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Summary of the NTNFC Postdoctoral Fellowship Program

PNNL.13.007 (April 2013 – March 2014)

JM Schwantes
LE Sweet
LW McDonald IV
BK McNamara
DG Abrecht
DD Reilly
CJ Barinaga

March 2014

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Richland, Washington 99352

1.0 Summary of Postdocs and Projects

Dallas Reilly

This FY Dallas was involved with multiple projects, including projects directly funded by NTNFC and other project work not directly funded by NTNFC but otherwise meaningful for the development of technical skills necessary for nuclear forensics.

Dallas participated in the Development of Predictive Signatures project (PNNL.13.005) by evaluating and summarizing the previous modeling efforts in order to train and prepare David Abrecht for working with the model upon his arrival, and has worked to help develop the database of thermodynamic constants and Pitzer parameters necessary to operate the database. More detail is available in the final report on the Development of a Predictive Signature Capability for Generating Contaminant Patterns for High Risk Reprocessing Methods task.

In the previous fiscal year, Dallas participated in a project that analyzed the natural aging and oxidation of uranium oxides that, under certain conditions, produces the hydrated uranium trioxide metaschoepite ($UO_3 \cdot 2H_2O$). This FY, Dallas extended this initial work and performed in-depth analysis of the growth and development of uranium trioxide phases under artificial annealing conditions in air, as a function of annealing time and temperature and starting material. The uranium-oxygen system has been studied in detail for extreme conditions in the literature, but few certainties in the formation of uranium trioxide phases under industrial processing conditions exist. Utilizing different uranium precursors commonly used in industrial processes, such as ammonium uranyl carbonate ($(NH_4)_4UO_2(CO_3)_3$, AUC) and uranyl peroxide (UO_4), various uranium trioxide compounds were produced by thermal oxidation in air at varying conditions of time and temperature, and the resulting compounds were analyzed by powder XRD, SEM, and micro-Raman spectroscopy. Some of the significant discoveries made in this FY include some of the first Raman spectra on a number of UO_3 phases, a phase diagram including the ranges of conditions that produce phases such as β-UO_3 and γ-UO_3, and answers to some basic questions not outlined in the literature (i.e. why does washed vs unwashed uranyl peroxide matter for producing α-UO_3?). Dallas's efforts are continuing on this project, with him currently assisting in the production of ~10 g batches of each UO_3 phase, based on the previously generated phase diagrams, for bulk characterization of the materials.

Dallas was instrumental in the preparation of materials for the International Technical Working Group Collaborative Materials Exercise (PNNL.13.002) this year. Dallas's previous experience made him a good candidate for this project, and included work at PNNL with controlled thermal oxidation of the materials and analysis of the prepared materials by SEM, XRD, and thermogravimetric analysis. After this preparation, Dallas worked for two weeks in Australia preparing the final materials and helping arrange for shipping back to the United States. For more information on this work, refer to the International Exercises task final report.

David Abrecht

David's efforts have primarily been to assist in the modeling aspects of the various projects he has been involved with. He has contributed significantly to the Development of Predictive Signatures project (PNNL.13.005) efforts to model trace elemental composition of the bismuth phosphate process, including development of the physical constants database and initial modeling efforts for the first precipitation stage. These efforts are detailed in the final report for that task.

David has also participated in the ongoing efforts at PNNL to monitor the fallout of the Fukushima-Daiichi Nuclear Power Plant accident. His efforts have involved the development of advanced free energy correlations capable of estimating the maximum reactor temperature during the accident and predicting the concentrations of unmeasured radionuclides in soil samples present from atmospheric venting.

