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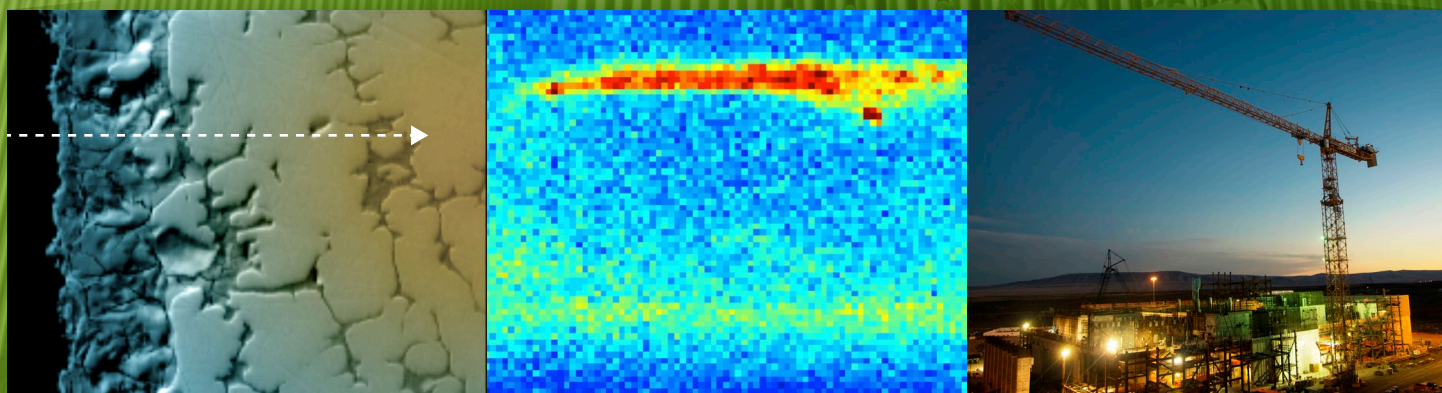


Workshop
Report

Technetium Chemistry

Science Challenges in Environmental Science and Waste Processing

March 17, 2015



Workshop Held
July 24-25, 2014

U.S. DEPARTMENT OF
ENERGY

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Technetium Chemistry

Science Challenges in Environmental Science
And Waste Processing

Workshop
Sponsored by Environmental Molecular Science Laboratory
Richland, Washington
July 24-25, 2014

Report Issued March 17, 2015

Prepared for the U.S. Department of Energy's Office of Biological and
Environmental Research under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

The Environmental Molecular Sciences Laboratory (EMSL) is a national Biological and Environmental Research (BER) U.S. Department of Energy (DOE) user facility. EMSL hosted a workshop entitled, “Technetium Chemistry – Science Challenges in Environmental Science and Waste Processing,” on July 24-25, 2014, in Richland, Washington. The primary objective of this workshop was to explore short- and long-term science challenges in fundamental technetium (Tc) chemistry that effect environmental biogeochemistry and its role in the nuclear fuel lifecycle, including waste tank chemistry, separations, and waste forms. Identifying these challenges is the first step in selecting key science gaps that are fundamental to understanding Tc reactivity, complexation. Identifying where EMSL, especially the new EMSL Radiochemistry Annex, could play an important role is the second step.

Workshop participants came from academic institutions and national laboratories, and brought considerable expertise in thermodynamics, solution chemistry, environmental chemistry and chemistry, and behavior of Tc in waste tank and potential waste forms for Tc disposal (see Appendix A for the workshop schedule and speaker list). Participants were asked to identify the role EMSL scientists and the new Radiochemistry Annex could play in addressing these challenges and what new capabilities would be needed.

The workshop participants identified the following key research challenges:

- Determine the solution speciation of Tc under extreme conditions such as those found in high-level nuclear waste tanks.
- Determine the factors that would result in the formation of low solubility Tc phases that are not subject to re-oxidation of reduced Tc(IV).
- Determine the chemical form of Tc in highly variable and complex waste forms both under *in situ* reaction conditions and *ex situ* in the final waste form.

The workshop participants identified the following principal roles for EMSL:

- Develop new experimental and computational approaches to identify and quantify Tc oxidation states and complex species at low concentration.
- Provide expertise and tools for investigating fundamental interactions of Tc with environmental materials.
- Serve as a coordinator/broker of distributed characterization resources for Tc at Pacific Northwest National Laboratory (PNNL), at partner universities, and at other national laboratories.

The Radiochemistry Annex houses complementary capabilities with instruments (see Appendix B), sample preparation and analysis facilities in a contiguous laboratory; however, participants noted additional capabilities were needed in four areas to address the above research challenges:

- Bench-top instrumentation such as ultra violet (UV) visible(VIS) and FTIR spectrometers to support existing experimental analyses
- Sample handling techniques requiring innovative development to prepare non-dispersible radioactive samples to be analyzed at EMSL

Executive Summary

- Variable temperature, electrochemical, and oxygen partial pressure *in situ* sample cells for nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR) and X-Ray Photoemission Spectroscopy (XPS).
- High-sensitivity chemical imaging approaches such as nano-Secondary Ion Mass Spectrometer (nano-SIMS) and Atomic Probe Tomography (APT) so the distribution of Tc and other elements can be determined at low concentrations.
- Ultra High Resolution Mass Spectrometry for the identification of actinide-ligand complexes that occur in the natural environment or under extreme conditions such as those found in high-level nuclear waste tanks.

We appreciate the time and thoughtful contribution from workshop participants and it is our pleasure to share the results of the Technetium Chemistry – Science Challenges in Environmental Science and Waste Processing Workshop, July 24-25, 2014.

Acronyms and Abbreviations

AIMD	ab initio molecular dynamics
DEPT	density functional perturbation theory
DOE	U.S. Department of Energy
EELS	electron energy loss spectroscopy
EMP	electron micro probe
EMSL	Environmental Molecular Sciences Laboratory
EPA	Environmental Protection Agency
EPR	electron paramagnetic resonance
EXAFS	extended x-ray absorption fine structure
Fe	iron
FTIR	Fourier transform infrared
HLW	high-level waste
ICP-MS	inductively-coupled plasma mass spectrometry
LLW	low-level waste
MCL	maximum contaminant level
MOB	metal oxidizing bacteria
MRB	metal reducing bacteria
NMR	nuclear magnetic resonance
PNNL	Pacific Northwest National Laboratory
Pu	plutonium
SIMS	secondary ion mass spectrometry
S/TEM	scanning tunneling electron microscopy
STXM	scanning tunneling x-ray Microscopy
Tc	technetium
Ti	titanium
U	uranium
XMCD	X-ray magnetic circular dichroism
XPS	X-ray photoelectron spectroscopy

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1.0 Introduction

Techneium-99 ($\beta = 292 \text{ keV}$; $T_{1/2} = 2.11 \cdot 10^5 \text{ y}$) generated from the fission of ^{235}U and ^{239}Pu is a particularly challenging isotope to manage. The element is readily oxidized to the highly mobile pertechnetate ion, TcO_4^- , in oxidizing subsurface environments (Figure 1.1).

