EMSL Research and Capability Development Proposal – March 2012

Sealed Probes for NMR Spectroscopy of Radioactive Solids

EMSL Proposal Authors

Nancy Washton

Jesse Sears

Additional EMSL Staff

Hardeep Mehta

Karl Mueller

David Hoyt

Non-EMSL (Partner) Investigators

Herman Cho (Fundamental and Computational Sciences Directorate, EMSL Wiley Research Fellow)

Background and Objectives

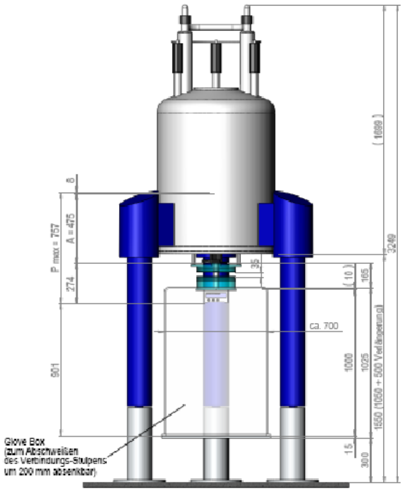
When the NMR facility in the EMSL Radiological Annex opens in FY 2013, it will have the most advanced and comprehensive array of NMR instrumentation of any radiochemistry laboratory in the world. To achieve the promise of full radiological operations by the opening date, it is imperative that work begin immediately to prepare the customized probes and accessories needed for safe experimentation with radioactive materials.

Much of the initial work on these instruments will involve high-resolution measurements of solid samples. Because of the need to ***spin solid samples at high speeds*** for resolution enhancement, the highest priority and most challenging task for radiological preparedness will be the development of methods to ensure the secure containment of radioactive materials during magic-angle-spinning (MAS) experiments. *The goal of this intramural project will be to achieve readiness for radiological NMR and demonstrate cutting-edge capabilities with preliminary experiments on radioactive samples in support of EMSL user projects. Three probes that provide secure containment of radioactive solid samples while maintaining state-of-the-art performance in spinning, temperature control, sensitivity, and power handling specifications will be designed, built, and tested in-house to achieve this goal.*

Technical Approach For Capability Development

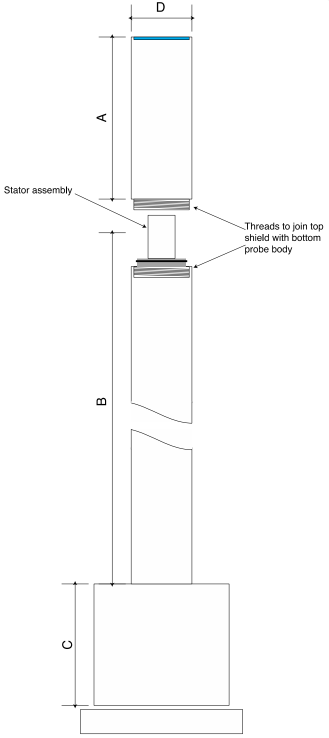
Two approaches have been previously proposed to meet the safety challenges of MAS experiments with radioactive solids. The **secure rotor** method,[1,2] first developed by a Cambridge University/PNNL collaboration and reported in 2004, involves the encapsulation of the radioactive sample in an MAS rotor with multiple layers of containment. An attractive feature of this approach is that off-the-shelf commercial probes may be used since the sample holder and not the probe serves as the primary fail-safe layer of radioactive containment. However, the extra layers of encapsulation of a secure rotor greatly reduce the amount of sample that can be inserted in the probe's sensitive volume; in the 7.5 mm MAS rotor design successfully used in past work, less than 25% of the usual sample volume remains in a triple containment secure rotor. Furthermore, this method requires the use of large rotors that cannot reach the high spinning speeds desired for optimal resolution enhancement.

A second strategy for radioactive containment of NMR samples is currently under development at the new radiological NMR facility at the Institute for Transuranic Elements (ITU) in Karlsruhe, Germany. The ITU group proposes to insert a plexiglass tube inside the bore of their wide-bore magnet to serve as a shield between the NMR probe and the laboratory environment. The tube is sealed at the top, and connected to a glove box at the bottom, forming a closed space where the probes and radioactive samples reside (concept drawing at right). As in the secure rotor method, the ***glove box*** approach allows the use of commercial probes. However, items that enter the glove box space would be considered contaminated, severely hampering the performance of everyday operations such as adjustment, servicing, and maintenance of probes. Moreover, the mounting of a glove box to a 750MHz magnet entails significant costs and laboratory modifications, including a magnet pedestal and ~7 m high ceiling heights. We note that the use of a glove box would also contravene PNNL's radiation safety policy, which is to confine radioactive contamination to the smallest spaces possible. At present, the glove box strategy is not feasible for the EMSL Radiological Annex facility.



Glove Box - Konfiguartion
NMR 400 mit WB Shimcoil S2 und Pobe S5
Magnetstand um 500 mm verlängert

The drawbacks of these previous approaches would be avoided if ***probes with primary and secondary sealed bodies*** could be constructed as the primary mode of radioactive containment. The figure at the top of the next page shows a concept drawing of such a probe. The concept incorporates design features that have been tested and validated in other contexts for the containment of radioactive materials. In the event of a rotor failure during a spinning experiment, the primary and secondary containers would completely contain the spread of radioactive contamination to within the enclosed rotor housing. This ensures the probe body, exterior, and surrounding areas are maintained in a contamination-free state.



Although the unique characteristic of this probe will be its sealed interior, the design will incorporate other noteworthy features that will improve its performance and enhance safety. For example, transmission line circuit elements will be used in the body of the probe, allowing the tuning and matching capacitors to be positioned outside the bore of the magnet and creating more room inside the probe and more flexibility in the placement of gas lines, cables, check valves, filters, etc. Another advantage to this type of containment is the ability to utilize larger sample volumes, thereby increasing signal to noise and decreasing overall experiment time.

Probes for both the new EMSL 750 MHz instrument and the RPL 300 MHz spectrometers will be constructed in this project. The availability of probes for two widely dispersed magnetic fields will be a particularly valuable asset for interpreting spectra of quadrupolar nuclides, *i.e.*, nuclides with nuclear spin quantum number ≥1, which are usually characterized by one interaction that scales linearly with magnetic field (the chemical shift) and one interaction that scales inversely with the field (the second order quadrupolar interaction). In NMR studies of quadrupolar nuclides, which comprise the large majority of NMR-active isotopes, the acquisition of spectra at two different fields can greatly improve the reliability of determinations of chemical shift and electric field gradient tensors.

