William R. Wiley
EMSL
Environmental Molecular Sciences Laboratory

EMSL Quarterly Highlights Report

1st Quarter, Fiscal Year 2008

(October 1, 2007, through December 31, 2007)

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

The W.R. Wiley Environmental Molecular Sciences Laboratory (EMSL) is a U.S. Department of Energy (DOE) national scientific user facility located at Pacific Northwest National Laboratory (PNNL) in Richland, Washington. EMSL is operated by PNNL for the DOE Office of Biological and Environmental Research. At one location, EMSL offers a comprehensive array of leading-edge resources and expertise.

Access to the instrumentation and expertise is obtained on a peer-reviewed proposal basis. Users are participants on accepted proposals. Staff members work with users to expedite access. The EMSL Quarterly Highlights Report documents research and activities of EMSL staff and users.

Research Highlights

Atmospheric Aerosol Chemistry

Heterogeneous Reaction of Deliquesced NaCl Particles with Gaseous HNO_3

Y. Liu,[a] JP Cain,[b] H Wang,[b] and A Laskin[a]
(a) Environmental Molecular Sciences Laboratory, Richland, Washington
(b) University of Southern California, Los Angeles, California

Reactions on atmospheric aerosol particles are known to impact atmospheric composition and chemistry, global radiative forcing and climate change, sky visibility, and public health. Understanding these processes is crucial for our ability to control and predict their effects on the environment.

Over the last few decades, a great deal of attention has been placed on the fundamental kinetics and mechanism of atmospheric heterogeneous reactions. Reactions involving aerosols are known to impact atmospheric composition and chemistry, global radiative forcing and climate change, sky visibility, and public health. Sea salt aerosols, generated by wind-induced wave action and bubble bursting of seawater, are the second largest component (by mass) of global aerosol burden. These aerosols may undergo heterogeneous reactions with trace species in the atmosphere, including OH, HNO_3, O_3, NO_2, N_2O_5, and $ClONO_2$. The net result is that inert halides may be converted to photochemically reactive halogen species, which lead to the production of reactive halogen species upon exposure to sunlight. There has been increasing evidence from laboratory and field studies that these halogen atoms play pivotal roles in the chemistry of the marine boundary layer. For these reasons, a quantitative understanding of the uptake and kinetics of reactive gases on sea salt particles is critical toward elucidating the overall halogen budget and tropospheric chemistry. Figure 1 shows a schematic of a mechanism to create halogens.

In this work, the authors report on the heterogeneous reaction kinetics of gaseous nitric acid with deliquesced sodium chloride particles, $NaCl(aq)+ HNO_3(g)$, to form aqueous sodium nitrate and gaseous hydrochloric acid, $NaNO_3(aq) + HCl(g)$, using a novel particle-on-substrate stagnation flow reactor (PS-SFR). This instrument allows the reactions to be studied under conditions, including particle size, relative humidity, and reaction time, directly relevant to the atmospheric chemistry of sea salt particles. Particles deposited onto an electron microscopy grid substrate were exposed to the reacting gas at atmospheric pressure and room temperature by impingement via a stagnation flow inside the reactor. The reactor design and choice of flow parameters were guided by computational fluid dynamics to ensure uniformity of the diffusion flux to all particles undergoing reaction. The reaction kinetics were followed by observing chloride depletion in the particles by computer-controlled scanning electron microscopy with energy-dispersive x-ray analysis (CCSEM/EDX).

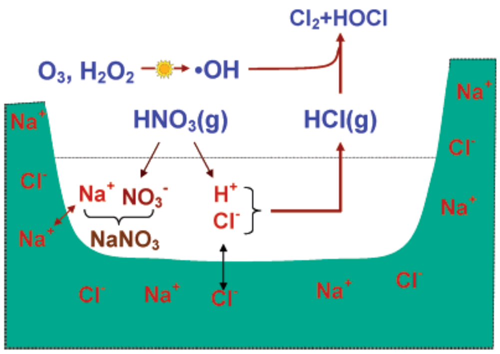

Figure 1. *Heterogeneous reactions occurring in the marine boundary layer: uptake of HNO_3 onto NaCl and reaction of its product, HCl, with OH.*

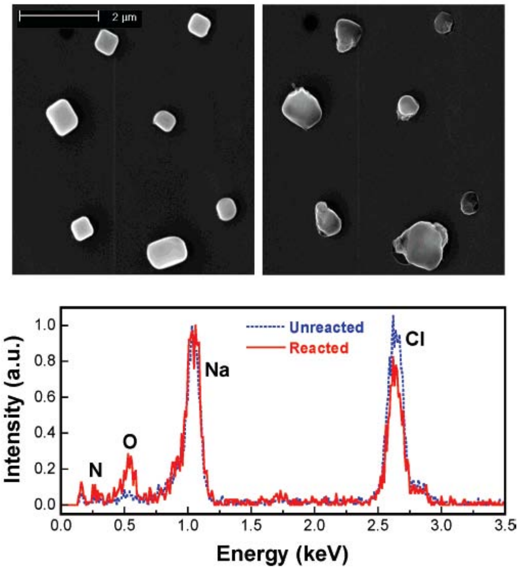

Figure 2. *Top panels: Scanning electron microscope images of NaCl particles before (left) and after (right) reaction with gaseous HNO_3 of 6 ppb concentration, 80% relative humidity and reaction time of 210 min. Bottom panel: Typical* energy-dispersive x-ray analysis *spectra of individual NaCl particle before and after reaction.*

Figure 2 shows a scanning electron microscope image of NaCl particles before and after exposure to HNO_3. A series of experiments was conducted in which the particle loading, free stream HNO_3 concentration, reaction time, particle size, and relative humidity were varied for one or more types of salt particles. Results show that the variation of the apparent, pseudo-first-order rate constant with particle loading and HNO_3 concentration in the free stream is entirely consistent with a diffusion-kinetic analysis.

The authors note that micron-size sea salt particles are ubiquitous in and near the marine boundary layer. These particles are responsible for a large fraction of light scattering and backscattering. However, the particles are too large to be efficiently transmitted to single-particle mass spectrometers (SPMS) commonly used to detect chloride depletion. In addition, the fact that the particles must be suspended in a gas requires the reaction to take place in a flow reactor for no longer than tens of seconds, far shorter than the lifetime of typical sea salt particles in atmospheric chemistry. For these reasons, reactions of micron-size particles are not "accessible" by FR-SPMS. However, the PS-SFR experiment coupled with the CCSEM/EDX technique adopted here allows the particles to undergo exposure to a reactive gas over a considerably longer period and is well suited for particles of micron size. The technique also offers options for multi-instrumental microanalysis and is applicable to both laboratory-generated and field-collected samples. It should be noted that this approach does have one important limitation: particles smaller than 0.5 microns may not be accurately probed because of the potential damage caused from the electron beam. These considerations lead the authors to believe that a combination of FR-SPMS and PS-SFR/CCSEM/EDX would be essential to understand uptake over a wide range of particle sizes and experimental conditions. Details of this exciting research have been published as a feature article in the *Journal of Physical Chemistry A*.

Citation

Liu Y, JP Cain, H Wang and A Laskin. 2007. "Kinetic Study of Heterogeneous Reaction of Deliquesced NaCl Particles with Gaseous HNO_3 using Particle-on-Substrate Stagnation Flow Reactor Approach." *Journal of Physical Chemistry A* 111(40):10026-10043.

Biological Interactions and Dynamics

Proteomic Characterization of the *Rhodobacter sphaeroides* 2.4.1 Photosynthetic Membrane: Identification of New Proteins

X Zeng,[a] JH Roh,[a] SJ Callister,[b] CL Tavano,[c] TJ Donohue,[c] MS Lipton,[b] and S Kaplan[a]
(a) University of Texas Health Science Center, Houston, Texas
(b) Pacific Northwest National Laboratory, Richland, Washington
(c) University of Wisconsin-Madison, Madison, Wisconsin

The bacterium Rhodobacter sphaeroides *2.4.1 is known for its diverse metabolic activities, including the ability to produce copious amounts of hydrogen, which could prove to be a source of renewable bioproduced energy. Many of these activities are linked to* R. sphaeroides' *photosynthetic apparatus that has served as a model for photosynthesis. Collaborative proteomic research being conducted at EMSL is increasing our understanding of this important link.*

This study builds upon previous proteomic research conducted at EMSL on *Rhodobacter sphaeroides* 2.4.1 (Callister et al. 2006a, 2006b) and details the discovery of new proteins associated with the intracytoplasmic membrane (ICM) (Figure 1), a specialized membrane dedicated to the photosynthetic processes used by *R. sphaeroides*. Subcellular fractionation combined with multichromatographic methods was coupled with Fourier transform ion cyclotron resonance mass spectrometry to test the hypothesis that a significant number of proteins associated with the ICM have not been previously been identified. The identification of these proteins could impact the understanding of how solar energy is used to the benefit of this organism.

To evaluate this hypothesis, EMSL's proteomic capabilities were applied to probe the ICM for potentially important structural and metabolic proteins. ICM vesicles were purified from *R. sphaeroides* cell cultures as well as surrounding sub-cellular fractions, such as the outer membrane, periplasm, and cytoplasmic membrane. Proteins extracted from the ICM and the other fractions were analyzed using a peptide-centric high-throughput liquid chromatography-mass spectrometry-based approach (Zimmer et al. 2006).

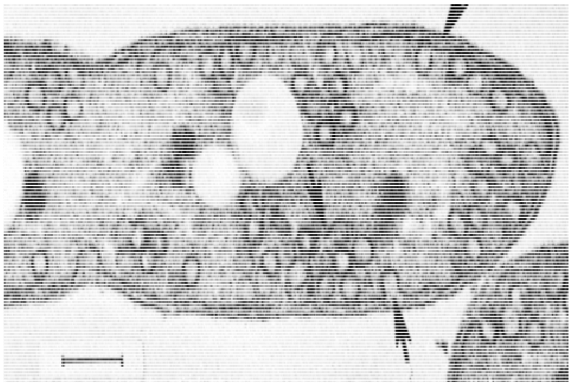

Figure 1. *The Intracytoplasmic Membrane (arrows) within* Rhodobacter sphaeroides 2.4.1 *houses proteins important for obtaining energy through photosynthesis. Using EMSL's proteomic capabilities, new proteins were discovered unique to the membrane.*

Purified ICM vesicles were shown to be enriched in several abundant, newly identified membrane proteins, including a protein of unknown function (AffyChip designation RSP1760) and a possible alkane hydroxylase (RSP1467). Deletion of the gene encoding for the RSP1760 protein resulted in the inability of *R. sphaeroides* to grow under conditions suitable for solar energy use, indicating the importance of this protein for *R. sphaeroides* to function as a photosynthesizing organism. Proteins necessary for other cellular functions, such as ATP synthesis, respiration, solute transport, protein translocation, and other physiological processes, were also identified to be in association with the ICM. This study is the first to provide a more global view of the protein composition of a photosynthetic membrane from any source. Results are provided in detail in the *Journal of Bacteriology* (Zeng et al. 2007).