David has also contributed significantly to a current LDRD effort to develop a PNNL capability for actinide Mössbauer spectroscopy. This effort is designed to incorporate Mossbauer spectroscopy into the suite of available techniques for non-destructive chemical characterization and isotopic quantification of actinide-containing bulk materials and powders, which will allow direct probing of chemical process signatures available within the materials. While this system in under construction, David's efforts in this FY have been supportive of future measurement efforts. He has begun development of a library of theoretical Mössbauer parameters for ^{237}Np compounds to compare to experiments using density functional theory, and has shown success in predicting the nuclear energy level splittings for $^{237}NpO_2$. In addition, David has developed a software filter based on the Kalman filter to improve the signal-to-noise ratio of the measurements in real time. In tests with ^{57}Fe Mossbauer, this filter is providing improvements in the signal-to-noise ratio of measurements of 50% and improvements in detection time of up to 60% when compared to the unfiltered data. These improvements in measurement time will be critical for actinide measurements, which typically have lower absorption cross-sections than iron.

Luther McDonald

Luther McDonald was responsible for performing multiple mass spectrometry projects during this FY. His largest project involved the construction of a Quadrupole-based, negative-ion mass spectrometer for thermal ionization mass spectrometric characterization of actinides fluorinated with NF_3 gas. This selective fluorinating agent allows controlled separation of actinide species from complex matrices and each other by thermal control of the extent of reaction. By coupling the mass spectrometer inlet to the outlet of a thermogravimetric analyzer with precise temperature control, which will allow precise measurement of mass deviations from a solid sample, the fluorinated species being volatilized can be controlled to reduce errors from isobaric effects and fragmentation. Luther was successful this FY in completing construction of the instrument and performing initial analysis of the instrument characteristics.

2.0 Postdoctoral Fellow Research Contributions

Below is a complete description of references which were supported by the NTNFC Postdoctoral Fellowship program.

Formal Reports (1)

Meier DE, JB Coble, DV Jordan, JB Forrester, K Unlu, S Landsberger, S Bender, KJ Dayman, DD Reilly, LW McDonald, IV, and JM Schwantes. 2013. *The Multi-Isotope Process (MIP) Monitor Project: FY13 Final Report*. PNNL-22799, Pacific Northwest National Laboratory, Richland, WA.

Presentations (4)

Schwantes JM, EJ Mausolf, and LW McDonald, IV. 2013. "Cs in Coastal and Marine Waters." Presented by Jon Schwantes (Invited Speaker) at Fukushima Daiichi Cleanup Workshop #3 , Tokyo, Japan on July 17, 2013. PNNL-SA-96682.

Sweet LE, DD Reilly, TA Blake, CH Henager, Jr, SY Hu, DE Meier, JM Schwantes, YF Su, JE Szecsody, and TJ Johnson. 2013. "Understanding the Polymorphic Nature of UO_3 to Infer Process History." Presented by Lucas Sweet (Invited Speaker) at SPIE Defense, Security and Sensing, Baltimore, MD on April 29, 2013. PNNL-SA-95427.

Johnson TJ, LE Sweet, DD Reilly, DG Abrecht, TA Blake, CH Henager, Jr, SY Hu, DE Meier, JM Schwantes, YF Su, and JE Szecsody. 2013. "Understanding the Polymorphic Nature of UO_3 to Infer Process History." Presented by Dallas Reilly (Invited Speaker) at ACS 246th National Meeting, Indianapolis, IN on September 9, 2013. PNNL-SA-98150.

Johnson TJ, LE Sweet, DD Reilly, DG Abrecht, TA Blake, CH Henager, Jr, SY Hu, DE Meier, JM Schwantes, YF Su, and JE Szecsody. 2013. "Spectroscopic Studies *of Several Isomers of UO_3 ." Presented by Tim J. Johnson (Invited Speaker) at SPIE Counterterrorism Conference, Dresden, Germany on September 23, 2013. PNNL-SA-98282.

Abstracts (4)

Reilly DD, LE Sweet, and JM Schwantes. 2013. "Understanding the Polymorphic Nature of UO_3 to Infer Process History." Abstract submitted to ACS Fall Conference, Indianapolis, IN. PNNL-SA-94484.