Construction of the 300 MHz probe (referred to as probe 1, below) before the construction of the 2nd and 3rd probes for the EMSL 750 instrument serves an important practical purpose. Since the RPL NMR laboratory is currently approved for experiments on radioactive samples, the construction of a probe for this instrument allows us to proceed with a realistic test of our design in advance of the opening date of the EMSL Radiological Annex. Testing of this first probe also minimizes the chance that flaws in the original design are propagated to subsequent probes.

The following deliverables will result from this project.

- *Three NMR probes for the EMSL Radiological Annex NMR Facility*. It is anticipated that these probes will be accessible to users when the NMR facility is commissioned for radiological experiments. The availability of these probes to users will advance the EMSL's reputation as the world's leader and destination laboratory for radiological NMR researchers.
- *Publications in peer-reviewed journals*. Scientific projects, especially in the area of the transport and fate of radionuclides in the environment, will be the main focus of the research that will be undertaken during this intramural project (see below). In addition, due to the novelty of these probes, we consider this work suitable for publications in journals such as *Review of Scientific Instruments*, *Solid State NMR*, *Journal of Magnetic Resonance*, etc. The test experiments we plan for these probes using the RPL 300 MHz instrument might well yield data on uranium and plutonium oxides that merits publication.
- *Invention reports and patents*. To our knowledge, no comparable sealed body NMR probe has yet been reported. In addition to radioactive samples, we expect that such probes will be of commercial interest in contexts requiring the examination of highly hazardous samples of all kinds, such as biological pathogens or toxic chemicals, where fail-safe containment is a primary consideration.

We propose a three-year duration for this project, encompassing a number of tasks. In addition to the actual construction of the probes, the plan below outlines the several other steps needed to achieve readiness for radiological NMR experiments. During each task, PNNL radiological engineers will be consulted to confirm that the hardware and procedures are proceeding along a path that will result in a final product approved for radiological use. Several of these tasks may proceed concurrently.

Task 1 (Year 1): Probe design, first iteration (Sears, Cho, Mueller). Three months

Task 2 (Year 1): Formulation of procedures for packing and test-spinning samples (Washton, Hoyt, Cho). Two months

Task 3 (Year 1): Probe construction and assembly (Sears, Mehta, Cho). Three months

Task 4 (Year 2): Probe testing (Cho, Washton, Mueller). Six months

Task 5 (Year 2): Writing of formal procedure documents (Washton, Cho). Two months

Task 6 (Year 2): Presentation of hardware and written procedures for final approval by Radiological Safety engineers (Cho, Hoyt, Washton). Two months

Task 7: Construction (Year 2) and testing (Years 2 and 3) of probes 2 and 3 (Sears, Cho, Mehta, Washton, Mueller). Six months

Task 8 (Year 3): Science projects, first science examples (Washton, Cho, Mueller). Six months

Task 9 (Year 3): Preparation of peer-reviewed publications (Washton, Cho, Mueller, Sears). Four months

First Science

The lead PI (Washton) and Dr. Karl Mueller are part of a multi-laboratory/university research team that is investigating the fate of uranium and strontium radionuclides in waste-weathered sediments. This project seeks to predict reactive contaminant migration in Hanford sediments that have received acidic uranium and strontium bearing waste streams. They hypothesize that acidic waste infusion results in silicate mineral transformations that exert strong controls on uranium and strontium speciation and mobility. Their research approach involves iterative laboratory, modeling and field scale studies. By combining bench-scale simulations of sediment weathering, spectroscopic investigation of contaminant speciation, (especially NMR studies) and meso-scale studies of contaminant transport, they are attempting to constrain the continued development of a mechanistic reactive transport model of coupled mineral transformation and radionuclide sequestration in the Hanford vadose zone.

Long-term, time series batch and flow-through column reactor experiments will be employed to assess coupled mineral transformation and contaminant partitioning reactions postulated to have affected Hanford vadose zone sediments when the cribs were active. *Each of these reacted samples will contain radioactive uranium (at natural abundance), which complicates analysis in standard analytical chemistry laboratories. Especially difficult is the use of techniques such as magic-angle spinning NMR, where a rotor crash could cause significant dispersal of the sample into the laboratory atmosphere.* Contaminant uptake to weathering sediments is expected to involve adsorption to native sediment minerals, as well as adsorption, co-precipitation, and occlusion with neoformed solids resulting from silicate mineral weathering promoted by the waste interaction.[4-8] To assess pathways of U and Sr uptake, solid phase reactants and products will be interrogated for quantitative mineral composition and contaminant bonding environment, and results will be subjected to direct comparison with core samples obtained in the field subsurface sampling at the crib sites. This lab/field dialogue will help to corroborate bench-scale results, and lab-generated sediments will also be used in subsequent experiments to assess contaminant release kinetics. Since much of the initial acid buffering and reaction with acidic waste occurred in Hanford formation (HF) sediments, those sediments will be the primary focus of this research. Each of the cribs received different types of waste when active. Although the chemical composition of the waste was not reported precisely during activity, it has been simulated by the Hanford Soil Inventory Model (SIM).[9] The SIM data guides the overall experimental approach to long-term batch and column reaction studies to employ three distinct solution compositions representative of the main waste streams discharged to the cribs. Time series characterizations of the experimental systems will provide a unique set of data to constrain mineral transformation rates as a function of treatment, and their influence on contaminant uptake or release from the solid phase.

Building on the approach used in prior studies of HF reaction with hyperalkaline solutions, 400 g of uncontaminated sediment will be reacted in triplicate with 20 L of synthetic crib waste leachate (SCWL, pre-equilibrated with atmospheric CO_2) over time scales ranging from 1 week to 30 months, similar to the group's prior studies for alkaline solutions.[3,4,10-12] Three SCWL solutions represent a best current estimate of the chemistry of the two main streams that were discharged to the cribs (Dilute/Concentrated miscellaneous uranium nitrate hexahydrate, UNH and Spent Nitric Acid, SNA). Whereas two of the streams represent acid and neutralized end-members (pH 1.6 and 7.0), we also use a third stream simulating a mixture of the two and comprising an intermediate pH (4.0). Based on SIM estimates, SCWL-1 (pH 1.6 SNA simulant), SCWL-2 (pH 7 UNH simulant), and SCWL-3 (pH 4 SNA and UNH mixture) will be prepared. At each sample point, a mass of 10 g of weathered sediment will be separated from solution by displacement and then freeze-dried prior to analysis. The elemental composition of the filtered solution will be determined by pH electrode, ICP-MS (for major and trace elements, including Sr and U), ion chromatography (for NO_3^-, PO_4^{3-}, SO_4^{2-}, F^- and Cl^-) and inorganic carbon analyzer. Elemental phase partitioning during weathering will help in identifying dissolution and precipitation dynamics.