Citations

Callister SJ, CD Nicora, X Zeng, JH Roh, MA Dominguez, CL Tavano, ME Monroe, S Kaplan, TJ Donahue, RD Smith, and MS Lipton. 2006a. "Comparison of Aerobic and Photosynthetic *Rhodobacter sphaeroides* 2.4.1 Proteomes." *Journal of Microbiological Methods* 67(3):424-436.

Callister SJ, MA Dominguez, CD Nicora, X Zeng, CL Tavano, S Kaplan, TJ Donahue, RD Smith, and MS Lipton. 2006b. "Application of the Accurate Mass and Time Tag Approach to the Proteome Analysis of Sub-cellular Fractions Obtained from *Rhodobacter sphaeroides* 2.4.1 Aerobic and Photosynthetic Cell Cultures." *Journal of Proteome Research* 5(8):1940-1947.

Zeng X, JH Roh, SJ Callister, CL Tavano, TJ Donahue, MS Lipton, and S Kaplan. 2007. "Proteomic Characterization of the *Rhodobacter sphaeroides* 2.4.1 Photosynthetic Membrane: Identification of New Proteins." *Journal of Bacteriology* 189(20):7464-7474.

Zimmer JSD, ME Monroe, WJ Qian, and RD Smith. 2006. "Advances in Proteomics Data Analysis and Display using an Accurate Mass and Time Tag Approach." *Mass Spectrometry Reviews* 25(3):450-482.

Making Genomes Accessible: Dealing with the Avalanche of Biological Sequence Data

VM Markowitz[(a)]

(a) Lawrence Berkeley National Laboratory, Berkeley, California

The Integrated Microbial Genome system and its metagenome extensions are software tools that provide data management, analysis, and annotation capabilities for all publicly available microbial, viral, and eukaryal isolate genomes and metagenomes. Managing this collection of several thousand genomes and metagenomes requires performing trillions of pairwise sequence analysis calculations—a job which requires several years of computational time to complete. Using the Molecular Science Computing Facility supercomputer MPP2 and ScalaBLAST (specially designed high-throughput sequence analysis software from Pacific Northwest National Laboratory), these calculations have been periodically performed, leading directly to recent releases of Integrated Microbial Genome system and its metagenome extensions.

The ability to recognize similarity in the DNA code that defines particular genes or proteins is a fundamental tool in molecular biology. When similar DNA or polypeptide sequences are observed, a biologist can infer homology, which is a family relationship based on inheritance from a common ancestor. Proteins that are homologous share a common three-dimensional structure that often allows their functions to be predicted. This type of evidence is powerful and underlies much of modern biology. The Integrated Microbial Genome (IMG) system and the metagenome extensions (IMG/M) (Markowitz 2007a, 2007b) are software resources built using homologous relationships between sequenced genomes for use by the biological research community. The IMG and IMG/M tool suites combine data management, analysis, and functional annotation capabilities based on pre-computed homologous relationships between publicly available genomes.

Two critical issues are exploding in importance in the large-scale sequence comparisons that must be performed to enable the IMG and IMG/M systems. First, building this basic map of sequence homology is becoming a significant obstacle because of the high throughput and cheap production of sequence data. The relatively few genes that have been *studied* experimentally must be projected against the majority that are *sequenced* but as yet uncharacterized. In 2007, there were about 400 microbial genomes alone that were completed, but this number is estimated to grow to 10,000 in just a few years. The scale of this dataset has outstripped various mechanisms that have been employed in the past to enhance the computational algorithm throughput of BLAST (Altschul et al. 1990), the basic method for comparing biosequences. The second issue relates to an exciting new type of analysis based on the comparison of genomes that has recently become possible precisely because there is so much data to work with. These genome comparison methods are essential for deciphering biological networks—a key step in enabling systems approach to biology. However, this more complex analysis typically consumes large numbers of sequence comparisons as raw material.

To deal with these large datasets, the researcher employed ScalaBLAST (Oehmen and Nieplocha 2006), which is a high-performance extension to the BLAST algorithm.

ScalaBLAST was used to accelerate the throughput of BLAST sequence analysis using the EMSL Molecular Science Computing Facility supercomputer MPP2 through a Computational Grand Challenge for several large-scale sequence analysis calculations. These calculations led directly to the 2.3 release of IMG and IMG/M and were directed at (1) integrating microbial genome and available metagenome data, and (2) applying this integrated data resource for specific scientific studies like advancing understanding of biological communities in the coastal margin between the Columbia River and Pacific Ocean.

Citations

Altschul SF, W Gish, W Miller, EW Myers, and DJ Lipman. 1990. "Basic Local Alignment Search Tool." *Journal of Molecular Biology* 215(3):403-410.

Markowitz VM, NN Ivanova, E Szeto, K Palaniappan, K Chu, D Dalevi, IA Chen, Y Grechkin, I Dubchak, I Anderson, A Lykidis, K Mavromatis, P Hugenholtz, and NC Kyrpides. 2007a. "IMG/M: A Data Management and Analysis System for Metagenomes." *Nucleic Acids Research*, Advance Access, in press.

Markowitz VM, E Szeto, K Palaniappan, Y Grechkin, K Chu, IA Chen, I Dubchak, I Anderson, A Lykidis, K Mavromatis, NN Ivanova, and NC Kyrpides. 2007b. "The Integrated Microbial Genomes (IMG) System in 2007: Data Content and Analysis Tool Extensions." *Nucleic Acids Research*, Advance Access, in press.

Oehmen C, and J Nieplocha. 2006. "ScalaBLAST: A Scalable Implementation of BLAST for High-Performance Data-Intensive Bioinformatics Analysis." *IEEE Transactions on Parallel and Distributed Systems* 17(8):740-749.

Geochemistry/Biogeochemistry and Subsurface Science

Carbon Tetrachloride Flow and Transport in the Subsurface of the 216-Z-9 Trench at the Hanford Site

M Oostrom,[a] ML Rockhold,[a] PD Thorne,[a] MJ Truex,[a] GV Last,[a] and VJ Rohay[a]
(a) Pacific Northwest National Laboratory, Richland, Washington

Using a combined modeling and experimental approach, this study determined that the future threat of carbon tetrachloride contamination of Hanford groundwater comes from the interaction between groundwater and carbon tetrachloride vapor and not migration of residual carbon tetrachloride liquid. As a result, remediation strategies are being refined to target the carbon tetrachloride vapor threat.

As a result of past practices, up to 580 m^3 carbon tetrachloride was discharged to waste sites at the 200 West Area of the U.S. Department of Energy's Hanford Site near Richland, Washington. Three-dimensional modeling was conducted to enhance the current conceptual model of CCl_4 distribution beneath the major disposal site (216-Z-9). The simulations, using the STOMP code, focused on migration of dense nonaqueous-phase liquid (DNAPL) consisting of CCl_4 and co-disposed organics under scenarios with differing sediment properties, sediment distribution, waste properties, and waste disposal history. Simulation results support a conceptual model for CCl_4 distribution where CCl_4 in the DNAPL phase migrated primarily in a vertical direction below the disposal site and where some CCl_4 DNAPL likely migrated across the water table into the regional aquifer. Results also show that the lower permeability Cold Creek unit retained more CCl_4 DNAPL within the vadose zone than other hydrologic units during the infiltration and redistribution process. Because of the relatively high vapor pressure of the CCl_4, the resulting vapor plumes are extensive and influenced by density-driven advection. Any continued migration of CCl_4 from the vadose zone to the groundwater is likely through interaction of vapor phase CCl_4 with the groundwater and not through continued DNAPL migration.

Additional simulations assessed the impacts of soil vapor extraction (SVE) as a remediation method. These simulations showed rapid CCl_4 removal associated with the assumed local equilibrium of CCl_4 between the phases. Additional efforts are needed to enhance the understanding of rate-limited volatilization to improve simulation of the SVE process and to provide a basis for refining the design and operation of SVE systems.

Plutonium recovery operations within the 200 West Area resulted in organic and aqueous wastes that were disposed of at several cribs, tile fields, and French drains. The organic wastes consisted of CCl_4 mixed with lard oil, tributyl phosphate, and dibutyl butyl phosphonate. The main disposal areas were the 216-Z-9 trench, the 216-Z-1A tile field, and the 216-Z-18 crib. These three major disposal facilities received a total of about 13,400,000 liters of liquid waste containing 363,000 to 580,000 liters of CCl_4. The disposal site locations are shown in Figure 1, with the 216-Z-9 site situated in the middle of the site-specific model domain and the 216-Z-1A and 216-Z-18 sites located to the southwest of the site-specific domain. The Plutonium Finishing Plant is directly to the west of the 216-Z-9 disposal site. Assuming a maximum aqueous CCl_4 solubility of 800 $mg \cdot L^{-1}$ and an organic liquid density of 1.59 $g \cdot cm^{-3}$ (Schwille 1988), the 13,400,000 liters of liquid waste would be able to contain approximately 6700 liters of CCl_4 in dissolved form, indicating that the majority of the CCl_4 entered the subsurface as an organic liquid.