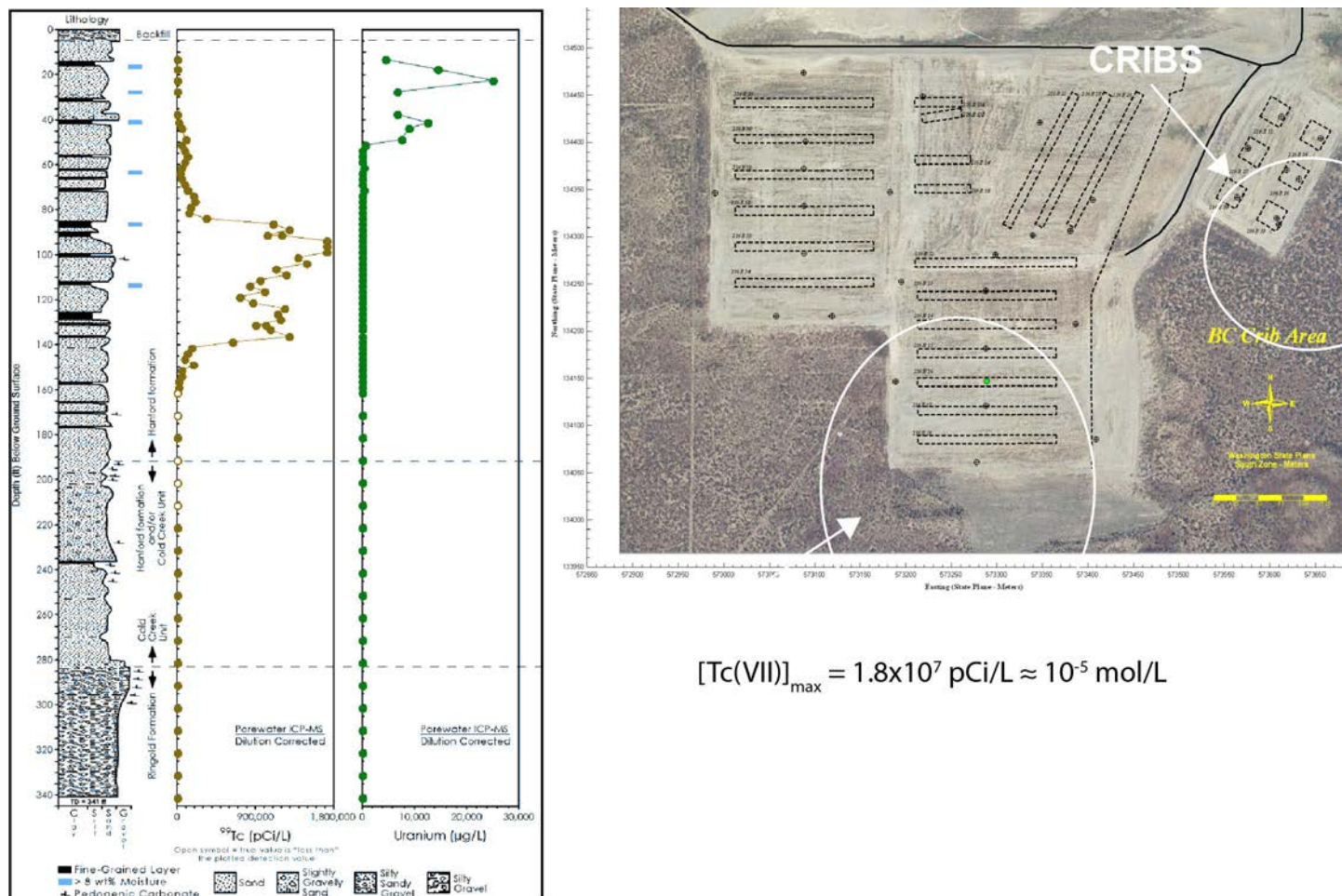


Figure 1.1 TC distribution in subsurface Hanford BC cribs illustrates potential subsurface migration. *Courtesy of John Zachara*

The high-fission yield, which leads to large inventories, long half-life, and high mobility, results in significant dose implications in performance assessments of Tc waste forms in oxidizing disposal environments such as the Waste Isolation Pilot Plant in New Mexico, Yucca Mountain in Nevada, and the Savannah River Site in South Carolina. This makes immobilization of Tc into high durability waste forms a critical technical challenge for nuclear waste management, especially when performance predictions may extend to millennia (Figure 1.2).

Techneium also displays a rich and varied chemistry due to the wide range of oxidation states (from +I to +VII) it can access and its ability to be present in either anionic or cationic forms under environmental conditions (Icenhower, et al. 2010). Therefore, understanding Tc speciation is key to several challenges including subsurface fate and transport, nuclear fuel cycle separations, and waste tank chemistry. Detailed understanding of reaction pathways of Tc from waste stream



Figure 1.2 Low-activity waste disposal in grout at the Savannah River Site shows volume of waste that may require long-term stabilization. *Courtesy of Dan Kaplan*

through processing and disposal waste form will scientifically underpin waste management strategies and result in reliable engineering solutions. Together, this improved understanding will result in reduced uncertainties, reduced risk, and reduced life-cycle cost for waste management.

With these factors in mind, this workshop report is organized by the three key challenges areas identified by workshop participants as: Tc thermodynamics and solution speciation, interfacial and surface-driven processes in environmental systems, and characterization of Tc in complex waste forms and secondary reaction products. A summary is provided for each challenge along with recommendations from the workshop participants for the role of EMSL and need for additional capabilities in addressing these challenges.

2.0 Tc Thermodynamics and Solution Speciation

A basic understanding of Tc thermodynamics and solution phase speciation is necessary for the development of enhanced technologies to separate Tc from complex waste streams as well as predict migration of Tc in the subsurface. While a great deal is known about the solution phase species of Tc(VII), much less is known about speciation of reduced forms of Tc including thermodynamic properties under variable ionic strengths and/or in complexing media found in chemically extreme environments, such as in the presence of high salt or base, or where radiolytic processes dominate. Furthermore, little is known about the effect of chelating agents or complexation reactions for reduced Tc species or the mechanisms that trigger and stabilize the formation of reduced Tc aggregates and colloidal species. The formation of reduced Tc species is complicated by Tc's multivalent nature that makes understanding details of its redox behavior critical for predictive models. This is especially important under the range of chemical conditions that typify waste tank or separations processing (Schroeder, et al. 1995).