Solid-state NMR (SSNMR) methods probe structure in crystalline minerals,[13] short-range order in amorphous phases,[14] and local binding environments of sorbed species.[15] SSNMR will be used in conjunction with XRD, EXAFS and vibrational studies of sediments and weathered materials for understanding of sediment structural transformation (at the molecular level) and contaminant sorption and siting. SSNMR has been utilized to follow the kinetics of transformation of clay minerals and Hanford sediments.[3,10-12,16-17] The NMR methods used in these studies will involve routine one-pulse characterization (for ^{23}Na, ^{27}Al, and ^{29}Si studies), double-resonance methods (^{1}H/^{29}Si, ^{1}H/^{27}Al, ^{27}Al/^{87}Sr, ^{29}Si/^{87}Sr, and others), and triple-resonance experiments (especially new ^{1}H/^{29}Si/^{87}Sr and ^{1}H/^{27}Al/^{87}Sr methods). The latter methods will provide the correlation of ^{29}Si or ^{27}Al resonances to the siting of cations such as ^{87}Sr. The advanced methods to be utilized include cross-polarization MAS, rotational-echo-double-resonance NMR[18] and transfer of populations in double-resonance NMR.[19] ^{27}Al multiple-quantum MAS (MQMAS) experiments[20] will also be utilized to follow changes in the local environments of aluminum atoms as samples are transformed via chemical weathering. For direct-detection of ^{87}Sr, both single-pulse and quadrupolar Carrr-Purcell Meiboom-Gill (QCPMG) echo sequences[21-24] will be utilized for discrimination of Sr in symmetric or highly-mobile environments from that in asymmetric binding sites. Various preparatory pulse schemes such as double frequency sweep (DFS), fast amplitude modulation (FAM), and rotor-assisted population transfer (RAPT) will also be used to further enhance the sensitivity of ^{87}Sr signals in echo and QCPMG experiments.[22,25-27]

Poor constraint on our knowledge of the *reactive surface area* of geological samples imposes limits on our ability to model field-scale weathering processes. Since this parameter is subject to change over the course of weathering processes, reactive surface area is expected to exhibit significant variability over the course of long-term contaminant aging in acidic-waste impacted sites. Washton, Mueller, and coworkers have recently demonstrated the use of ^{19}F MAS NMR of a reactive probe molecule (a fluorinated chlorsilane) for the determination of reactive surface area in low- to moderate-surface area materials.[28-30] This new technique will be directly applied to Hanford sediment samples before and after the weathering process.

EMSL User Program and Science-Theme Related Objectives and Benefits

A survey of additional experiments that would be made possible by the construction of the three radiological MAS NMR probes has been presented in the 2006 report and proceedings of the "EMSL Radiological NMR Spectroscopy Meeting" (published as Report No. PNNL-16045, Pacific Northwest National Laboratory, Richland, Washington, 2006).[31] The design parameters of these probes have been selected to provide maximum coverage of the diverse array of solid-state NMR experiments described in this document. Of special note is the target bandwidth, which will be extended to access the high NMR frequency of the ^{3}H isotope and the low frequencies of actinide isotopes such as ^{239}Pu. The frequencies of these isotopes fall outside the standard range of commercial probes.

As is true for non-radioactive samples, NMR can be used for many different purposes in **radiological contexts**, which fit well within the bounds of the EMSL Science Themes. In particular, the *Biogeosciences* and *Science of Interfacial Phenomena* Science Themes would be well represented by proposals to utilize these novel probes. As noted above, fundamental studies of interfacial reactions that include Sr, Cs, and U radionuclides from the Hanford Site and elsewhere are studied by K. T. Mueller, N. M. Washton (PNNL/EMSL) and collaborators (J. Chorover, P. O'Day, W.Um) in a currently funded User Proposal (Science Theme Proposals 40064), and would utilize these probes. In another proposal, Joe Ryan (APEL/PNNL) is studying nuclear waste forms (through Open Call Proposal 46043), and an extended Science Theme proposal will be submitted next year that would include radioactive elements. Other proposals will be solicited exploring highly active, fissile radioisotopes, and particularly the transuranics.

Development Team

Qualifications of Investigators

The members of this project team have the demonstrated expertise to ensure successful completion of all phases of this project, including high-resolution solid state NMR spectroscopy (Mueller, Washton, Cho), probe design and construction (Sears, Mehta), and radiological sample handling (Cho). Many of the early innovations in radiological NMR spectroscopy were first developed and tested at PNNL.

References

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BIOGRAPHICAL SKETCH	
Name (Last, first, middle initial) Mueller, Karl T.	**Position Title** Laboratory Fellow (Level VI) Science Lead in Magnetic Resonance

Education/Training (Begin with baccalaureate or other initial professional education and include postdoctoral training)

Institution and Location	**Degree** (if applicable)	**Year(s)**	**Field of Study**
University of Rochester Rochester, NY	B.S.	1981 - 1985	Chemistry
Cambridge University Cambridge, UK	C.P.G.S.	1985 -1986	Natural Sciences/Chemistry
University of California, Berkeley Berkeley, CA	Ph.D.	1986 - 1991	Chemistry
University of British Columbia Vancouver, BC	Postdoctoral researcher	1991-1993	Chemistry

Research and Professional Experience

Appointments.

2010 - present Magnetic Resonance Science Lead and Laboratory Fellow
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
2007 - present Professor, Department of Chemistry
Penn State University
1999 - 2007 Associate Professor, Department of Chemistry
Penn State University
1993 - 1999 Assistant Professor, Department of Chemistry
Penn State University

Publications.