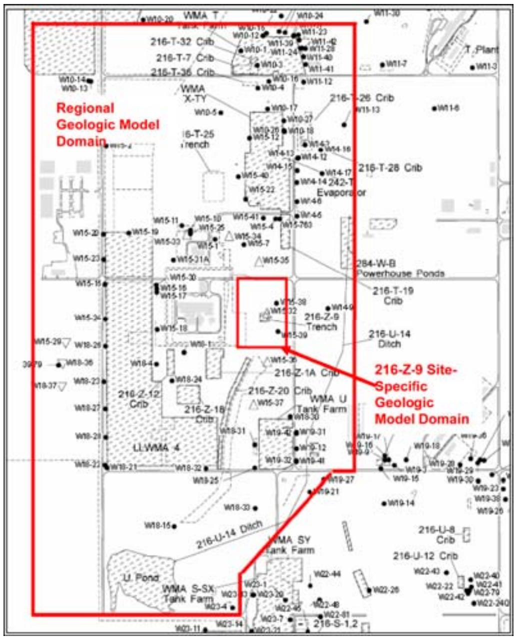

Figure 1. *Outline of regional and 216-Z-9 trench geologic model domains at the Hanford Site.*

In recent years, two major remediation technologies have been applied to remove CCl_4 from the vadose zone and groundwater at the Hanford Site. Beginning in 1991, about 78,000 kg of CCl_4 was removed using an SVE system in the vadose zone (Fluor Hanford 2006). In addition, a pump-and-treat system for the unconfined aquifer removed 9700 kg of CCl_4 from the groundwater beginning in 1994 (DOE 2006).

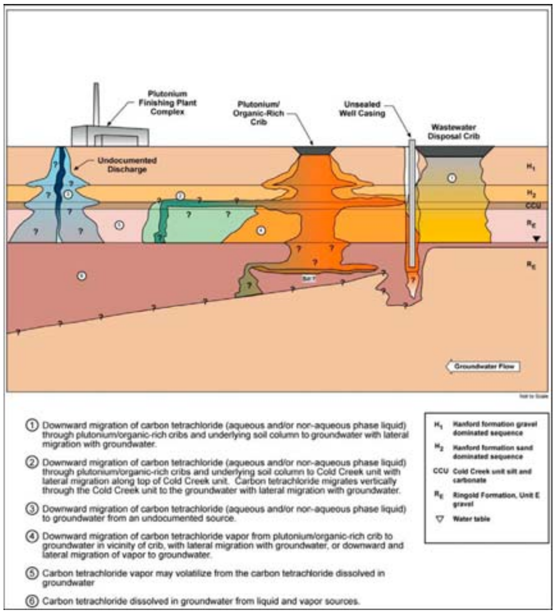

Figure 2. *Current conceptual model of subsurface carbon tetrachloride behavior* (after DOE 2004).

The main objective of the current study is to develop an updated conceptual model for CCl_4 behavior under the 216-Z-9 site, based on a series of multifluid flow simulations, and compare the updated conceptual model with the existing model described by DOE (2004), as shown in Figure 2. The numerical simulations focus on the 216-Z-9 site because of the three major DNAPL disposal sites, the 216-Z-9 has the smallest footprint and has received the most DNAPL waste. Because of these characteristics, it is expected that DNAPL disposed at the 216-Z-9 trench may have moved deeper into the subsurface compared to the other Hanford CCl_4 disposal sites. A series of three-dimensional multifluid flow simulations was conducted using the STOMP code (White and Oostrom 2006), including a base case simulation and 28 sensitivity analysis simulations, to examine the impact of parameter variation on the simulated migration of CCl_4 in the subsurface beneath the 216-Z-9 disposal area from 1954 to 2005. An additional objective was to investigate the impact of SVE, implemented at the site in 1993, on CCl_4 distributions and fluxes. This research was recently published in *Vadose Zone Journal* (Oostrom et al. 2007).

Citations

Fluor Hanford. 2006. Performance Evaluation Report for Soil Vapor Extraction Operations at the 200-PW-1 Carbon Tetrachloride Site, Fiscal Year 2005. WMP-30426, Fluor Hanford, Richland, Washington.

Oostrom M, ML Rockhold, PD Thorne, MJ Truex, GV Last, and VJ Rohay. 2007. "Carbon Tetrachloride Flow and Transport in the Subsurface of the 216-Z-9 Trench at the Hanford Site." *Vadose Zone Journal* 6(4):971-984.

Schwille F. 1988. *Dense Chlorinated Solvents*. Lewis Publishers, Chelsea, Michigan.

U.S. Department of Energy. 2004. *Plutonium/Organic-Rich Process Condensate/Process Waste Group Operable Unit RI/FS Work Plan, Includes: 200-PW-1, 200-PW-3, and 200-PW-6 Operable Units*. DOE/RL-2001-01, Rev. 0, reissue. DOE, Richland Operations Office, Richland, Washington.

U.S. Department of Energy. 2006. *Fiscal Year 2005 Annual Summary Report for 200-UP-1 and 200-ZP-1 Pump-and-Treat Operations.* DOE/RL-2005-91. DOE, Richland Operations Office, Richland, Washington.

White MD, and M Oostrom. 2006. *STOMP Subsurface Transport Over Multiple Phases, Version 4.0 Users Guide.* PNNL-15782. Pacific Northwest National Laboratory, Richland, Washington.

Geochemical Controls on Contaminant Uranium in Vadose Hanford Formation Sediments at the 200 Area and 300 Area, Hanford Site, Washington

JP McKinley,[a] JM Zachara,[a] J Wan,[b] DE McCready,[c] and SM Heald[d]
(a) Pacific Northwest National Laboratory, Richland, Washington
(b) Lawrence Berkeley National Laboratory, Berkeley, California
(c) Environmental Molecular Sciences Laboratory, Richland, Washington
(d) Argonne National Laboratory, Argonne, Illinois

Using combined experimental analysis and electron microscope imaging, this study determined that secondary mineral formation is the dominant control of uranium contamination of Hanford Site groundwater.

Long-term historic spills of uranium at the Hanford Site's 300 Area fuel fabrication site (58,000 kg of disposed uranium over 32 years) and at the 200 East Area BX tank farm (7000 kg of spilled uranium in one event), both within the Hanford formation near Richland, Washington, were investigated by subsurface sampling and subsequent microscale investigations of excavated samples. The 200 Area sediments contained uranyl silicate mineralization (sodium boltwoodite) in restrictive microfractures in granitic clasts, in the vadose zone over a narrow range in depth. Well logging and column experiments indicated that tank wastes migrated deeper than observed in core samples. The 300 Area sediments included metatorbernite and uranium at low concentrations associated with detrital aluminosilicates, along with other mineral phases that could accommodate uranyl, such as uranophane and calcium carbonate. The association of contaminant uranyl with Hanford formation sediments provided a persistent source of uranium to groundwater. The results of both studies suggest that the formation of secondary solid uranyl-bearing phases influences the subsequent release of uranium to the environment and that our understanding of these processes and individual waste sites is incomplete.

The Hanford Site produced plutonium from 1943 until 1989 for weapons applications. The Site occupies about 1500 km^2 in an arid environment, bounded by a broad bend of the Columbia River to the east and by Rattlesnake Mountain to the west. Fuel fabrication occurred at the Site's southern extremity (300 Area); fuel was irradiated near the Columbia River to the north (100 Area); and the rods were processed in chemical facilities on the Site's central plateau (200 Area). Each of the manufacturing components had a characteristic waste stream or streams, and while some streams were disposed directly onto the ground surface, others were retained for long-term storage or isolation. Materials research and fabrication at the 300 Area generated wastes that were sluiced into process ponds (Figure 1, top), constructed and maintained to avoid contamination of the nearby Columbia River.

The ponds received constant and intermittent releases of a broad variety in composition and volume, including caustic alkaline and acidic fluids and slurries containing uranium, aluminum, and copper. After irradiation, the chemical processing steps in the 200 Area included dissolution of irradiated fuel rods and subsequent industrial-scale chemical manipulations to form distinct compositional streams that were managed to extract useful materials and to isolate wastes. The storage of chemical process intermediates and the disposal of unwanted wastes presented (and continues to present) a significant challenge. During the years of plutonium production, highly radioactive and hazardous wastes were disposed in underground tanks (Figure 1, bottom), which were initially of single-wall construction.

The unintended release of uranium and other wastes to the environment produced contaminated zones in the vadose sediments. This study focused on two distinct contaminant events: (1) a historic, episodic leak of alkaline uranium wastes to the thick and deep 200 East Area vadose zone, and (2) the long-term seepage of acidic or neutral uranium wastes to the thin and shallow 300 Area vadose zone. Both released uranium into the same surficial sedimentary deposit, and each represents the source or potential source of uranium to groundwater.

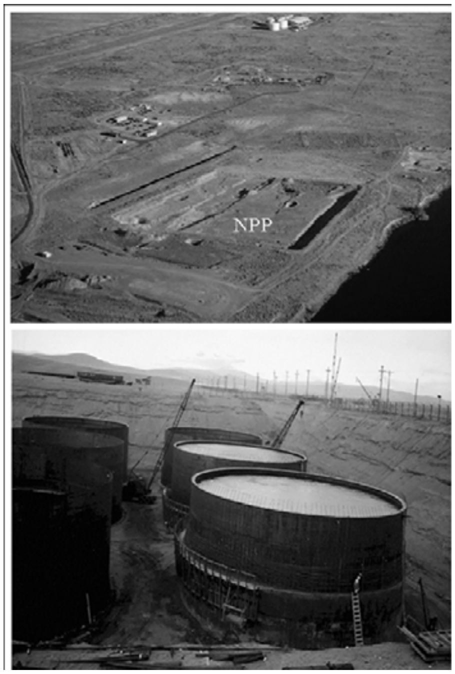

Figure 1. *Top: Aerial photograph of the 300 Area North Process Pond, in 2003, after excavation of the residual pond wastes. Samples described here were removed from the site after this photo was taken. Bottom: Photograph of the 200 East Area BX tank farm under construction, 1944.*

The mobility of uranium is a complex function of the chemical and physical properties and the geological and lithological variations in the subsurface. The present-day geochemical behavior of the wastes appears to be controlled by the composition and morphologic character of the secondary waste-bearing solid phases, which in turn result from the composition and reactivity of the original aqueous waste, which migrated through the vadose environment. The results of these investigations also illustrate the uncertainties and difficulties in understanding the geochemical factors controlling potential environmental hazards of long-resident contaminants in the vadose regime. More detail is provided in *Vadose Zone Journal* (McKinley et al. 2007).