Sweet LE, DD Reilly, TA Blake, JE Szecsody, DE Meier, YF Su, CS Brauer, EC Buck, and TJ Johnson. 2013. "Spectroscopic Studies of the Several Isomers of UO_3." Abstract submitted to SPIE Security + Defence 2013--Optics and Photonics for Counterterrorism, Crime Fighting and Defence , Dresden, Germany. PNNL-SA-94762.

Abrecht DG, and JM Schwantes. 2013. "Thermodynamic Modeling of Fission Product Release from the Fukushima Daiichi Nuclear Accident." Abstract submitted to 247th ACS National Meeting, Dallas, TX. PNNL-SA-98981.

Sweet LE, DG Abrecht, DD Reilly, and JM Schwantes. 2013. "Contaminants of the Bismuth Phosphate Process as Signifiers of Nuclear Reprocessing History." Abstract submitted to the IAEA International Conference on Advances in Nuclear Forensics, scheduled for July 7-10 2014. PNNL-SA-99739.

Conference Papers (1)

Sweet LE, DD Reilly, DG Abrecht, EC Buck, DE Meier, YF Su, CS Brauer, JM Schwantes, RG Tonkyn, JE Szecsody, TA Blake, and TJ Johnson. 2013. "Spectroscopic Studies of the Several Isomers of UO_3." In *Optics and Photonics for Counterterrorism, Crime Fighting and Defence IX; and Optical Materials and Biomaterials in Security and Defence Systems Technology X, September 23, 2013, Dresden, Germany. Proceedings of the SPIE* , vol. 8901, ed. R Zamboni, et al, p. Paper No. 890107. SPIE, Bellingham, WA. doi:10.1117/12.2029408

A manuscript entitled "The Solubility of $^{242}PuO_2$ in the presence of Aqueous Fe(II): The Impact of Precipitate Preparation" has been produced by **AR Felmy, DA Moore, EC Buck, SD Conradson, RK Kukkadapu, LE Sweet, DG Abrecht, and ES Ilton** and includes collaborative work with David Abrecht on his Mössbauer efforts. This manuscript has been submitted to *Radiochimica Acta.*

David Abrecht was a contributing author on a manuscript with **Edward Mausolf, Kenny Dayman, Bruce McNamara, Chuck Soderquist, Sheldon Landsberger, Edgar Buck, and Jon Schwantes** entitled "Implication of the Presence of Silver Iodide in Used Nuclear Fuel," submitted to the *Journal of Nuclear Materials.*

David Abrecht has prepared a manuscript entitled "Linear Free Energy Correlations for Fission Product Release from the Fukushima-Daiichi Nuclear Accident" describing his work with thermodynamic modeling of the Fukushima-Daiichi fallout spread. This article will be submitted to *Environmental Science and Technology.*

David's work is also the topic of a presentation "Thermodynamic Modeling of Fission Product Release from the Fukushima-Daiichi Nuclear Accident" which will be presented at the ACS National Meeting in Dallas, TX, on March 18th.

3.0 Benefits (to the laboratory, the mentors, and postdocs)

The NTNFC Postdoctoral Fellows program has offered a number of benefits to our laboratory, our staff, and the postdoctoral fellows. First and foremost, this fellowship program has offered critical training and mentoring opportunities to the next generation of nuclear forensic scientists. Due to the particular nature of the research, many skills necessary for the development of these young scientists and their transition into successful careers are only available in a National Laboratory setting. This fellowship program has provided support for these young scientists during this difficult transition period.

Secondarily, this program offers some support to staff participation in mentoring and training activities. Although training of new scientists is often a normal part of a staff members' day, this necessary and important task for the development of the next generation is not typically captured within the scope of "research and development" activities. This program has provided support for these normally unfunded training activities, allowing improvements in the consistent transfer of skills and career development for this young talent.

4.0 Challenges

In December, Luther McDonald left the laboratory to join the faculty of the University of Utah as an Assistant Professor. The project has advertised for a replacement for Luther and is in the process of down-selecting a new Post-Doc.