Five Publications Most Closely Related to the Proposed Project (from over 80 publications in refereed journals since 1986)

N. M. Washton, S. L. Brantley, and K. T. Mueller, "Probing the Molecular-Level Control of Aluminosilicate Dissolution: A Sensitive Solid-State NMR Proxy for Reactive Surface Area", *Geochimica et Cosmochimica Acta* **72**, 5949-5961 (2008).

M. C. Davis, W. J. Brouwer, D. J. Wesolowski, L. M. Anovitz, A. S. Lipton, and K. T. Mueller, "Magnesium Silicate Dissolution Investigated by ^{29}Si MAS, ^{1}H-^{29}Si CP MAS, ^{25}Mg QCPMG, and ^{1}H-^{25}Mg CP QCPMG NMR", *Physical Chemistry Chemical Physics* **11**, 7013-7021 (2009).

J. C. Johnston, Robbie J. Iuliucci, J C. Facelli, G. Fitzgerald, and K. T. Mueller, “Intermolecular Shielding Contributions Revealed by Modeling the ^{13}C Chemical-Shift Tensors of Organic Single Crystals with Plane Waves”, *Journal of Chemical Physics* **131**, 144503-144513 (2009).

C. P. Morrow, J. D. Kubicki, K. T. Mueller, and D. R. Cole, “A Description of Mg^{2+} Release from Forsterite using Ab-Initio Methods”, *Journal of Physical Chemistry C* **114**, 5417–5428 (2010).

R. L. Sanders, N. M. Washton, and K. T. Mueller, “Measurement of the Reactive Surface Area of Clay Minerals Using Solid-State NMR Studies of a Probe Molecule”, *Journal of* Physical *Chemistry C* **114**, 5491–5498 (2010).

Five Additional Publications

N. Tsomaia, S. L. Brantley, J. P. Hamilton, C. G. Pantano, and K. T. Mueller, “NMR Evidence for Formation of Octahedral and Tetrahedral Al and Repolymerization of the Si Network During Dissolution of Aluminosilicate Glass and Crystal”, *American Mineralogist* **88**, 54-67 (2003)

R. Fry, N. Tsomaia, C. G. Pantano, and K. T. Mueller, “^{19}F MAS NMR Quantification of Accessible Hydroxyl Sites on Fiberglass Surfaces”, *Journal of the American Chemical Society* **125**, 2378-2379 (2003).

L. J. Criscenti, S. L. Brantley, K. T. Mueller, N. Tsomaia, J. D. Kubicki, “Theoretical and ^{27}Al CPMAS NMR Investigation of Aluminum Coordination Changes During Aluminosilicate Dissolution”, *Geochimica et Cosmochimica Acta* **69**, 2205-2220 (2005).

R. A. Fry, K. Kwon, J. D. Kubicki, and K. T. Mueller, “A Solid-State NMR and Computational Chemistry Study of Mononucleotides Adsorbed to Alumina”, *Langmuir* **22**, 9281-9286 (2006).

S. Nangia, N. M. Washton, K. T. Mueller, J. D. Kubicki, and B. J. Garrison, “Study of a Family of 40 Hydroxylated β-Cristobalite Surfaces Using Empirical Potential Energy Functions”, *Journal of Physical Chemistry C* **111**, 5169-5177 (2007).

Synergistic Activities and Experience

Research Corporation Cottrell Scholar (1996), Beckman Young Investigator (1996), Camille Dreyfus Teacher-Scholar (1997), Sloan Research Fellow (1999), Varian Lecturer (2007), and AAAS Fellow (2011).

Moderator of discussions on “Ethics in Chemical Research” for students at many different stages of their careers (high school, undergraduate, graduate) (1996 – present).

Member of Executive Committee for Penn State’s *Center for Environmental Chemistry and Geochemistry* (1997–2008); Director of the Center (2004 – 2008).

Member of organizing committee for NMR Symposium for Rocky Mountain Conference on Analytical Chemistry (2000-2006); Symposium chair (2006).

Member of PSU Graduate Council (2001 – 2008); chair of Graduate Council Committee on Fellowships and Awards (2005 – 2008).

BIOGRAPHICAL SKETCH			
Name (Last, first, middle initial) Washton, Nancy M.		**Position Title** Experimental, Analytical Chemist/Scientist (Level III)	
Education/Training (Begin with baccalaureate or other initial professional education and include postdoctoral training)			
Institution and Location	**Degree** (if applicable)	**Year(s)**	**Field of Study**
University of Nevada Las Vegas Las Vegas, NV	B.S.	1997 - 2001	Chemistry
Penn State University University Park, PA	Ph.D.	2001 - 2007	Chemistry

Research and Professional Experience

Appointments.

2010-present Experimental, Analytical Chemist/Scientist
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
2008-2010 Senior Research Chemist in Fiberglass Sciences and Technology
PPG Industries, Inc
2007-2008 Assistant Professor of Chemistry
The Community College of Baltimore County (CCBC)
2005 (summer) Research Intern
ExxonMobil Research & Engineering Corporation, Annandale NJ

Publications.

Five Publications Most Closely Related to the Proposed Project

N. Washton, S. L. Brantley, and K. T. Mueller, "Toward a Quantitative Understanding of Reactive Surface Hydroxyl Density in Feldspar Minerals". Proceedings of the Eleventh International Symposium on Water-Rock Interaction (WRI-11), R. Wanty & R. Seal II, Eds., Saratoga Springs NY USA. pp. 1665-1669, 2004.

V. L. Budarin, J. H. Clark, S. E. Hale, S. J. Tavener, K. T. Mueller, and N. M. Washton, "NMR and IR Study of Fluorobenzene and Hexafluorobenzene Adsorbed on Alumina", *Langmuir* **23**, 5412-5418 (2007).

S. Nangia, N. M. Washton, K. T. Mueller, J. D. Kubicki, and B. J. Garrison, "Study of a Family of 40 Hydroxylated β-Cristobalite Surfaces Using Empirical Potential Energy Functions", *Journal of Physical Chemistry C* **111**, 5169-5177 (2007).

N. M. Washton, S. L. Brantley, and K. T. Mueller, "Probing the Molecular-Level Control of Aluminosilicate Dissolution: A Sensitive Solid-State NMR Proxy for Reactive Surface Area", *Geochimica et Cosmochimica Acta* **72**, 5949-5961 (2008).