Citation

McKinley JP, JM Zachara, J Wan, DE McCready, and SM Heald. 2007. "Geochemical Controls on Contaminant Uranium in Vadose Hanford Formation Sediments at the 200 Area and 300 Area, Hanford Site, Washington." *Vadose Zone Journal* 6(4):1004-1017.

Science of Interfacial Phenomena

Direct Synthesis of Nanoceria in Aqueous Polyhydroxyl Solutions

AS Karakoti,[a] SV Kuchibhatla,[a,b] KS Babu,[a] and S. Seal[a,c]
(a) Advanced Materials Processing and Analysis Center, University of Central Florida, Orlando, Florida
(b) Environmental Molecular Sciences Laboratory, Richland, Washington
(c) Nanoscience and Technology Center, University of Central Florida, Orlando

One-step synthesis and stabilization of cerium oxide (ceria) nanoparticles is a most important challenge in order to efficiently use them in applications such as sensors, catalysis, and biomedical materials. This study proposes an efficient, low-cost, green chemical route to synthesize nanoceria in saccharides, while simultaneously retaining the regenerative, oxidation state switching (Ce^{3+} to Ce^{4+} and back) property of ceria nanoparticles. These nanoparticles are expected to have potential use in future biomedical applications such as preventing retinal damage, preventing radiation damage of healthy cells during cancer treatment, and UV absorption.

Nanoceria has potential applications in catalysis, sensors, and biomedicine, including protecting cells again reactive oxygen species and radiation. These applications stem from cerium oxide's ability to switch oxidation states between +4 and +3, depending on the ambience (oxidizing and reducing environment). This renders nanoceria an important biomedical property for radical quenching. A whole new world of biological applications of nanoceria is opening with several interesting findings.

However, nanoceria needs to be stabilized in aqueous or non-aqueous media for all practical applications in biology. Thus, it is imperative to find a suitable delivery medium for carrying nanoceria to specific locations as an alternative route to intravenous administration. In this study, synthesis and redox chemistry of nanoceria in the presence of polyhydroxyl groups such as glucose and dextran are reported.

The effect of both acidic and basic medium on the synthesis and oxidation-state stability of nanoceria in the absence of buffer was examined using UV-visible spectroscopy and transmission electron microscopy (TEM). The basic and acidic mediums show differences in the synthesis of nanoceria in terms of size and structure without interfering with the redox chemistry. Pure and aqueous saccharides suspension of nanoceria in acid/base media undergoing redox transformation were also compared in this study.

The vital points in the mechanism for engineering functionalized nanoceria are as follows:

- Ce(IV) is reduced to Ce(III) in the process of oxidation of glucose to arabinose.
- Polysaccharides have stronger tendency to complex Ce(IV) than the monosaccharides.
- Reduction of Ce(IV) to Ce(III) takes place in only highly acidic mediums (pH <2), and at this concentration no colloidal particles were detected by light-scattering photometry.

Both dextran and glucose can be used efficiently to synthesize nanoceria with enhanced stability in dextran. No significant differences were observed with respect to particle size in both dextran and glucose suspensions. However, the acidic media was found to induce higher agglomeration tendencies as compared to the basic media. Some representative TEM images are shown in Figure 1. A possible mechanism of ceria-saccharides superstructure formation by cross linking of groups due to further complexation of free hydroxyl groups of glucose with cerium(IV) is shown in Figure 2. This study clearly demonstrates that nanoceria can be synthesized directly in mono/polysaccharides by oxidizing the species in both acidic and basic environment

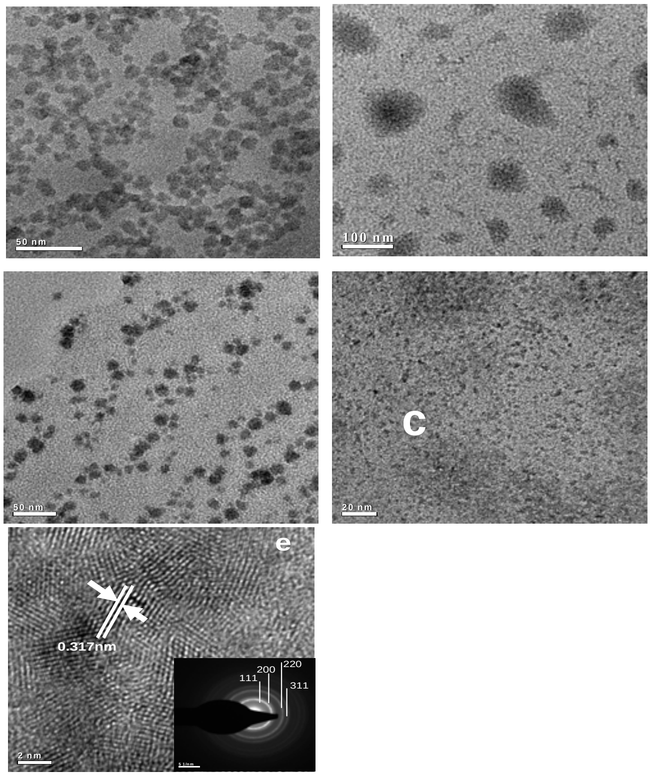

Figure 1. *Transmission electron micrographs for ceria synthesized in different conditions. Ceria synthesized in glucose using (a) 20-mM glucose/acid; (b) 20-mM glucose/base and in dextran; (c) 5-mM dextran/acid; and (d) 5-mM dextran/base. (e) High-resolution transmission electron microscope image and diffraction confirming the fluorite structure of ceria.*

Importantly, the initial complex formed between cerium and sugars does not hinder the property of ceria to switch its oxidation state based on the environment. The kinetics of switching of oxidation states in solution specifically regenerated from the Ce(IV) to Ce(III) oxidation state was slower in basic medium compared to acidic medium. Moreover, from UV-visible light spectroscopy results, it is clear that the +IV oxidation state was retained in the basic medium for more than 2 months as a stable suspension, which proves the tunability of nanoceria with respect to ambience and aging. The extended stability range of ceria in saccharides over a pH range from 2.0 to 8.0 is illustrated in Figure 3.

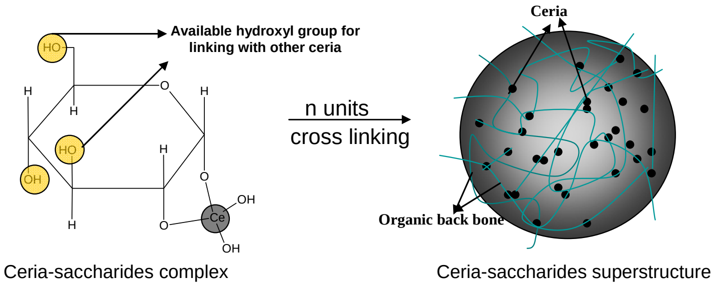

Figure 2. *Possible mechanism for complexation and ceria–saccharide superstructure formation.*

Citation
Karakoti AS, S Kuchibhatla, KS Babu, and S Seal. 2007. “Direct Synthesis of Nanoceria in Aqueous Polyhydroxyl Solutions.” *Journal of Physical Chemistry C* 111(46):17232-17240.

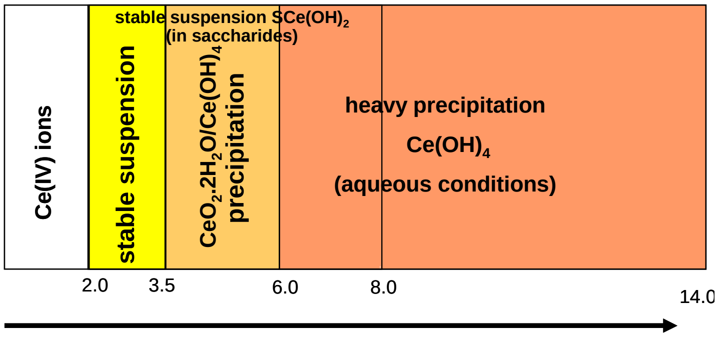

Figure 3. *Precipitation behavior of cerium (IV) with respect to change in pH in oxidizing environment. The narrow stability range of ceria suspension can be extended up to a pH of 8.0 by the use of saccharides (dashed lines). Cerium is present as Ce(IV) ions (pH 0 – 2.0), stable suspension* $CeO_2.2H_2O$ *(pH 2.0 – 3.5), precipitate as* $CeO_2.2H_2O$ *(pH 3.5 – 6.0), precipitate heavily as* $Ce(OH)_4$ *(pH 6.0 and above), stable suspension in saccharides as S-Ce(OH)X (pH 2.0 -8.0).*

Transient Mobility of Oxygen Adatoms upon O_2 Dissociation on Reduced TiO_2 (110)

Y Du,[(a)] Z Dohnálek[(b)] and IV Lyubinetsky[(a)]
(a) Environmental Molecular Science Laboratory, Richland, Washington
(b) Pacific Northwest National Laboratory, Richland, Washington

The interaction of molecular oxygen with TiO_2*–based materials can affect many chemical and photochemical processes. In particular, it plays an important role in a wide range of applications such as photocatalysis, degradation of organic pollutants, and water splitting for hydrogen production.*

Oxygen vacancy-mediated dissociation of O_2 molecules on TiO_2 (110) is shown to be energetically favorable by a number of theoretical investigations. On the basis of temperature-programmed desorption observations, researchers have suggested that for each O_2 molecule dissociated at the vacancy, one oxygen atom fills a vacancy while the other oxygen atom resides on the surface as an adatom, bound to the nearest-neighbor five-fold coordinated titanium site in the adjacent titanium row. The oxygen adatoms are found to significantly perturb the surface chemistry of adsorbed water, ammonia, and methanol, and may as well alter the surface chemistry of other adsorbate species on the TiO_2(110).

Recently, using *in-situ* scanning tunneling microscopy, the researchers studied at the atomic level the initial stages of O_2 dissociation at room temperature by tracking the same surface area before and after oxygen exposure. The results confirm that O_2 molecules dissociate only at the bridging oxygen vacancies, resulting in the healing of a vacancy by one oxygen atom, O_v, and the deposition of the other oxygen as an adatom, O_a, on a neighboring five-fold coordinated titanium site as shown in Figure 1.