2.1 Key Research Challenge

Determine the aqueous speciation of Tc under extreme conditions such as those found in high-level nuclear waste tanks.

A major research challenge is to determine the aqueous speciation of Tc under extreme conditions such as those found in high-level nuclear waste storage tanks. Research in Tc speciation will provide the scientific basis for advanced separations chemistry and appropriate waste storage forms. This information is also needed in subsurface reactive transport models to predict Tc mobility in the subsurface should Tc-containing waste leak from underground storage tanks.

The chemical forms of Tc in nuclear waste streams are exceedingly complex and Tc speciation can be highly variable. For example, in highly basic nuclear waste streams, such as those at the Hanford and Savannah River Sites, Tc is thought to be present both as Tc(VII) pertechnetate as well as Tc(I) carbonyl complexes (Figure 2.1). Under the highly alkaline conditions of the Hanford tanks, it is likely that $[\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_3]^+$ will be deprotonated to form $\text{Tc}(\text{CO})_3(\text{H}_2\text{O})_2(\text{OH})$ (Gorshkov, et al. 2000). In addition, it is likely that intermediate valence states also exist (Levitskaia, et al. 2014a; 2014b). Multiple oxidation states and the presence of complexants will necessitate careful design of separations processes to extract Tc as well as change the design of the Tc waste forms.

Unfortunately, progress has been limited by the lack of facilities where Tc can be handled in macroscopic quantities and characterized under conditions that prevent hydrolysis or oxidation of reduced species, the lack of model compounds for thermodynamic studies, comprehensive experimental studies under relevant solution conditions, and attention of scientists who can derive the relevant and qualified thermodynamic data. Additionally, recent advances in computational chemistry have yet to be applied broadly to Tc research. Recent advances in quantum chemistry now allow calculation of thermodynamic properties from first-principles

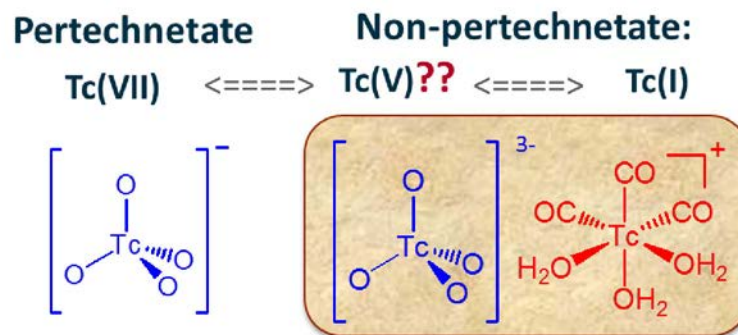


Figure 2.1 Possible forms of Tc in tank waste solutions. Non-pertechnetate species change the ability to separate Tc from low-activity waste and performance of alternative low-temperature waste forms.

Courtesy of Tatiana Levitskaia

and very limited computation studies have focused on Tc compounds and complexes. For example, using a combination of density functional perturbation theory (DFPT) and phonon analysis, the thermodynamic properties of layered technetium dichalcogenides were predicted (Weck, et al. 2013). Such theoretical methods can be applied systematically to tackle these fundamental, yet very complex challenges in Tc research and fill existing knowledge gaps; however, the computed data will need experimental verification and validation whenever possible.

2.2 Role of EMSL

Develop new experimental and computational approaches to identify and quantify Tc oxidation states and complex species at low concentration.

The primary role of EMSL is to develop enhanced methods to identify and quantify Tc oxidation states and determine the nature of Tc complexes at low concentration. The EMSL Radiochemistry Annex houses many spectroscopic and imaging components needed to partially address this challenge. These include the sub-ppm O₂ environmental chambers to conduct solubility studies under controlled redox conditions and for sample preparation. The radiological nuclear magnetic resonance spectroscopy (NMR) and electronparamagnetic resonance spectroscopy (EPR) and X-Ray Photoemission Spectroscopy (XPS) provide characterization of the oxidation state and coordination environment (bonding, number, and identity of nearest neighbors) of both solid and solution phases. However, with few exceptions, the current experimental capabilities are limited to relatively high Tc concentrations (millimolar) and solutions of simple chemical complexity.

Additionally there is a great potential to advance Tc chemistry by exploiting computational capabilities at EMSL including computational chemistry expertise, state-of-the-art computational resources (Cascade supercomputer), and software (NWChem) for thermochemical calculations and insights into Tc chemical bonding to support interpretation of spectroscopic results. For thermochemistry of Tc species in solution, NWChem has highly accurate multireference coupled-cluster methods particularly suitable for variant oxidation states, as well as exchange-correlation density functionals designed for accurate thermochemical calculations for large systems. For spectroscopic characterization of Tc species, NWChem can characterize properties using first principles methods to directly compare with experimental results. Furthermore, theoretical calculations can also provide information to systems that are inaccessible to experimental techniques such as transition states. The calculated properties include NMR and EPR quantities (e.g., chemical shifts, electric field gradients, g-shifts, hyperfine tensors) and infrared spectroscopy as well as time-dependent density functional theory methods for the calculation of UV/visible spectra and x-ray absorption spectra. For Tc solution species, solvent molecules change the chemistry through the formation of ordered first and second solvation shells. NWChem has ab initio molecular dynamics (AIMD) methods to treat Tc solutions with explicit solvent molecules at first principles level. NWChem also has an implicit solvation model Conductor-like Screening Model, which can be coupled with thermochemistry and spectroscopic calculations to include solvation effects.

The capabilities in the EMSL Radiochemistry Annex need to be expanded to facilitate Tc speciation in solutions under a wider range of controlled redox conditions where intermediate oxidation states and associated complexes can be stabilized. Specifically, electrochemical capabilities for NMR and EPR experiments are needed to exploit the synergy with the two techniques to cover the range of possible Tc oxidation states. Currently only a few spectra are available in the literature for the less common Tc oxidation states.

In addition, synthetic capabilities for the preparation of Tc solid state-compounds are needed as reference compounds for the calibration of spectroscopic techniques available at EMSL. EMSL should consider partnering with PNNL, other national and international laboratories, and academic institutions with both facilities and expertise in this area.

3.0 Interfacial and Surface-driven Processes in Environmental Systems

The Tc oxidation state changes the chemical form and attendant mobility in groundwater, soils, and the subsurface. Under most environmental conditions, Tc is present as the oxidized anionic species, pertechnetate (TcO_4^-), and migrates freely in the aqueous phase. For reduced solution species, such as $\text{TcO}(\text{OH})_2$, solubility is much lower and these species form surface complexes with iron-bearing mineral phases more readily. Three primary pertechnetate reduction mechanisms include homogeneous reduction, heterogeneous reduction, and biological reduction (Figure 3.1). Rates of reduction vary significantly and are dependent on additional processes such as sorption, presence of surface complexes, and speciation of the reductant. Primary environmental abiotic reductants are largely iron (Fe) or sulfur based.