R. L. Sanders, N. M. Washton, and K. T. Mueller, "Measurement of the Reactive Surface Area of Clay Minerals Using Solid-State NMR Studies of a Probe Molecule", *Journal of* Physical *Chemistry C* **114**, 5491–5498 (2010).

Additional Publications

L. Sapochak. A. Padmaperuma, N. Washton, F. Endrino, G. Schmett, J. Marshall, D. Fogarty, P. Burrows, S. Forrest. “Effects of systematic methyl substitution of metal (III) tris(n-methyl-8-quinolinolato) chelates on material properties for optimum electroluminescence device performance.” *Journal of the American Chemical Society* **123**, 6300-6307 (2001).

N. M. Washton, K. C. Earnheart, D. G. Sykes, M. Ucak-Astarlioglu, and K. T. Mueller, “Towards the Integration of Liquid- and Solid-State NMR Across the Undergraduate Curriculum”, *ACS Symposium Series 969*, “Modern NMR in Undergraduate Education”, 20-35 (2007).

Synergistic Activities and Experience

Best Oral Presentation, 9th Annual Environmental Chemistry Student Symposium, 2006
NSF-EMSI Center for Environmental Kinetics Analysis (CEKA) Fellow, 2005-2007
NSF-IGERT Biogeochemical Research Initiative in Education (BRIE) Fellow, 2002-2004
Dan Waugh Teaching Award, 2002
Roberts Fellowship for Graduate Studies, 2001-03
Nowak-Notre Dame Prize in Chemistry, 2000
Mitzi Hughes Alumni Scholarship, 2000
University of Nevada, Las Vegas Department of Chemistry Scholarship, 1998

BIOGRAPHICAL SKETCH			
Name (Last, first, middle initial) Meehta, Hardeep S.	**Position Title** Engineer/Scientist (Level II)		
Education/Training (Begin with baccalaureate or other initial professional education and include postdoctoral training)			
Institution and Location	**Degree** (if applicable)	**Year(s)**	**Field of Study**
Maharishi Dayanand University Rohtak, India	B.E.	2000 - 2004	Electronics Engg.
Michigan Technological University Houghton, MI	M.S.	2004 - 2006	Electrical Engg.

Research and Professional Experience

Appointments.

2009-present Engineer/Scientist II
Environmental Molecular Sciences Laboratory
Pacific Northwest National Laboratory
2006-2009 Electrical Engineer
Doty Scientific, Inc

Publications.

Jian Zhi Hu, Jesse A. Sears, Hardeep S. Mehta, Joseph J. Ford, Ja Hun Kwak, Kake Zhu, Yong Wang, Jun Liu, David W. Hoyt and Charles H. F. Peden. “A large sample volume magic angle spinning nuclear magnetic resonance probe for *in situ* investigations with constant flow of reactants”, Journal of Physical Chemistry Chemical Physics 2012

Hu, J., Feng, J., Mehta, H, “A Non-, or Minimal Invasive High Resolution 1H NMR Metabolic Profiling Using Slow MAS”, 11th International Conference on Magnetic Resonance Microscopy, Beijing, China *2011*

Mehta, H. and Zekavat, S.A. “Dynamic Resource Allocation via Clustered MC-CDMA in Multi-Service Wireless Ad-hoc Networks Achieving Low Interference Temperature and Code Reuse Distance”, *IEEE DYSPAN 2007*

Presentations and Posters

Hoyt, D., Sears, J., Burton, S., Isern, N., Washton, N., Rommereim, D., Froehlke, M., Lipton, A., Hu, J.Z., Cho, H., Walter, E., Majors, P., Mehta, H., Mueller, K. “Innovative Capabilities at the EMSL User Facility to Support the Study of Materials and Biosystems with Advanced NMR Spectroscopy”, *ENC 2011*.

Hu, J., Feng, J., Mehta, H, “A Non-, or Minimal Invasive High Resolution 1H NMR Metabolic Profiling Using Slow MAS”, *ENC 2011*.

Isern, N., Mehta, H., Hoyt, D., Sears, J., Walter, E., Burton, S., Ford, J., Rommereim, D., Froehlke, M., Lipton, A., Hu, J.Z., Majors, P., Minard, K., Ellis, P. “Technologies for Tommorow: Expanded Capabilities at the EMSL User Facility Supporting Innovative Solid and Liquid State Research in Biosystems and Materials”, *ENC 2010*.

Shevgoor, S., Entzminger, G., Mehta, H., Staab, J., Spitzmesser, J.B. and Doty, F. “Preliminary Experimental Results for Development of ^{1}H/^{13}C/^{15}N CryoMASTM Probe for 500 MHz”, *ENC 2009*.

Staab, J., Shevgoor, S., Entzminger, G., Mehta, H., Cothran, V., Wylde, R., Dupree, R. and Doty, F. “Improving Low-temperature MAS for DNP and Other LT-NMR Applications”, *ENC 2009*.

Entzminger, G., Staab, J., Holte, L., Mehta, H., Doty, F. “An Ultra-high power, High-S/N, 1H/13C/15N Narrow-bore PISEMA Probe”, *ENC 2008*.

Synergistic Activities and Experience

2011 EMSL Director’s Award

Maharishi Dayanand University Tuition Waiver, 2000 - 2004

BIOGRAPHICAL SKETCH	
Name (Last, first, middle initial) Cho, Herman M.	**Position Title** Scientist, Fundamental Computational Sciences Directorate

Education/Training (Begin with baccalaureate or other initial professional education and include postdoctoral training)

Institution and Location	Degree (if applicable)	Year(s)	Field of Study
Amherst College, Amherst, MA	A.B.	1981	Chemistry
University of California, Berkeley, CA	Ph.D.	1987	Chemistry

Research and Professional Experience

Appointments.

1992-present	Senior Research Scientist, Fundamental and Computational Sciences Directorate Pacific Northwest National Laboratory, Richland, Washington
1989-1992	Myron A. Bantrell Research Fellow, California Institute of Technology
1987-1989	U.S. NSF Postdoctoral Fellow, ETH Zürich, Switzerland

Publications.

Five Publications Most Closely Related to the Proposed Project

I. Farnan, **H. Cho**, W. J. Weber, R. D. Scheele, N. R. Johnson, and A. E. Kozelisky, "High-Resolution Solid-State Nuclear Magnetic Resonance Experiments on Highly Radioactive Ceramics," *Rev. Sci. Instr.* **75**, 5232–5236 (2004).