After dissociation, the majority (~81 %) of O adatoms were found to separate from the original vacancy positions by up to two lattice constants along [001] direction. The majority of the adatoms (~74 %) were one lattice constant apart along [001] direction from the original vacancy positions shown as configuration *B* in Figure 2 (published as cover of *The Journal of Physical Chemistry C*). Other O_a atoms were separated by two lattice constants (~7 %, configuration *C* in Figure 2) or bonded at the nearest-neighbor titanium sites (~19 %, configuration *A* in Figure 2). Studies showed that a limited nonthermal, transient mobility resulting from energy release during O_2 dissociation, rather than thermal diffusion was accounted for the observed distribution. Effect of the hyperthermal transient mobility of the oxygen adatoms may lead to an enhanced reactivity, which could be of a general relevance for the chemical and photochemical processes involving oxygen interaction with TiO_2-based systems.

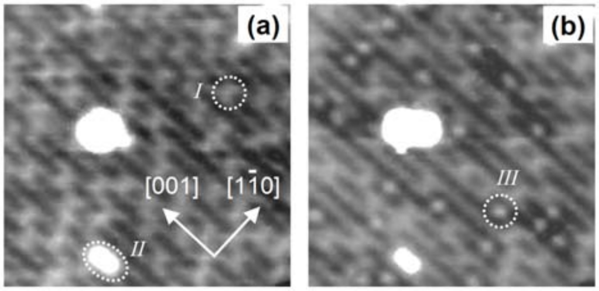

Figure 1. *Scanning tunneling microscopy images of the same (11 × 10) nm^2 area of the TiO_2 (110) surface (a) before and (b) after adsorption of 0.03 ML of O_2 at 300 K. One of the oxygen vacancies, double hydroxyl group, and oxygen adatom are labeled with I, II, and III, respectively.*

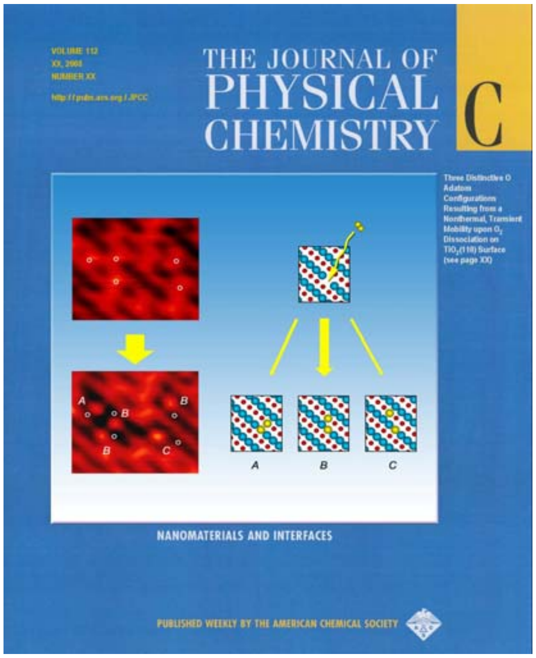

Figure 2. *Three different oxygen adatom configurations resulting from a nonthermal transient mobility upon O_2 dissociation on TiO_2 (110) surface.*

Citation

Du Y, Z Dohnálek, and I Lyubinetsky. 2007. "Transient Mobility of Oxygen Adatoms upon O_2 Dissociation on Reduced TiO_2 (110)." *Journal of Physical Chemistry C*. In press.

One Step Closer to Hydrogen-Powered Cars

J Knudson,(a) AU Nilekar,(b) RT Vang,(a) J Schadt,(a) EL Kunkes,(b) JA Dumesic,(b) M Mavrikakis,(b) and F Besenbacher(a)
(a) University of Aarhus, Aarhus, Denmark
(b) University of Wisconsin-Madison, Madison, Wisconsin

One key technological advance needed to enable efficient widespread use of hydrogen fuel cells for transportation involves the water-gas-shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$). This reaction is a crucial step in hydrogen production from fossil fuels. There is need for a better catalyst for small-scale applications before this process can be used in hydrogen fuel cell powered vehicles. Part of an EMSL Computational Grand Challenge project on Computational Design of Catalysts focuses on uncovering the details of the WGS reaction and is led by Manos Mavrikakis at the University of Wisconsin, Madison. High-performance computing using EMSL's supercomputer is an essential tool in probing the molecular details of how a proposed copper-platinum alloy might facilitate the WGS reaction.

Scientists using EMSL's supercomputer have been running calculations on a new alloy as a potential catalyst for the water-gas-shift (WGS) reaction—a key capability in making hydrogen fuel cell vehicles a commercially viable reality. The crux of the study is to characterize the energy requirements for creating the alloy and understanding the details of how it interacts with the WGS reaction. Using computational chemistry software, the energetics of constructing a copper/platinum (Cu/Pt) near-surface alloy and its catalytic properties were analyzed. The alloy was found to have copper preferentially incorporated in the subsurface layer of platinum, meaning that creating the alloy is energetically favorable. Large-scale calculations and experimental x-ray photoelectron spectroscopy results both show copper is most stable in the first subsurface layer of a platinum lattice. A comparison between the experimental and theoretically simulated scanning tunneling microscope images (Figure 1) reveals that post-annealing, the subsurface layer of the alloy is copper-rich. Additionally, experiments on carbon-monoxide (CO) desorption from the catalyst suggest that with increasing copper coverage, the CO-desorption temperature would decrease. Using computational methods, this relationship between CO desorption and temperature holds only if copper is in the subsurface layer. These

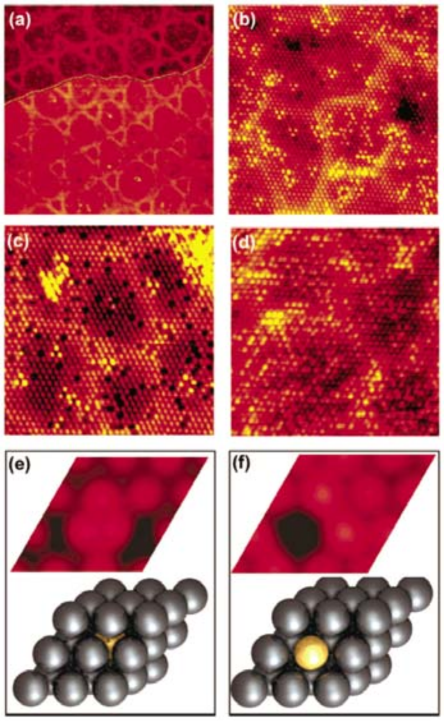

Figure 1. *Experimental and density functional theory-simulated scanning tunneling microscopy images. A comparison between the experimental and theoretically simulated scanning tunneling microscopy images reveals that post-annealing, the subsurface layer of the alloy is copper-rich.*

calculations and observations confirm the ideal configuration of copper and platinum can be assembled in an energy-efficient process because incorporation of copper into the platinum lattice is chemically favored at typical annealing temperatures.

The study also found that the Cu/Pt alloy has promising properties as a potential catalyst for the WGS reaction. CO binds more weakly to a special form of the alloy—Cu/Pt nitrosyl sulfuric acid (NSA)—than to a pure platinum surface. In addition, a common spectator/poison of WGS catalysts, formate (HCOO), binds more weakly than copper, suggesting that formate will not fatally interfere with this catalyst. Perhaps most importantly, Cu/Pt NSA activates water—the rate limiting step for WGS—as efficiently as copper, and yet binds the water dissociation products much more weakly than copper. This facilitates subsequent steps in the hydrogen production pathway. All these properties make the Cu/Pt NSA alloy a promising candidate for WGS catalysis, one that could be more active with a higher stability against poisoning by dominant reactive intermediates. The results were published in the *Journal of the American Chemical Society* (Knudson et al. 2007).

Citation

Knudson J, AU Nilekar, RT Vang, J Schnadt, EL Kunkes, JA Dumesic, M Mavrikakis, and F Besenbacher. 2007. “A Cu/Pt Near-Surface Alloy for Water-Gas-Shift Catalysis.” *Journal of the American Chemical Society* 129(20):6485-6490.

900-MHz NMR Enables Novel Catalysis Studies

JH Kwak,[a] JZ Hu,[a] DH Kim,[a] J Szanyi,[a] and CHF Peden[a]

(a) Pacific Northwest National Laboratory, Richland, Washington

γ-alumina is an important material both as a catalyst and a support to bind with other materials to form a new catalyst. When barium oxide is bound to γ-alumina, it forms a catalyst that is potentially useful in preventing pollution from diesel engines. This work discovers structural details of this complex that have been unobtainable by other techniques.

The ability to tailor catalysts one atom at a time is a step closer to reality, in part, because of EMSL’s 900-MHz nuclear magnetic resonance (NMR) spectrometer. A research team from the Institute for Interfacial Catalysis, located at the Pacific Northwest National Laboratory, used the 900-MHz NMR spectrometer to generate the highest-resolution spectra ever obtained of a common catalyst support and observed, for the first time, how the support interacts with a catalyst at the atomic scale.

To really understand catalysts, they must be studied in molecular and atomic detail. The team characterized a model system of the common γ-alumina support, γ-Al_2O_3, and the catalyst, barium oxide (BaO). γ-alumina materials serve as a support material for many catalysts, including BaO. Because BaO absorbs NO_x, a family of vehicle emissions products—the model system is a promising combination for emissions control. Despite the importance of γ-alumina materials, technology has previously not allowed detailed studies of them. The chemical properties of γ-alumina compounds are such that using traditional surface structure techniques to study them is not feasible.

The data from EMSL's 900-MHz NMR system indicates that in addition to the internal structural tetrahedral and octahedral coordinated aluminum atoms, there are also penta-coordinated aluminum atoms on the surface of the material. These atoms have different NMR relaxation times from the bulk aluminum, which is consistent with them being restricted to the surface. As BaO is added to the catalyst, the peak for these aluminum atoms becomes smaller and changes shape, showing that they are responding to the addition of the BaO. The tetrahedral and octahedral peaks do not change with the addition of BaO. Additionally, comparison of the number of BaO molecules added to the γ-alumina with the number of penta-coordinated aluminum sites that disappear in the NMR spectrum showed a nearly mole-per-mole correlation between the penta-coordinated Al^{3+} ions consumed and catalyst deposited. This is strong evidence that the binding site for BaO on γ-alumina is the penta-coordinated aluminum sites. Research results are provided in detail in *Journal of Catalysis* (Kwak et al. 2007).

