes/enzymes responsible (for use as molecular markers for in situ studies).
- Quantify oxidation kinetics in ways that are meaningful to the field. Incorporate understanding into biogeochemical models at different scales.
- Identify diffusive and advective transport effects on oxidation in relevant materials in both laboratory studies and field sites.
- Perform a comprehensive, integrative, multi-investigator, multi-scale field experiment on radionuclide oxidation at an appropriate field location.

Workshop Attendees (77)

Barcelona, Michael	Holden, Trish	Peyton, Brent
Bayer, Paul	Hubbard, Susan	Phelps, Tommy
Beazley, Melanie	Istok, Jack	Puzon, Geoffrey
Benner, Shawn	Jacobs, Gary	Ravel, Bruce
Blake, Diane	Jardine, Phil	Reed, Donald
Bolton, Harvey	Katz, Arthur	Reeder, Matthew
Borch, Thomas	Kelly, Shelly	Roden, Eric
Boyamon, Maxim	Kemner, Ken	Sani, Rajesh
Brooks, Scott	Khare, Tripti	Santschi, Peter
Burgos, Bill	Kitanidis, Peter	Sapp, Mandy
Busson, Gilles	Kothari, Vijendra	Shelobolina, Zhenya
Coates, John	Krumholz, Lee	Shuh, David
Criddel, Craig	Lesmes, David	Taillefest, Martial
Dayvault, Dick	Liu, Chongxuan	Tokunaga, Tetsu
Dhungana, Suraj	Livens, Francis	Turick, Charles
DiChristina, Tom	Lloyd, Jon	Vazquez, G.
Elias, Dwayne	Long, Phil	Wan, Jiamin
Fang, Yilin	Lovley, Derek	Watson, David
Fendorf, Scott	Marshall, Mathew	Webb, Sam
Fitts, Jeff	Matin, A. C.	Weber, Karrie
Fredrickson,	Melora, Melora	White, Dave
Ginder-Vogel, Mathew	Neu, Mary	Williams, Ken
Gu, Boahua	Northrup, Paul	Wu, Weimin
Hansel, Colleen	O'Loughlin, Edward	Yabusaki, Steve
Hersman, Larry	Parker, Jack	Yeh, George
	Payne, Rayford	Zachara, John