H. Cho and A. R. Felmy, "Environmental Molecular Sciences Laboratory Radiological NMR Spectroscopy Meeting," published as Report No. PNNL-16045, Pacific Northwest National Laboratory, Richland, Washington, 2006.

I. Farnan, **H. Cho**, and W. J. Weber, "Quantification of actinide alpha-radiation damage in minerals and ceramics," *Nature* **445**, 190–193 (2007).

H. Cho, W. A. de Jong, and C. Z. Soderquist, "Probing the oxygen environment in UO_2^{+2} by solid-state ^{17}O NMR spectroscopy and relativistic density functional calculations," *J. Chem. Phys.* **132**, 084501 (2010).

H. Cho, W. A. de Jong, A. P. Sattelberger, F. Poineau, and K. R. Czerwinski, "Comprehensive Solid State NMR Characterization of Electronic Structure in Ditechnetium Heptoxide," *J. Am. Chem. Soc.* **132**, 13138 (2010).

Additional Publications from the Past Five Years

H. Cho, "2-D Homonuclear Correlation and Separated Local Field Experiments for Solids with Strong Homonuclear Dipolar Couplings," *Solid State NMR* **29**, 219–226 (2006).

H. Cho, A. R. Felmy, R. Craciun, J. P. Keenum, N. Shah, and D. A. Dixon, "Solution State Structure Determination of Silicate Oligomers by ^{29}Si NMR Spectroscopy and Molecular Modeling," *J. Am. Chem. Soc.* **128**, 2324–2335 (2006).

I. Farnan, **H. Cho**, and W. J. Weber, “Identifying and Quantifying Actinide Radiation Damage in ZrSiO4 Minerals and Ceramics with Nuclear Magnetic Resonance,” in *Recent Advances in Actinide Science*, R. Alvares, N. D. Bryan, and I. May, Eds. Royal Society of Chemistry, Cambridge, UK, 2006.

E. Harel and **H. Cho**, “A General Numerical Analysis of Time-Domain NQR Experiments,” *J. Magn. Reson.* **183**, 308–314 (2006).

A. R. Felmy, **H. Cho**, D. A. Dixon, Y. Xia, N. J. Hess, and Z. Wang, “Stoichiometry and Structure of Aqueous Thorium Citrate Complexes under Neutral to Basic Conditions” *Radiochim. Acta* **94**, 205–212 (2006).

B. McNamara, L. Snow, C. Soderquist, S. Sinkov, **H. Cho**, and J. Friese, “The Radiation Induced Chemistry of the Uranyl Cation in Carbonate-Bicarbonate Solutions as Followed by NMR Spectroscopy,” in *Actinides 2005*, L. Soderholm, Ed. Materials Research Society, Warrendale, Pennsylvania, 2006.

H. Cho, W. J. Shaw, V. Parvanov, G. K. Schenter, A. Karkamkar, N. J. Hess, C. Mundy, S. Kathmann, J. Sears, A. S. Lipton, P. D. Ellis, and S. T. Autrey, “Molecular Structure and Dynamics in the Low Temperature (Orthorhombic) Phase of NH_3BH_3,” *J. Phys. Chem. A* **112**, 4277–4283 (2008).

H. Cho, W. A. de Jong, and C. Z. Soderquist, “Probing the oxygen environment in UO_2^{+2} by solid-state ^{17}O NMR spectroscopy and relativistic density functional calculations,” *J. Chem. Phys.* **132**, 084501 (2010).

H. Cho, W. A. de Jong, A. P. Sattelberger, F. Poineau, and K. R. Czerwinski, “Comprehensive Solid State NMR Characterization of Electronic Structure in Ditechnetium Heptoxide,” *J. Am. Chem. Soc.* **132**, 13138 (2010).

H. Cho, W. A. de Jong, A. R. Felmy, and C. Z. Soderquist, “Structure Determination of Actinide Complexes by Nuclear Magnetic Resonance Spectroscopy,” in *Plutonium Futures – The Science 2010*. American Nuclear Society, LaGrange Park, Illinois (2010).

J. R. Cort and **H. Cho**, “^{1}H and ^{13}C NMR Chemical Shift Assignments and Conformational Analysis for the Two Diastereomers of the Vitamin K Epoxide Reductase Inhibitor Brodifacoum”, *Magn. Reson. Chem.* **47**, 897–901 (2009).

H. Cho, W. A. de Jong, A. R. Felmy, and C. Z. Soderquist, “Structure Determination of Actinide Complexes by Nuclear Magnetic Resonance Spectroscopy in *Plutonium Futures The Science 2010*. American Nuclear Society, LaGrange Park, Illinois (2010).

A. Jain, J. C. Linehan, S. Raugei, **H. Cho**, D. L. DuBois, W. J. Shaw, ”Incorporating Peptides in the Outer Coordination Sphere of Bio-inspired Electrocatalysts for Hydrogen Production,” *Inorg. Chem.* **50**, 4073 (2011).

J. R. Cort, P. J. Alperin, and **H. Cho**, “Measurement and analysis of diastereomer ratios for forensic characterization of brodifacoum,” *Forensic Sci. Int.*, in press.

Synergistic Activities and Experience

2011-present	Member, Scientific Advisory Committee, EURACT-NMR Project at the Institute for Transuranic Elements, Karlsruhe, Germany
2010-present	Category 40 Senior Scientist/Expert Fellow at the Joint Research Centre of the European Commission, Institute for Transuranic Elements, Karlsruhe, Germany
2010-present	Member, Radiochemistry Capability Advisory Committee at the Environmental Molecular Sciences Laboratory, Richland, Washington
2009-present	Wiley Research Fellow at the Environmental Molecular Sciences Laboratory, Richland, Washington
2007-present	Member, Organizing Committee, American Chemical Society National Meeting Symposium on Analytical Chemistry in Nuclear Technology

BIOGRAPHICAL SKETCH			
Name (Last, first, middle initial) Sears Jr., Jesse A		**Position Title** Senior Technologist	
Education/Training (Begin with baccalaureate or other initial professional education and include postdoctoral training)			
Institution and Location	**Degree** (if applicable)	**Year(s)**	**Field of Study**
Southeast Community College Milford, NE	A.A.S	1979	Electronic Engineering

Research and Professional Experience

1997 - Present	Sr. Technologist VII, NMR/EPR - EMSL, PNNL
1992 - 1997	Field Service Engineer, Varian/Otsuka Electronics, Fort Collins, CO
1991 - 1992	Electronic Technician, Varian/Otsuka Electronics, Fort Collins, CO
1979 - 1990	Electronic Technician, Woodward Governor, Fort Collins, CO

Publications.