This work is possible only with the high sensitivity and resolution provided by the 900-MHz NMR spectrometer at EMSL.

Citation

Kwak JH, JZ Hu, DH Kim, J Szanyi, and CHF Peden. 2007. "Penta-Coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ -Al_2O_3: An Ultra-High Magnetic Field ^{27}Al MAS NMR Study." *Journal of Catalysis* 251(1):189-194.

Professional/Community Service

EMSL user awarded U.S. Coast Guard Achievement Medal. Environmental Molecular Sciences Laboratory's Ken Beck (Figure 1) received the U.S. Coast Guard (USCG) Achievement Award for enabling maritime patrols to reliably communicate in the gullies and gorges of the Columbia and Snake rivers. Beck received the award for superior performance of duty while serving as USCG Auxiliary Flotilla 85 Communications Staff Officer from February 2007 to November 2007, in direct support of USCG Aids to Navigation.


Figure 1. *Ken Beck testing a radio in a U.S. Coast Guard patrol craft at the Kennewick station on Clover Island.*

For 45 years, U.S. Coast Guard patrols have dealt with spotty communications along sections of the Columbia and Snake rivers, especially on 130 miles of the Upper Snake River and 140 miles of the Lake Roosevelt/Spokane River arm. In these areas, steep cliffs block satellite phones, and cell phone reception is intermittent at best and nonexistent at worst. So, patrol teams maintaining the navigational aids for barges and others river traffic may be out of touch with their home base for hours, constituting a dangerous situation.

As the newly installed Communications Staff Officer for USCG Flotilla 85, Beck took on this problem. He developed and implemented a protocol using a Near Vertical Incident Skywave (NVIS) system, developed in the 1970s. The NVIS system sends high-frequency transmissions into the ionosphere. The signal is reflected and refracted back to earth, creating a circular communication zone with a radius of 25 to 250 miles. Beck designed and assembled the NVIS and extensively field tested the prototype. Further, he modeled the radiofrequency emitted to make sure the field team's exposure was within permissible environmental exposure limits. The NVIS system that Beck designed is now a model for USCG stations where communications are blocked by the local topography.

Awards and Recognition

EMSL user receives prestigious American Chemical Society award. EMSL user Gerard F. R. Parkin, Columbia University, was awarded the Organometallic Chemistry Award by the American Chemical Society. He has focused his research career on synthetic, structural, mechanistic, and theoretical studies of organometallic complexes. An article announcing the news was published in the January 8, 2008, issue of *C&E News*.

EMSL user elected Fellow of the American Association for the Advancement of Science. Nanoscientist Lai-Sheng Wang, Professor of Physics and Materials Science at Washington State University and Affiliate Senior Chief Scientist at Pacific Northwest National Laboratory, has been elected to the rank of Fellow in the American Association for the Advancement of Science (AAAS). Wang is being recognized for "distinguished and innovative contributions to the field of atomic clusters and for pioneering work on gaseous multiply-charged anions." He will be honored at the AAAS National Meeting on February 16, 2008, in Boston.

EMSL user receives Presidential Early Career Award for Scientists. Julia Laskin, EMSL user from Pacific Northwest National Laboratory, received the U.S. government's highest honor for researchers at the beginning of their careers when she accepted the Presidential Early Career Award for Scientists and Engineers at the White House on November 1. Laskin was honored for her work in fundamental reaction kinetics and ion surface reactions at EMSL. Her work provides a foundation for understanding the mass spectrometry of high molecular weight compounds and preparation of novel biomaterials.

EMSL user appointed to the 2008 Editorial Advisory Board of the *Journal of Physical Chemistry*. Lai-Sheng Wang, Professor of Physics and Materials Science at Washington State University and Affiliate Senior Chief Scientist at Pacific Northwest National Laboratory, was selected for the three-year term on the journal's editorial advisory board based on his distinguished contributions to the field of atomic clusters and for pioneering work on gaseous multiply-charged anions. In this role, Wang will influence the current policies and future direction of the publication.

Visitors and Users

During the first quarter of Fiscal Year 2008, a total of 347 users benefited from EMSL capabilities and expertise. This total included 231 onsite users and 116 remote users.

Publications

Journal Articles

Averkiev BB, AI Boldyrev, X Li, and LS Wang. 2007. "Planar Nitrogen-Doped Aluminum Clusters AIxN- (x=3-5)." *Journal of Chemical Physics* 125(12): Art. No. 124305. doi:10.1063/1.2335449

Boily JF, J Szanyi, and AR Felmy. 2007. "Effects of Surface Coordination on the Temperature-Programmed Desorption of Oxalate from Goethite." *Journal of Physical Chemistry C* 111(45):17072-17081. doi:10.1021/jp075576q

Boily JF, O Qafoku, and AR Felmy. 2007. "A Potentiometric, Spectrophotometric and Pitzer Ion-Interaction Study of Reaction Equilibria in the Aqueous H^+-Al^{3+}, H^+-Oxalate and H^+-Al^{3+}-Oxalate Systems up to 5 mol*dm^{-3} NaCl ." *Journal of Solution Chemistry* 36(11-12):1727-1743. doi:10.1007/s10953-007-9203-9

Bondarchuk O, and I Lyubinetsky. 2007. "Preparation of TiO_2(110)-(1x1) Surface via UHV Cleavage: An Scanning Tunneling Microscopy Study." *Review of Scientific Instruments* 78(11): Art. No. 113907. doi:10.1063/1.2814160

Bonini N, M Lazzeri, N Marzari, and F Mauri. 2007. "Phonon Anharmonicities in Graphite and Graphene." *Physical Review Letters* 99(176802):1-4. doi:10.1103/PhysRevLett.99.176802

Chambers SA, SH Cheung, V Shutthanandan, S Thevuthasan, MK Bowman, and AG Joly. 2007. "Properties of Structurally Excellent N-doped TiO_2 Rutile." *Chemical Physics* 339(1-3):27-35. doi:10.1016/j.chemphys.2007.04.024

Chambers SA. 2007. "Surface Science Opportunities in the Electronic Structure of ZnO (A Perspective on the Article, "Quantitative Analysis of Surface Donors in ZnO", by D.C. Look)." *Surface Science* 601(23):5313-5314. doi:10.1016/j.susc.2007.10.004

Chimentão RJ, JE Herrera, JH Kwak, F Medina, Y Wang, and CHF Peden. 2007. "Oxidation of Ethanol to Acetaldehyde over Na-Promoted Vanadium Oxide Catalysts." *Applied Catalysis. A, General* 332(2):263-272. doi:10.1016/j.apcata.2007.08.024

Cygan RT, CT Stevens, RW Puls, SB Yabusaki, RD Wauchope, CJ McGrath, GP Curtis, MD Siegel, LA Veblen, and DR Turner. 2007. "Research Activities at U.S. Government Agencies in Subsurface Reactive Transport Modeling." *Vadose Zone Journal* 6(4):805-822. doi:10.2136/vzj2006.0091

Devanathan R, A Venkatnathan, and M Dupuis. 2007. "Atomistic Simulation of Nafion Membrane. 2. Dynamics of Water Molecules and Hydronium Ions." *Journal of Physical Chemistry B* 111(45):13006-13013. doi:10.1021/jp0761057

Dixon DA, T Wang, DJ Grant, KA Peterson, KO Christe, and GJ Schrobilgen. 2007. "Heats of Formation of Krypton Fluorides and Stability Predictions for KrF_4 and KrF_6 from High Level Electronic Structure Calculations." *Inorganic Chemistry* 46(23):10016-10021. doi:10.1021/ic701313h

Elias DA, SL Tollaksen, DW Kennedy, HM Mottaz, CS Giometti, JS McLean, EA Hill, GE Pinchuk, MS Lipton, JK Fredrickson, and YA Gorby. 2007. "The Influence of Cultivation Methods on *Shewanella oneidensis* Physiology and Proteome Expression." *Archives of Microbiology*. doi:10.1007/s00203-007-0321-y

Farber R. 2007. "The Future Looks Bright for Teraflop Computing." *Scientific Computing* 24(10):34.

Glezakou VA, M Dupuis, and CJ Mundy. 2007. "Acid/Base Equilibria in Clusters and their Role in Proton Exchange Membranes: Computational Insight." *Physical Chemistry Chemical Physics* 9(43):5752-5760. doi:10.1039/b709752b

Goodman DW, CHF Peden, and MS Chen. 2007. "CO Oxidation on Ruthenium: The Nature of the Active Catalytic Surface." *Surface Science* 601(19):L124 - L126. doi:10.1016/j.susc.2007.08.003

Goodman DW, CHF Peden, and MS Chen. 2007. "Reply to Comment on "CO Oxidation on Ruthenium: The Nature of the Active Catalytic Surface" by H Over, M Muhler, and AP Seitsonen." *Surface Science* 601(23):5663–5665. doi:10.1016/j.susc.2007.09.042

Hadjar O, JH Futrell, and J Laskin. 2007. "First Observation of Charge Reduction and Desorption Kinetics of Multiply Protonated Peptides Soft Landed onto Self-Assembled Monolayer Surfaces." *Journal of Physical Chemistry C* 111(49):18220-18225. doi:10.1021/jp075293y

Hammond JR, K Kowalski, and WA de Jong. 2007. "Dynamic Polarizabilities of Polyaromatic Hydrocarbons Using Coupled-Cluster Linear Response Theory." *Journal of Chemical Physics* 127(14): Art. No. 144105. doi:10.1063/1.2772853

Han P, S Axnanda, I Lyubinetsky, and DW Goodman. 2007. "Atomic-Scale Assembly of a Heterogeneous Catalytic Site." *Journal of the American Chemical Society* 129(46):14355-14361. doi:10.1021/ja074891n

Hooker BS, DJ Bigelow, and CT Lin. 2007. "Methods for Mapping of Interaction Networks Involving Membrane Proteins." *Biochemical and Biophysical Research Communications* 363(3):457-461. doi:10.1016/j.bbrc.2007.09.031

Ibrahim Y, ME Belov, AV Tolmachev, DC Prior, and RD Smith. 2007. "Ion Funnel Trap Interface for Orthogonal Time-of-Flight Mass Spectrometry." *Analytical Chemistry* 79(20):7845-7852. doi:10.1021/ac071091m