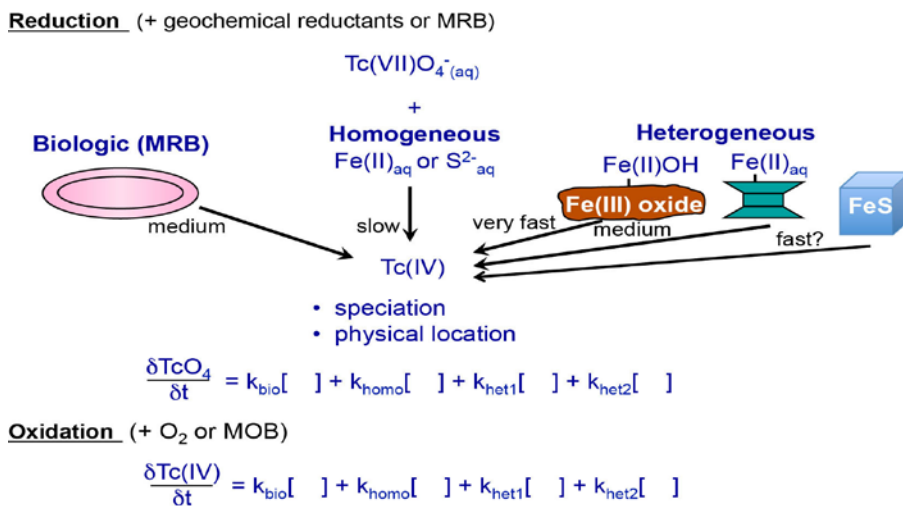


Figure 3.1 Possible Tc reduction and oxidation mechanisms include biological, heterogeneous, and homogeneous mechanisms. In the environmental biogeochemistry context, heterogeneous and biological mechanisms dominate. MRB = metal reducing bacteria, MOB = metal oxidizing bacteria. *Courtesy of John Zachara*

Reduced Tc can form both amorphous and crystalline solid oxide phases that can be incorporated in both Fe oxides and sulfides. Ionic radii and structural similarities suggest co-precipitation with Fe(III) is possible (Lukens, et al. 2012). Characterization by extended x-ray absorption fine structure (EXAFS) suggests that Tc forms polynuclear species (monomers, dimers, and trimers) coordinated to Fe-O as a result of heterogeneous reduction on goethite, hematite, and magnetite surfaces (Peretyazhko, et al. 2011; Um, et al. 2012; Liu, et al. 2012). The reduction products of Tc(VII) by sulfur species (either S^{2-} or S^0) are mixed Fe-Tc sulfides or TcS_2 (Fan, et al. 2014).

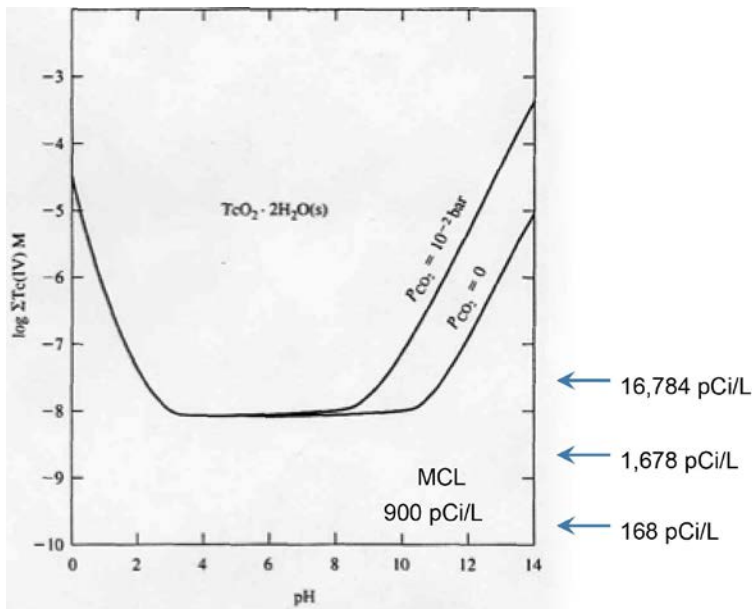


Figure 3.2 Calculated solubilities of Tc(IV) species in equilibrium with $TcO_2 \cdot 2H_2O$ as a function of partial pressure of CO_2 . Concentration of Tc species converted to radionuclide activity to compare against EPA standard MCL.

Courtesy of John Zachara

Typical products of bioreduction by metal reducing bacteria (MRB) include $TcO_2 \cdot nH_2O$ and Tc(IV) associated with ferrihydrite and phyllosilicates. Experimental studies suggest these products generally have higher solubility products than abiotic reduction products of comparable composition. The solubility of sparingly soluble Tc(IV) compounds, such as crystalline TcO_2 or amorphous $TcO(OH)_2$, are still greater than the maximum contaminant level (MCL) established by the Environmental Protection Agency (EPA) (Figure 3.2).

3.1 Key Research Challenge

Determine the factors that would result in the formation of low solubility Tc phases that are not subject to re-oxidation of reduced Tc(IV).

Remediation strategies based on *in situ* sequestration of Tc will require Tc be incorporated into a lower solubility solid phase than pure phase compounds. In addition, such lower solubility phases must be resistant to re-oxidation should the original reducing agent be removed from the subsurface system in the future. Therefore, a major research challenge is to determine factors that would result in the formation of low solubility phases that are not subject to re-oxidation of the reduced Tc(IV). This is a difficult challenge since the reduced Tc(IV) is often associated with the reducing species (e.g., Fe); hence, a potential electron transport pathway may be present in the precipitated phase (Figure 3.3).