Five Publications Most Closely Related to the Proposed Project

Lipton AS, JA Sears, and PD Ellis. 2001. "A General Strategy for the NMR Observation of Half -Integer Quadrupolar Nuclei in Dilute Environments." Journal of Magnetic Resonance 151(1):48-59.

Hoyt DW, RVF Turcu, JA Sears, Jr, KM Rosso, SD Burton, AR Felmy, and JZ Hu. 2011. "High-pressure Magic Angle Spinning Nuclear Magnetic Resonance ." Journal of Magnetic Resonance. doi:doi:10.1016/j.jmr.2011.07.019

Hu JZ, JA Sears, Jr, HS Mehta, JJ Ford, JH Kwak, K Zhu, Y Wang, J Liu, CHF Peden, and DW Hoyt. 2011. "A Large Sample Volume Magic Angle Spinning Nuclear Magnetic Resonance Probe for In Situ Investigations with Constant Flow of Reactants." PNNL-SA-81858, Pacific Northwest National Laboratory, Richland, WA

Vijayakumar M, SN Kerisit, KM Rosso, SD Burton, JA Sears, Jr, Z Yang, GL Graff, J Liu, and JZ Hu. 2011. "Lithium Diffusion in Li4Ti5O12 at High Temperatures." Journal of Power Sources 196(4):2211-2220.

Kwak JH, JZ Hu, RVF Turcu, KM Rosso, ES Ilton, CM Wang, JA Sears, Jr, MH Engelhard, AR Felmy, and DW Hoyt. 2011. "The Role of H2O in the Carbonation of Forsterite in Supercritical CO2." International Journal of Greenhouse Gas Control 5(4):1081-1092. doi:10.1016/j.ijggc.2011.05.013

Additional Publications

Lipton AS, GW Buchko, JA Sears, MA Kennedy, and PD Ellis, "Zn-67 Solid-State NMR Spectroscopy of the Minimal DNA Binding Domain of Human Nucleotide Excision Repair Protein XPA." Journal of the American Chemical Society, 2001, 123 (5) 992

Lipton AS, JA Sears, Robert W. Heck, and Paul Ellis 2003. " Low Temperature Solid-state NMR Experiments of Half-Integer Quadrupolar Nuclides: Caveats and Data Analysis". Journal of Magnetic Resonance, 151(1), 48.

Ellis PD, JA Sears, Jr, P Yang, M Dupuis, T Boron, V Pecoraro, T Stich, RD Britt, and AS Lipton. 2010. "Solid-State 55Mn NMR Spectroscopy of bis(μ-oxo)dimanganese(IV) [Mn2O2(salpn)2], a Model for the Oxygen Evolving Complex in Photosystem II." Journal of the American Chemical Society 132(47):16727-16729. doi:10.1021/ja1054252

Synergistic Activities and Experience

Cryogenic probe designs:

800MHz double resonance low gamma CP probe, 500MHz triple resonance {H1, Zn67, N15} CP, and a 400MHz double resonance {Zn67, H1} CP probe. All of the tuning elements are inside of the sample cryostat and are exposed to extremely low temperatures. Because of this the tuning capacitors had to be special ordered from the vendor. Also because the probe operates in a vacuum, a new vacuum motion feed-thru had to be designed and built in house because there is nothing available on the market that met our requirements. All of these probes have gone through many design changes and updates; the 800's probe alone went through 3 major design changes before we had a reliable design. As a result of these improvements new probes were built for the 400 and 500 MHz systems.

Low gamma probe designs:

900MHz triple resonance Zn{N, H} probe, 900MHz double resonance low gamma CP probe, and the 800MHz double resonance low gamma CP probe. All of these probes were built around the same technology. Transmission lines are use to transform impedances so that the use of ceramic chip capacitors can be reduced or eliminated, this eliminates artifacts in the spectra due to the chip caps when observing low gamma nuclei.

CPMAS low gamma probe designs:

750MHz medium gamma CPMAS, and 750MHz low gamma CPMAS probes. These probes make use of transmission lines as mentioned above to eliminate artifacts. Because they are also Magic Angle Spinning probes, and have a large sample volume, a new rotor housing and proton RF coil was designed in house to meet this challenge.

Specialty probe designs:
500MHz, slow MAS probe.
850/500MHz, in-situ Flow probe.
300MHz, 5mm CPMAS, DRAWS Probe.
300MHz, 7.5mm CPMAS/DMAT probe.
300MHz, 7.5mm CPMAS Xe123 flow probe, with variable temperature (350 C).
900MHz, 3.2mm CPMAS probe.
900MHz, 5mm CPMAS probe, with variable temperature (400 C).
1.4 Tesla, 5mm DNP, cryogenic probe (4.4 to 295 K

BIOGRAPHICAL SKETCH			
Name Hoyt, David W	Position Title: Sr. Research Scientist (SE4) - EMSL MR Group		
Education/Training			
Institution and Location	**Degree**	**Year(s)**	**Field of Study**
Millersville University, Millersville, PA	BS	1979 – 1983	Chemistry
University of Delaware, Newark, DE	MA	1983 – 1987	Biochemistry
University of Texas Southwestern Medical Center at Dallas, Dallas, TX	Ph.D.	1987 - 1990	Biochemistry

- Research and Professional Experience

  - *Appointments:*

2011 - Present Sr. Research Scientist IV, NMR/EPR - EMSL, PNNL
2002 - 2011 Sr. Research Scientist IV, Technical Group Lead, NMR/EPR - EMSL, PNNL
2001 - 2002 Sr. Research Scientist IV, Macromolecular Structure and Dynamics -FSD, PNNL
1997 - 2001 Sr. Research Scientist III, Macromolecular Structure and Dynamics, FSD, PNNL
1995 - 1997 Postdoctoral Fellow, Macromolecular Structure and Dynamics, FSD, PNNL
1991 - 1995 Postdoctoral Fellow, Dept. of Biochemistry, University of Alberta