Iddir H, V Komanicky, S Öğüt, H You, and P Zapol. 2007. "Shape of Platinum Nanoparticles Supported on $SrTiO_3$: Experiment and Theory." *Journal of Physical Chemistry C* 111(40):14782-14789. doi:10.1021/jp073041r

Jacob RE, G Laicher, and KR Minard. 2007. "3D MRI of Non-Gaussian ^3He Gas Diffusion in the Rat Lung." *Journal of Magnetic Resonance* 188(2):357-366. doi:10.1016/j.jmr.2007.08.014

Jacobs JM, KM Waters, LE Kathmann, DG Camp, II, HS Wiley, RD Smith, and BD Thrall. 2007. "The Mammary Epithelial Cell Secretome and Its Regulation by Signal Transduction Pathways." *Journal of Proteome Research.* ASAP Article. doi:10.1021/pr0704377

Joly AG, W Chen, J Zhang, and SP Wang. 2007. "Electronic Energy Relaxation and Luminescence Decay Dynamics of Eu^{3+} in $Zn_2SiO_4:Eu^{3+}$." *Journal of Luminescence* 126(2):491-496. doi:10.1016/j.jlumin.2006.09.004

Joslin EJ, LK Opresko, A Wells, HS Wiley, and DA Lauffenburger. 2007. "EGF-Receptor-Mediated Mammary Epithelial Cell Migration Is Driven by Sustained ERK Signaling from Autocrine Stimulation." *Journal of Cell Science* 120(20):3688-3699. doi:10.1242/jcs.010488

Kannan S and M Zacharias. 2007. "Folding of a DNA Hairpin Loop Structure in Explicit Solvent Using Replica-Exchange Molecular Dynamics Simulations." *Biophysical Journal* 93:3218-3228. doi:10.1529/biophysj.107.108019

Karakoti AS, SVNT Kuchibhatla, KS Babu, and S Seal. 2007. "Direct Synthesis of Nanoceria in Aqueous Polyhydroxyl Solutions." *Journal of Physical Chemistry C* 111(46):17232-17240. doi:10.1021/jp076164k

Kim Y, BD Kay, JM White, and Z Dohnálek. 2007. "Alcohol Chemistry on Rutile TiO_2(110): The Influence of Alkyl Substituents on Reactivity and Selectivity." *Journal of Physical Chemistry C* 111(49):18236-18242. doi:10.1021/jp075608+

Kim Y, BD Kay, JM White, and Z Dohnálek. 2007. "Inductive Effect of Alkyl Chains on Alcohol Dehydration at Bridge-Bonded Oxygen Vacancies of TiO_2(110)." *Catalysis Letters* 119(1-2):1-4. doi:10.1007/s10562-007-9199-1

Kokubo H, J Rösgen, DW Bolen, and BM Pettitt. 2007. "Molecular Basis of the Apparent Near Ideality of Urea Solutions." *Biophysical Journal* 93(10):3392-3407. doi:10.1529/biophysj.107.114181

Kowalski K, JR Hammond, and WA de Jong. 2007. "Linear Response Coupled Cluster Singles and Doubles Approach with Modified Spectral Resolution of the Similarity Transformed Hamiltonian." *Journal of Chemical Physics* 127(16):164105 (9). doi:10.1063/1.2795708

Kwak JH, JZ Hu, DH Kim, J Szanyi, and CHF Peden. 2007. "Penta-Coordinated Al^{3+} Ions as Preferential Nucleation Sites for BaO on γ-Al_2O_3: An Ultra-High-Magnetic Field ^{27}Al MAS NMR Study." *Journal of Catalysis* 251(1):189-194. doi:10.1016/j.jcat.2007.06.029

Lane CD, NG Petrik, TM Orlando, and GA Kimmel. 2007. "Electron-Stimulated Oxidation of Thin Water Films Adsorbed on TiO_2(110)." *Journal of Physical Chemistry C* 111(44):16319-16329. doi:10.1021/jp072479o

Lau K, W Zheng, N Wong, and W Li. 2007. "Theoretical Prediction of the Ionization Energies of the C_4H_7 Radicals: 1-Methylallyl, 2-Methylallyl, Cyclopropylmethyl, and Cyclobutyl Radicals." *Journal of Chemical Physics* 127:154302. doi:10.1063/1.2774972

Li S, and DA Dixon. 2007. "Low-Lying Electronic States of $M_3O_9^-$ and $M_3O_9^{2-}$ (M = Mo, W)." *Journal of Physical Chemistry A* 111(43):11093-11099. doi:10.1021/jp074187t

Liu C, JM Zachara, NS Foster, and J Strickland. 2007. "Kinetics of Reductive Dissolution of Hematite by Bioreduced Anthraquinone-2,6-Disulfonate." *Environmental Science & Technology* 41(22):7730-7735. doi:10.1021/es070768k

Liu G, and Y Lin. 2007. "Nanomaterial Labels in Electrochemical Immunosensors and Immunoassays." *Talanta* 74(3):308-317. doi:10.1016/j.talanta.2007.10.014

Liu G, Y Lin, H Wu, and Y Lin. 2007. "Voltammetric Detection of Cr (VI) with Disposable Screen-Printed Electrode Modified with Gold Nanoparticles." *Environmental Science & Technology* 41(23):8129-8134. doi:10.1021/es071726z

Liu G, Y Lin, J Wang, H Wu, CM Wai, and Y Lin. 2007. "Disposable Electrochemical Immunosensor Diagnosis Device Based on Nanoparticle Probe and Immunochromatographic Strip." *Analytical Chemistry* 79(20):7644-7653. doi:10.1021/ac070691i

Liu Y, JP Cain, H Wang, and A Laskin. 2007. "Kinetic Study of Heterogeneous Reaction of Deliquesced NaCI Particles with Gaseous HNO3 Using Particle-on-Substrate Stagnation Flow Reactor Approach." *Journal of Physical Chemistry A* 111(40):10026-10043. doi:10.1021/jp072005p

Ma L, Y Wang, J Xue, Q Chen, W Zhang, and W Zhang. 2007. "Energy Loss and Straggling of MeV Ions through Biological Samples." *Journal of Applied Physics* 102(8):084702, 1-6. doi:10.1063/1.2800996

Marginean N, RT Kelly, JS Page, K Tang, and RD Smith. 2007. "Electrospray Characteristic Curves: In Pursuit of Improved Performance in the Nanoflow Regime." *Analytical Chemistry* 79(21):8030-8036. doi:10.1021/ac0707986

Marsili E, H Beyenal, L Di Palma, C Merli, A Dohnalkova, JE Amonette, and Z Lewandowski. 2007. "Uranium Immobilization by Sulfate-Reducing Biofilms Grown on Hematite, Dolomite, and Calcite." *Environmental Science & Technology* 41(24):8349-8354. doi:10.1021/es071335k

McKinley JP, JM Zachara, J Wan, DE McCready, and SM Heald. 2007. "Geochemical Controls on Contaminant Uranium in Vadose Hanford Formation Sediments at the 200 Area and 300 Area, Hanford Site, Washington." *Vadose Zone Journal* 6(4):1004-1017. doi:10.2136/vzj2006.0184

Mei D, NA Deskins, and M Dupuis. 2007. "A Density Functional Theory Study of Formaldehyde Adsorption on Ceria." *Surface Science* 601(21):4993-5001. doi:10.1016/j.susc.2007.08.027

Oostrom M, ML Rockhold, PD Thorne, MJ Truex, GV Last, and VJ Rohay. 2007. "Carbon Tetrachloride Flow and Transport in the Subsurface of the 216-Z-9 Trench at the Hanford Site." *Vadose Zone Journal* 6(4):971-984. doi:10.2136/vzj2006.0166

Ouyang J, JA Ripmeester, X Wu, D Kingston, K Yu, AG Joly, and W Chen. 2007. "Upconversion Luminescence of Colloidal CdS and ZnCdS Semiconductor Quantum Dots." *Journal of Physical Chemistry C* 111(44):16261-16266. doi:10.1021/jp074416b

Petrik NG, and GA Kimmel. 2007. "Hydrogen Bonding, H-D Exchange, and Molecular Mobility in Thin Water Films on TiO_2(110)." *Physical Review Letters* 99(19):Art.No.196103. doi:10.1103/PhysRevLett.99.196103

Riley BJ, SK Sundaram, BR Johnson, and LV Saraf. 2007. "Differential Etching of Chalcogenides for Infrared Photonic Waveguide Structures." *Journal of Non-Crystalline Solids* 354(10-11):813-816. doi:10.1016/j.jnoncrysol.2007.08.061

Rong Z, F Gao, WJ Weber, and G Hobler. 2007. "Monte Carlo Simulations of Defect Recovery within a 10 keV Collision Cascade in 3C-SiC." *Journal of Applied Physics* 102(10):103508, 1-7. doi:10.1063/1.2812701

Schuchardt KL, BJ Palmer, JA Daily, TO Elsethagen, and AS Koontz. 2007. "IO Strategies and Data Services for Petascale Data Sets from a Global Cloud Resolving Model." *Journal of Physics: Conference Series* 78:Art. No. 012089 (6pp). doi:10.1088/1742-6596/78/1/012089

Senko JM, SD Kelly, AC Dohnalkova, JT McDonough, KM Kemner, and WD Burgos. 2007. "The Effect of U(VI) Bioreduction Kinetics on Subsequent Reoxidation of Biogenic U(IV)." *Geochimica et Cosmochimica Acta* 71(19):4644-4654. doi:10.1016/j.gca.2007.07.021

Shchukarev A, JF Boily, and AR Felmy. 2007. "XPS of Fast-Frozen Hematite Colloids in NaCl Aqueous Solutions: I. Evidence for the Formation of Multiple Layers of Hydrated Sodium and Chloride Ions Induced by the {001} Basal Plane." *Journal of Physical Chemistry C* 111(49):18307-18316. doi:10.1021/jp075321c

Shukla AK. 2007. "Bimodal Energy Distributions in the Scattering of Ar^+ Ions from Modified Surfaces at Hyperthermal Energies." *Chemical Physics Letters* 449(1-3):53-56. doi:10.1016/j.cplett.2007.10.043

Shukla AK. 2007. "Fragmentation Dynamics of CS22+ on Collision with a Self-Assembled Monolayer Surface." *Chemical Physics Letters* 448(4-6):156-158. doi:10.1016/j.cplett.2007.09.083