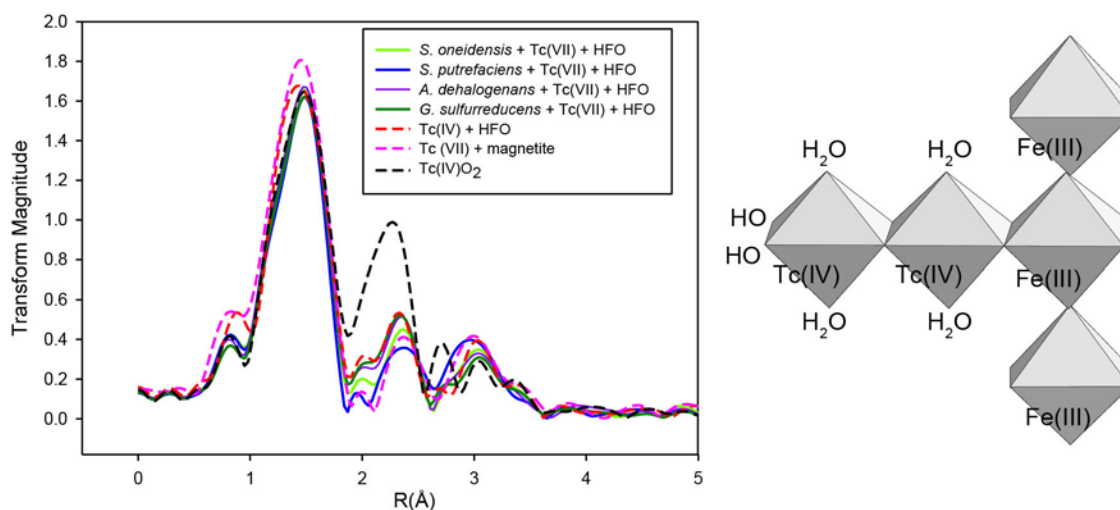


Figure 3.3 Left: Comparison of Fourier Transform of EXAFS of microbially-reduced and Abiot Tc(IV) solid phases. Right: Proposed association of reduced Tc(IV) with oxidized Fe(III) resulting from reduction of Tc(VII) by Fe(II). The close association of Tc(IV) with Fe makes TC susceptible to reoxidation via electron transfer pathways involving Fe(II).
Courtesy of John Zachara

Traditional models of Tc environmental behavior rely upon surface adsorption or pure phase solubility experiments and do not encompass processes such as incorporating Tc into mineral structures and identifying effects to Tc residence and reactivity. To address this science challenge, studies with powerful new tools are needed, such as linking advanced electron microscopy techniques (scanning tunneling electron microscopy (S/TEM)) and optical imaging with synchrotron-based scanning transmission x-ray microscopy and x-ray-magnetic circular dichroism spectroscopy (scanning transmission x-ray microscope (STXM) and X-ray magnetic circular dichroism (XMCD) techniques that are well suited to interrogate Tc distribution, oxidation state, bulk/interfacial reactivity and structural changes occurring at the atomic scale with site-specificity, in model micro- and nano-particulate Tc phases, as well as in Tc field samples (Pearce, et al. 2014). In addition, the capability to use these tools while working with radioactive samples, careful control of experimental redox conditions, and working with samples at low concentration must be developed. In this regard, experimental studies involving Tc are challenging both because of radioactivity and the specialized facilities needed to accommodate safe handling of radiological materials. Equally challenging is the need to control the redox conditions of the Tc experimental system. The interpretation of experimental results and Tc oxidation state determination without such controls can be misleading.

In environmental samples, the Tc concentration is generally quite low (e.g., less than $< 10^{-5}$ mol/L in Hanford Site sediments). While determinations of the amount of Tc present are generally possible, challenges remain in applying spectroscopic measurements to define the nature of the Tc-host relationship. As a result, many spectroscopic studies are conducted at concentrations orders of magnitude higher than that measured at environmental sites. It is not clear what the effect concentration has on chemical species present, reaction rates, or reaction processes. Nonetheless, the fundamental knowledge gained from these studies is needed to inform the design of effective waste forms and engineered barriers in long-term waste repositories and drives the need for Tc speciation at low concentrations. Understanding Tc behavior in disposal settings also remains elusive primarily because of the expected temporal and spatial changes in waste forms and engineered barriers resulting in steep and dynamic geochemical gradients. This scientific understanding will also lead to more accurate predictions of Tc mobility under far-field subsurface conditions at longer timeframes and under a broad range of environmental conditions.

3.2 Role of EMSL

Provide expertise and tools for investigating fundamental interactions of Tc with environmental materials.

EMSL's Radiochemistry Annex has resident expertise and many tools needed for investigating fundamental interactions of Tc with environmental materials. These include spectroscopic probes such as NMR, EPR, XPS, advanced imaging approaches like electron micro probe (EMP), TEM, S/TEM-EELS, and computational approaches to interpret spectroscopic results. Figure 3.4 shows an example of S/TEM-EELS used to map the incorporation, distribution, and oxidation state of Ti in ferrite spinel nanoparticles; research suggests that, as the ionic radius of Tc(IV) is very similar to that of Ti(IV) and Fe(III), Tc(IV) can also be incorporated into the spinel ferrite structure (Marshall, et al. 2014). EMSL also has environmental chambers necessary to prepare samples and prevent oxidation of reduced species and modest analytical capabilities (e.g., inductively-coupled plasma mass spectrometry (ICP-MS)). Additional capabilities available in the Radiochemistry Annex that have the potential to contribute to Tc studies include fluorescence spectroscopy.