  - *Publications (partial list ~ 40):*

1. Hu, JZ, Sears, JA, Mehta, HS, Ford, JJ, Kwak, JH, Zhu, K, Wang, Y, Liu, J, **Hoyt, DW**, and CHF Peden. 2011 "A Large Sample Volume Magic Angle Spinning Nuclear Magnetic Resonance Probe for In Situ Investigations with Constant Flow of Reactants". PCCP (Accepted – In Press).
2. **Hoyt DW**, Turcu RVF, Rosso KM, Burton, SD, Felmy AR, and JZ Hu. 2011 "High Pressure Magic Angle Spinning Nuclear Magnetic Resonance." *J. Magnetic Resonance,* 212: 378-385.
3. U.S. Patent Submission E-16894 Hoyt DW, JA Sears, RVF Turcu, KM Rosso, and JZ Hu. "Devices and Process for High-Pressure Magic Angle Spinning Nuclear Magnetic Resonance," filed July 28, 2011 (provisional patent submitted December 13 2010).
4. U.S. Patent No. 7,535,224 B2 entitled "Discrete Magic Angle Turning System, Apparatus and Process for In Situ Magnetic Resonance Spectroscopy and Imaging" issued May 19, 2009, JZ. Hu, JA. Sears, DW Hoyt, and RAWind.
5. Hu JZ, JA Sears, JH Kwak, **DW Hoyt**, Y Wang and CHF Peden. 2009. "An isotropic chemical shift–chemical shift anisotropic correlation experiment using discrete magic angle turning." *Journal of Magnetic Resonance* 198(1):105-110.
6. Kwak JH, Hu JZ, Turcu RVF, Rosso KM, Ilton ES, Wang C, Sears JA, Engelhard MH, Felmy AR, and **DW Hoyt**. 2011 "The Role of H_2O in the Carbonation of Forsterite in Supercritical CO_2." *Int. J. Greehouse Gas Control.* 5(4): 1082-1092.
7. White MD, McGrail BP, Schaef, HT, Hu JZ, **Hoyt DW**, Felmy AR, Rosso KM and SK Wurstner. 2011. "Multiphase sequestration geochemistry: Model for mineral carbonation." *Energy Procedia*, 4, 5009-5016.

8. Teklemichael SM, Hlaing Oo WM, McCluskey MD, Walter ED, and **DW Hoyt**. 2011.”Acceptors in ZnO nanocrystals” *Applied Physics Letters* 98 (23): 232112), doi:10.1063/1.3598411 .
9. Kwak JH, JZ Hu, **DW Hoyt**, JA Sears, C. Wang, KM Rosso, and AR Felmy. 2010. “Metal Carbonation of Forsterite in Supercritical CO_2 and H_2O Using Solid State ^{29}Si, ^{13}C NMR Spectroscopy.” *Journal of Physical Chemistry C* 114:4126-4134.
10. Bryant, PL, CR Hartwell, AA Mrse, EF Emery, Z Gan, T Caldwell, AP Reyes, P Kuhns, **DW Hoyt**, LS Simeral, RW Hall, and LG Butler. 2001. “Structural Characterization of MAO and Related Aluminum Complexes. 1. Solid–State MAS ^{27}Al NMR with Comparison to EFG Tensors from ab Initio Molecular Orbital Calculations.” *Journal of the American Chemical Society* 123 (48):12009-12017
11. Yang Y, **DW Hoyt**, and J Wang. 2007. " A complete NMR spectral assignment of the lipid-free mouse apolipoprotein A-I (apoAI) C-terminal truncation mutant, apoAI(1-216). " Biomolecular NMR Assignments 1(1):109-111
12. Smirnov S, NG Isern, ZG Jiang, **DW Hoyt**, and CJ McKnight. 2007. "The Isolated Sixth Gelsolin Repeat and Headpiece Domain of Villin Bundle F-Actin in the Presence of Calcium and Are Linked by a 40-Residue Unstructured Sequence." *Biochemistry* 46(25):7488-7496.
13. Brzovic P, AV Lissounov, D Christensen, **DW Hoyt**, and RE Klevit. 2006. "A UbcH5/Ubiquitin Noncovalent Complex is Required for Processive BRCA1-Directed Ubiquitination." *Molecular Cell* 21(6):873-880.
14. Lowry DF, **DW Hoyt**, FA Khazi, J Bagu, AG Lindsey, and DM Wilson. 2003. “Investigation of the Role of the Histidine-Aspartate Pair in the Human Exonuclease III-like Abasic Endonuclease, Ape1.” *Journal of Molecular Biology* 329 (5):311-322.
15. Brzovic PS, P Rajagopal, **DW Hoyt**, MC King, and RE Klevit. 2001. “Structure of a BRCA1-BARD1 Heterodimeric Complex.” *Nature Structural Biology* 8 (10):833-837.
16. Briknarova K, S Takayama, L Brive, ML Havert, DA Knee, J Velasco, S Homma, E Cabezas, J Stuart, **DW Hoyt**, AC Satterthwait, M Llinas, JC Reed, and KR Ely. 2001. “Structural Analysis of BAG1 Co-chaperone and its Interactions with Hsc70 Heat Shock Protein.” *Nature Structural Biology* 8 (4):349-352.

Synergistic Activities and Experience

Dr. Hoyt has 25 years of experience with research related to NMR. His traditional research focus has been on the structure and dynamics of bio-complexes via NMR, but more recently has broadened his interests to include geochemistry and NMR specialty-probe development projects. Dr. Hoyt has co-authored 40 peer-reviewed publications including articles in *Nature Structural Biology*, *Molecular Cell*, *JACS*, *Biochemistry*, and *Journal of Magnetic Resonance*.

Dr. Hoyt has been the PI of a PNNL LDRD project (10/01/08 - 9/30/11) for developing unique technology for *In Situ* NMR Investigations of Geologic Trapping Mechanisms in CO2 Storage and is successfully operating at the relevant geological temperature (from -20 to 80°C) and pressure (from less than 1.0 to 170+ atmospheres). Project award FY09: $280K, FY10: $476K. FY11: $380K.

PNNL LDRD Carbon Sequestration Initiative –Hoyt, D (Co-PI) 6/2011 – 09/30/2013 – 10% effort
Task Title: “In Situ Molecular-Scale Investigations of Reactions between Supercritical C and Minerals Relevant to Geologic Carbon Storage” JS Loring (PI), Z Wang, CJ Thompson, J-Z Hu, DW Hoyt, AS Lea, HT Schaef, KM Rosso.