Song C, RA Zaveri, ML Alexander, JA Thornton, S Madronich, JV Ortega, A Zelenyuk, X Yu, A Laskin, and DA Maughan. 2007. "Effect of Hydrophobic Primary Organic Aerosols on Secondary Organic Aerosol Formation from Ozonolysis of α-Pinene." *Geophysical Research Letters* 34(20):L20803. doi:10.1029/2007GL030720

Thurber A, KM Reddy, V Shutthanandan, MH Engelhard, C Wang, J Hays, and A Punnoose. 2007. "Ferromagnetism in Chemically Synthesized CeO_2 Nanoparticles by Ni Doping." *Physical Review. B, Condensed Matter* 76(16):165206 (p 1-8). doi:10.1103/PhysRevB.76.165206

Tuma J, S Tonzani, GC Schatz, AH Karaba, and FD Lewis. 2007. "Structure and Electronic Spectra of DNA Mini-hairpins with G_n:C_n Stems." *Journal of Physical Chemistry B* 111(45):13101-13106. doi:10.1021/jp072303m

Valiev M, J Yang, JA Adams, SS Taylor, and JH Weare. 2007. "Phosphorylation Reaction in cAPK Protein Kinase-Free Energy Quantum Mechanical/Molecular Mechanics Simulations." *Journal of Physical Chemistry B* 111(47):13455-13464. doi:10.1021/jp074853q

Wang CM, DR Baer, JE Amonette, MH Engelhard, JJ Antony, and Y Qiang. 2007. "Electron Beam-Induced Thickening of the Protective Oxide Layer around Fe Nanoparticles." *Ultramicroscopy* 108(1):43-51. doi:10.1016/j.ultramic.2007.03.002

Wang D and WM Huo. 2007. "An Eight-Degree-of-Freedom, Time-Dependent Quantum Dynamics Study for the H_2+C_2H Reaction on a New Modified Potential Energy Surface." *Journal of Chemical Physics* 127(15):Art. No. 154304. doi:10.1063/1.2794757

Wang LQ, XD Zhou, GJ Exarhos, LR Pederson, CM Wang, CF Windisch, Jr, and C Yao. 2007. "Proton Dynamics in ZnO Nanorods Quantified by *In Situ* Solid-State ^1H Nuclear Magnetic Resonance Spectroscopy." *Applied Physics Letters* 91(17):Art. No. 173107. doi:10.1063/1.2799734

Wellman DM, EM Pierce, and MM Valenta. 2007. "Efficacy of Soluble Sodium Tripolyphosphate Amendments for the In-Situ Immobilisation of Uranium." *Environmental Chemistry* 4(5):293-300.

Wigginton NS, KM Rosso, and MF Hochella Jr. 2007. "Mechanisms of Electron Transfer in Two Decaheme Cytochromes from a Metal-Reducing Bacterium." *Journal of Physical Chemistry B* 111(44):12857-12864. doi:10.1021/jp0718698

Yang F, DG Camp, II, MA Gritsenko, Q Luo, RT Kelly, TRW Clauss, WR Brinkley, RD Smith, and DL Stenoien. 2007. "Identification of a Novel Mitotic Phosphorylation Motif Associated with Protein Localization to the Mitotic Apparatus." *Journal of Cell Science* 120(22):4060-4070. doi:10.1242/jcs.014795

Yang F, N Jaitly, H Jayachandran, Q Lou, ME Monroe, X Du, MA Gritsenko, R Zhang, DJ Anderson, SO Purvine, JN Adkins, RJ Moore, HM Mottaz, S Ding, MS Lipton, DG Camp, II, HR Udseth, RD Smith, and S Rossie. 2007. "Applying a Targeted Label-free Approach using LC-MS AMT Tags to Evaluate Changes in Protein Phosphorylation Following Phosphatase Inhibition." *Journal of Proteome Research* 6(11):4489-4497. doi:10.1021/pr070068e

Yang Z, G Xia, MS Walker, CM Wang, JW Stevenson, and P Singh. 2007. "High Temperature Oxidation/Corrosion Behavior of Metals and Alloys Under a Hydrogen Gradient." *International Journal of Hydrogen Energy* 32(16):3770-3777. doi:10.1016/j.ijhydene.2006.08.056

Yantasee W, Y Lin, K Hongsirikarn, GE Fryxell, R Addleman, and C Timchalk. 2007. "Electrochemical Sensors for the Detection of Lead and Other Toxic Heavy Metals: The Next Generation of Personal Exposure Biomonitors." *Environmental Health Perspectives* 115(12):1683-1690.

Yao C, Y Shin, LQ Wang, CF Windisch, JR, WD Samuels, BW Arey, CM Wang, WM Risen Jr., and GJ Exarhos. 2007. "Hydrothermal Dehydration of Aqueous Fructose Solutions in a Closed System." *Journal of Physical Chemistry C* 111(42):15141-15145. doi:10.1021/jp074188l

Yi CW and J Szanyi. 2007. "D_2O Adsorption on an Ultrathin Alumina Film on NiAl(110)." *Journal of Physical Chemistry C* 111(47):17597-17602. doi:10.1021/jp074459s

Yi CW, JH Kwak, and J Szanyi. 2007. "Interaction of NO_2 with BaO: From Cooperative Adsorption to $Ba(NO_3)_2$ Formation." *Journal of Physical Chemistry C* 111(42):15299-15305. doi:10.1021/jp074179c

Yi CW, JH Kwak, CHF Peden, CM Wang, and J Szanyi. 2007. "Understanding Practical Catalysts Using a Surface Science Approach: The Importance of Strong Interaction between BaO and Al_2O_3 in NO_x Storage Materials." *Journal of Physical Chemistry C* 111(41):14942-14944. doi:10.1021/jp0763376

Zhai HJ, J Döbler, J Sauer, and LS Wang. 2007. "Probing the Electronic Structure of Early Transition-Metal Oxide Clusters: Polyhedral Cages of $(V_2O_5)_n^-$ (n=2-4) and $(M_2O_5)_2^-$ (M=Nb, Ta)." *Journal of the American Chemical Society* 129(43):13270-13276. doi:10.1021/ja0750874

Zhu M, J Wang, BC Holloway, RA Outlaw, X Zhao, K Hou, V Shutthanandan, and DM Manos. 2007. "A Mechanism for Carbon Nanosheet Formation." *Carbon* 45(11):2229-2234. doi:10.1016/j.carbon.2007.06.017

Zubkov T, RS Smith, TR Engstrom, and BD Kay. 2007. "Adsorption, Desorption, and Diffusion of Nitrogen in a Model Nanoporous Material. I. Surface Limited Desorption Kinetics in Amorphous Solid Water." *Journal of Chemical Physics* 127(18):Art. No. 184707. doi:10.1063/1.2790432

Book Chapter

Liu G, J Wang, Y Lin, and J Wang. 2007. "Nanoparticle-Based Biosensors and Bioassays." Chapter 14 in *Electrochemical Sensors, Biosensors and their Biomedical Applications*, ed. X Zhang, H Ju, J Wang, pp. 441-457. Academic Press, Burlington, MA.

Conference Papers

Krupka KM, WJ Deutsch, HT Schaef, BW Arey, SM Heald, MJ Lindberg, and KJ Cantrell. 2007. "Characterization of Solids in Residual Wastes from Underground Storage Tanks at the Hanford Site, Washington, U.S.A." In *30th International Symposium on Scientific Basis for Nuclear Waste Management, Boston, November 27 – December 1, 2006. Materials Research Society Symposium Proceedings*, vol. 985, ed. DE Dunn, C Poinssot, and B Begg, pp. 473-482. Materials Research Society, Warrendale, PA.

Perkins WA, MC Richmond, and GA McMichael. 2007. "Two-Dimensional Modeling of Time-Varying Hydrodynamics and Juvenile Chinook Salmon Habitat in the Hanford Reach of the Columbia River." In *World Water and Environmental Resources Congress 2004, June 27 – July 1, 2004, Salt Lake City, Utah, USA*, ed. Gerald Sehlke, Donald F Hayes, David K Stevens, p. 180. American Society of Civil Engineers, Reston, VA. doi:10.1061/40737(2004)180

Wei W, G Xiong, Y Sun, AG Joly, KM Beck, JM White, and WP Hess. 2007. "Real Time Study of Cu Diffusion Through a Ru Thin Film by Photoemission Electron Microscopy (PEEM)." In *Materials, Technology and Reliability of Low-k Dielectrics and Copper Interconnects. Materials Research Society Symposium Proceedings; 2006*, vol. 914, ed. Ting Y Tsui, pp. 185-190 (Paper no. 0914-F05-07). Material Research Society, Warrendale, PA.

Conferences and Presentations

During the first quarter of Fiscal Year 2008, EMSL staff presented on research performed at the user facility or attended conferences at the following meetings or locations:

- 2007 American Geophysical Union Fall Meeting, San Francisco, California
- 2007 Biobased Industry Outlook Conference, Ames, Iowa
- 2007 Geological Society of America Annual Meeting, Denver, Colorado
- Advanced Science Research 2007 Symposium, Tokai, Japan
- American Vacuum Society International 54th Symposium, Seattle, Washington
- Center for Environmental Kinetics Analysis All-Hands 4th Annual Meeting, State College, Pennsylvania
- Exploring Actinide Chemistry through a Combination of Computational Modeling and Experiment Seminar, Ames, Iowa
- Hanford Integrated Field Center Field Research Executive Committee Teleconference, Richland, Washington
- International Symposium on Materials Issues in a Hydrogen Economy, Richmond, Virginia
- Juvenile Salmon Tracking, North Bonneville, Washington
- Lawrence Berkeley National Laboratory, San Francisco, California
- National Academy of Sciences Review, Richland, Washington
- Office of Naval Research Research Tools Program, Arlington, Virginia
- Presentation to Bioinformatics and Statistics students, Texas A&M, College Station, Texas
- Presentation to CH2M HILL Hanford Group, Fluor Hanford, and Pacific Northwest National Laboratory, Richland, Washington
- Sixth International Association of Hydrological Sciences Groundwater Quality Conference 2007, Fremantle, Australia
- Supercomputing 2007, Reno, Nevada
- Washington State University, School of Chemical Engineering and Bioengineering, Pullman, Washington