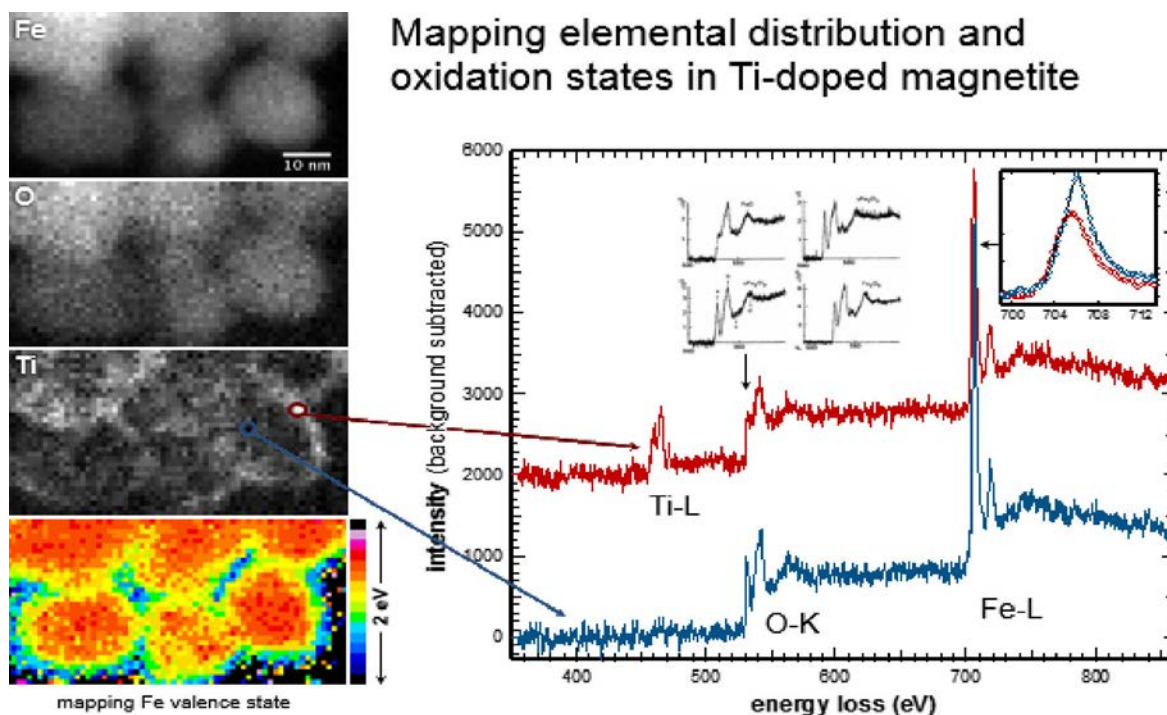


Figure 3.4 Mapping elemental distribution and oxidation state in Ti-doped magnetite using S/TEM-EELS at EMSL. *Courtesy of Pearce, Rosso, Colby and Kabius*

New capabilities that would enable impactful science outcomes include electrochemical cells for NMR and EPR to isolate and measure complexes of fixed Tc oxidation state, ultra-fast spectroscopy to capture short-lived, intermediate oxidation state species, and development of spectroscopic methods with enhanced sensitivity to measure Tc speciation at environmentally relevant concentrations. Other capabilities available in EMSL that could benefit Tc studies in the Radiochemistry Annex include Mössbauer spectroscopy to study the effect of Tc incorporation on Fe(II)/Fe(III) crystallographic distribution in Fe oxides and sulfides. In parallel, first principles studies will help interpretation of the

measured data. The plane-wave module in NWChem can study the interaction of Tc complexes with mineral surface to identify the stable configuration, characterize properties, and predict redox reactivity using density functional theory. In addition, NWChem can simulate interactions between liquid-solid interfaces using AIMD.

Microfluidic studies of reactive transport have resulted in a number of impactful studies that highlighted the importance of pore-scale mass transfer phenomena like advective and diffusive mass transfer on chemical reaction rates and the creation of steep redox gradients that can stabilize oxidized and reduced species at micron spatial scales (Zhang, et al. 2013; Boyd, et al. 2014). Applying microfluidic approaches to studies of pertechnetate and Tc incorporation in Fe oxides and sulfides could inform reactive transport models of Tc migration in the subsurface. Modeling and simulations using high-performance computing facilities and scalable computational chemistry tools developed at EMSL (e.g., NWChem) can help gain a better fundamental understanding of Tc surface chemistry and Tc incorporation and migration mechanisms in relevant oxides and sulfides.

3.3 Collaboration for Greater Scientific Impact

EMSL's Radiochemistry Annex has imaging capabilities that are complementary to synchrotron-based investigations. Coupling the light-source-based techniques of STXM and XMCD with aberration-corrected Titan S/TEM to study Fe/Tc-bearing phases will produce breakthroughs in determining reaction rates and mechanisms for important nanometer-scale processes occurring at Fe-oxide surfaces central to the form and chemical stability of Tc in nuclear waste containment and contaminated subsurface environments.

A library of model compounds with Tc stabilized in oxidation states ranging from +1 to +7 and a determination of their spectroscopic signatures would greatly facilitate understanding Tc redox reaction *in situ* and the development of mechanistic models. While the synthesis of library model compounds is largely outside EMSL's scope, EMSL could form partnerships with other research groups or serve as a mediator to direct users to these partners who have facilities and expertise to synthesize model compounds.

4.0 Characterization of Tc in Complex Waste Forms and Secondary Reaction Products

The design of nuclear waste forms is constrained by waste stream chemistry on the front end and by repository design that takes into account human and environmental risk on the back end. Additionally, nuclear waste streams are extremely diverse and complex (Poineau, et al. 2013).

4.1 Key Research Challenge

Determine the chemical form of Tc in highly variable and complex waste forms both under in situ reaction conditions and ex situ in the final waste form.

It is unlikely that a single waste form will be sufficient to accommodate the full range in waste stream chemistry. For a given waste chemistry, the corresponding waste form should accommodate variations in the waste stream composition with a minimal degree of pretreatment. In regard to Tc behavior, the fuel type and burn-up, waste stream chemistry, and any pretreatment change the amount and chemical form of Tc in the final waste form. For example, Tc could be present as solution species or incorporated in solid phases like metallic epsilon phases (Crum, et al. 2013), Fe oxy-hydroxides, and oxides (Um, et al. 2012) among others.

Currently there are both dedicated Tc waste forms and co-disposal of Tc with LLW and HLW in existing technologies (e.g., glass, cement) and emerging technologies (mineral waste forms, etc.) each with potential benefits and challenges. An additional complication exists for glass waste forms: pertechnetate solution species are volatile above 300 °C, well below typical glass formation temperatures. As a result, a large amount of Tc partitions into the volatile phase (Figure 4.1).

Several strategies for reincorporation of off-gas Tc species have been developed, yet there is a need to understand this process in greater detail. Additionally, the structure of glassy mid-range order continues to evolve over the 104-106 year time scales typical of waste repositories, and may effect Tc speciation. This is a particularly vexing challenge for the cementitious waste forms described below.

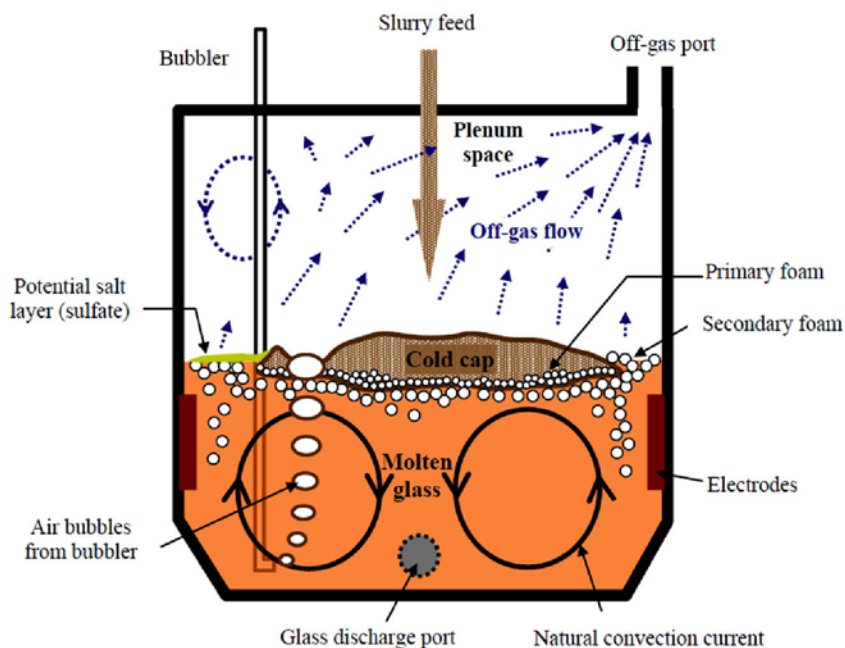


Figure 4.1 Formation of molten glass and possible phases for incorporation of Tc, including volatile off gas. *Courtesy of John Vienna*

While low temperature waste forms, such as cementitious based grouts, avoid the Tc volatility issue, the structure and chemistry of the solid crystalline, poorly crystalline and amorphous phases, and pore solutions evolve over time and can

result in transient alteration phases (Cantrell and William 2013; Kaplan, et al. 2008, 2011). Technetium initially incorporated in solid phases can be incorporated preferentially in weakly or poorly crystalline secondary alteration phases and clays. In this regard, while there has been a great deal of research in construction-grade Portland cements, relatively little high-end material characterization and structural chemistry have been conducted on cementitious waste forms with high amounts of reducing and reactive components (blast furnace slag, silica fume). Furthermore, the details of Tc speciation (type, mechanisms) are poorly understood in many waste forms. In particular, little is known about the reduction processes in cement controlling Tc speciation. Understanding the effect of aging cement on Tc speciation is a significant research challenge.

The development of Tc-specific waste forms is an emerging area of research. Research in this area is motivated in some regard by significant concentrations of Tc present in epsilon metallic phases in UO_2 waste streams, which are recalcitrant to many waste pretreatments and persist even under glass melter conditions. The fate of epsilon phases and their effect on waste form durability is not well understood and in itself presents a research challenge (McNamara, et al. 2014). Further investigation of chemically resistant mineral-based Tc-waste forms that can be incorporated into glass or cementitious waste forms has the potential to address the known weakness associated with these waste forms.

There are experimental challenges associated with the characterization of Tc in most waste forms. Even though Tc concentrations in waste forms (i.e., glass) are significantly higher than found in contaminated environmental samples, the Tc concentration in waste forms can be near the detection limit of many instruments (EPR, EMP) even under ideal conditions. Additionally, waste form matrices can be chemically complex, adding high background signals that can make measuring Tc spectra at low concentrations problematic. The lack of physical and spectroscopic data for reference compounds, even simple ones like TcO_2 or Tc metal, may not exist or the composition of important Tc phases is variable and the relevant compounds do not exist. Technetium may partition to multiple phases in a given waste form during processing (e.g., cold cap, salt phase, glass, off-gas, etc. in glass waste forms), and the ability to observe Tc behavior simultaneously in all phases during waste form processing does not exist. Both the chemical complexity of waste forms and the long time scales for which waste forms need to be certified make these systems difficult to simulate computationally. In this research challenge area, as well as others, the preparation of Tc materials for any characterization requires specialized facilities to accommodate both the radioactivity hazard and the need to control redox conditions. Therefore, a major research challenge is to determine the chemical form of Tc in diverse waste forms and their secondary alteration products both under waste form generation conditions and during aging under repository conditions.

4.2 Role of EMSL

Serve as a coordinator/broker of distributed characterization resources for Tc at Pacific Northwest National Laboratory (PNNL), at partner universities, and at other national laboratories.

The high resolution spectroscopic and imaging capabilities at EMSL's Radiochemistry Annex will enable characterization of relevant crystalline and amorphous Tc compounds. Furthermore, the annex can provide detailed characterization of waste forms and perhaps the design of new waste forms. EMSL's high performance computing facilities and the computational chemistry tools developed at EMSL can provide invaluable help to predict the existence of new Tc-containing structures and guide the experimental effort. These capabilities can assess thermal-hydro-mechanical-chemical (THMC) properties and be used for prediction of possible Tc structures, physical and spectroscopic properties (Levitskaia, et al. 2014a; Weck, et al. 2010; Weck, et al. 2011; Weck, et al. 2013).

EMSL could serve as a coordinator/broker of distributed characterization resources for Tc within PNNL and with partner universities, DOE sites/national laboratories, and international institutions. In this role, EMSL could facilitate a user's contact and collaboration with distributed radiological facilities and expertise for the synthesis of Tc model compounds or measurements that are not available within the Radiochemistry Annex. EMSL could also help initiate and nurture interactions between elements of the radiological community that focus primarily on waste form development and environmental geochemistry.

5.0 Capability Needs

While the Radiochemistry Annex houses a suite of state-of-the-art instruments, as well as specialized facilities for working with low-level radionuclides, it lacks some necessary, but routine bulk characterization instrumentation such as ultra violet visible and FTIR spectroscopy. These instruments are needed to support and complement the experimental measurements made by more advanced approaches.

The development of sample handling techniques to reduce the contamination risk of potentially dispersible samples would greatly expand possible material characterization capabilities. For example, nanoparticles are believed to significantly effect observed chemical properties, yet examination of nanoparticles, or loose powders, using TEM currently would be prohibited due to their potential dispersibility without new sample handling approaches.

There is a need to develop *in situ* sample cells for variable temperature, electrochemical and oxygen partial pressure conditions to stabilize intermediate species and to enable *in situ* tracking of Tc in solid, liquid, and gas phases under simulated waste form processing. These specialized sample environments are especially recommended for the NMR and EPR spectroscopic capabilities.

High-sensitivity chemical imaging approaches such as nano-Secondary Ion Mass Spectrometer (nano-SIMS) and Atomic Probe Tomography (APT) so the distribution of Tc and other elements can be determined at low concentrations. Both NanoSIMS and APT approaches are under high demand within EMSL for non-radiological samples.

Ultra High Resolution Mass Spectrometry for the identification of actinide-ligand complexes that occur in the natural environment or under extreme conditions such as those found in high-level nuclear waste tanks. Currently there are only a few high resolution mass spectrometry instruments that are available for the analysis of radiological samples, especially for samples that contain radionuclides other than Uranium.

6.0 Conclusion

Technetium chemical behavior remains an enigma in for both the environmental remediation of groundwater and subsurface sediments and the processing of nuclear waste for incorporation into waste forms. Its multivalent chemistry results in highly variable chemical behavior under both environmental and in engineered chemical processing systems. From a fundamental chemistry perspective there is a need for the synthesis, spectroscopic examination, and computational modeling of Tc model compounds as well as Tc incorporation into environmentally relevant minerals and wasteforms. Research conducted at EMSL's Radiochemistry Annex and in coordination with other radiological research facilities can play important role in addressing these needs.

Appendix A

Workshop Agenda

Appendix A

Radiochemistry Annex Workshop

July 24-25, 2014
EMSL Room 1077

Objective: Determine short and long term science challenges in Tc chemistry related to nuclear fuel lifecycle including waste tank chemistry, separations, waste forms, and environmental biogeochemistry

AGENDA

Thursday, July 24	
7:30 a.m.	Breakfast
8:00 a.m.	Introductory Remarks: Nancy Hess/Andy Felmy
8:15 a.m.	Plenary Speaker: Joe Rard (LLNL Retired), <i>Tc chemistry and thermodynamics overview</i>
8:45 a.m.	Plenary Speaker: John Zachara (PNNL), <i>Tc environmental chemistry</i>
9:15 a.m.	Overview Talk: Al Sattelberger (ANL), <i>Tc chemistry</i>
9:30 a.m.	Overview Talk: John Vienna (PNNL), <i>Tc in wastefoms</i>
9:45 a.m.	Overview Talk: Frederic Poineau (UNLV), <i>Tc in nuclear fuel cycle</i>
10:00 a.m.	Break
10:30 a.m.	Science Challenges: <ul style="list-style-type: none"> • Carolyn Pearce (University of Manchester) • Nathalie Wall (WSU) • Eunja Kim (UNLV) • Sam Bryan (PNNL) • Lynn Francesconi (Hunter College) • Tatiana Levitskaia (PNNL) • Dan Kaplan (SRNL) • John McCloy (WSU) • Wooyong Um (PNNL) • George Goff (LANL)

12:00 p.m.	Lunch - NW Chem presentation by Ping Yang (PNNL)
1:00 p.m.	Rad Annex Tour and PNNL Speakers: <ul style="list-style-type: none"> • Herman Cho – NMR • Mark Engelhard/Eugene Ilton – XPS • Jim McKinley – EMP • Zheming Wang – LIFS • Tom Wietsma – Analytics • Bruce Arey – FIB/SEM • Danny Edwards - TEM
3:00 pm	Science Challenge - discuss and selection of topics
5:00 p.m.	Adjourn for the day
6:00 p.m.	Dinner (location to TBD)
Friday, July 25	
8:00 a.m.	Kurt Gerdes (EM–20) EM perspective on Tc challenges
8:15 a.m.	Writing Working Group Session (Rooms 1077, 1185, 2185, 1385)
10:30 a.m.	Report out from working groups
11:30 a.m.	Summary discussion
12:00 p.m.	Adjourn

Other Attendees

Albert Kruger (ORP)	Scott Lea (EMSL)
Alex Telmouri (EM-20)	Dave Koppenaar (EMSL)
John Stuart (WSU)	Larissa Gribat (WSU)
Sue Clark (WSU)	Jamie Weaver (WSU)
Dawn Wellman (PNNL)	Marc Bowden (EMSL)
Ian Farnan (Cambridge)	Chris Brown (PNNL)
Karl Mueller (EMSL)	Eric Walter (EMSL)
Nancy Washton (EMSL)	

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Appendix B

Radiochemistry Annex Instrumentation

Radiochemistry Annex Instrumentation

The Radiochemistry Annex offers instruments for advanced imaging and chemical speciation for characterization of radioactive environmental samples including elemental composition, chemical speciation, oxidation state determination, mineral identification, spatial associations, mineral/microbe association, chemical solubility, and calorimetry.

Advanced Imaging

Focused Ion Beam/Scanning Electron Microscope – FEI Quanta 3D FEG

- 3D section analysis morphology, structure and composition and using focused ion beam
- Electron backscattering diffractions/energy dispersive x-ray spectroscopy software for elemental mapping

Scanning Electron Microscope – JEOL 7600F

- Ultra high resolution imaging, 1.5 nm, with analytical functionality
- Large variety of detectors for secondary electrons, backscattered electrons, EDS, WDS, EBSD, CL

Transmission Electron Microscope - JEOL Atomic Resolution Microscope 200F

- Operates in either TEM or STEM-CS spherical aberration corrected mode
- Useful magnification: sub-angstrom on ideal samples
- Narrow field emission source with 0.33 eV resolution producing a coherent electron beam
- Gatan Electron Energy Loss Spectrometer (EELS) provides oxidation state and chemical speciation information at high spatial resolution
- JEOL Centurio energy dispersive detector
- High angle, dark field detector

Electron Microprobe - JEOL JXA-8530F

- Analysis solid-phase elemental concentrations at ppm levels with 5 independent detectors
- High spatial resolution scanning electron microscope with combined compositional information
- Cathodoluminescence imaging

Atomic Force Microscope (Scanning Probe Microscope) - DI Nanoscope IV

- *In situ* examination of chemical reactions, mineral precipitation/dissolution on mineral surfaces at atomic resolution

Chemical Speciation

Nuclear Magnetic Resonance Spectrometer - Bruker 750 MHz 89 mm wide bore

- Highest-field radiological NMR in world
- High sensitivity and spectral resolution
- Liquid and MAS solid capability for the study of environmental and radiological samples
- Provides chemical state/structure information

Nuclear Magnetic Resonance Spectrometer - Magnex 100 MHz 130 mm wide bore

- Ideal for direct measurement of actinide nuclei or samples with paramagnetic content

Electron Paramagnetic Resonance Spectrometer - Bruker ESP 300E CW with the following:

- Measurement of paramagnetic solid or liquid samples
- X, S, Q-band
- Liquid He sample stage

X-ray Photoelectron Spectrometer - Kratos Axis 165/Ultra

- Dual Al K_{α} (1486.6 eV) / Ag L_{α} (2984.7 eV) monochromatic X-ray sources
- Guaranteed spatial resolution in imaging mode $< 3 \mu\text{m}$
- Variable temperature sample environment (-150°C to 600°C)
- Multi-technique XPS system – this system also provides UPS, ISS, and TPD from the same sample surface.
- Cluster Ar ion gun – possible to obtain chemical state information from XPS depth-profiling of soft materials because of the minimal ion beam modification of the material

Fluorescence spectrometer – Photon Technology International TimeMaster

- Fluorescence lifetime measurements
- Wavelength coverage from 240 to 990 nm with N2 laser pump dye laser
- Pulsed excitation, low rep rate

Fluorescence Spectrometer – Photon Technology International QuantaMaster 400

- Xenon arc lamp
- 185-1010 nm emission, PMT detection and single shot transient digitizer
- 0.022 nm spectral resolution
- Attomolar detection (fluorescein in 0.1 M NaOH)

Sample Preparation and Quantitation

- Four dual-station environmental chambers sub ppm O₂
- ICP-MS
- GC-MS
- IC
- Powder X-ray diffractometer
- CNS analyzer
- Alexsys molten solvent Calorimeter