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Co-PIs:

Institution: Stony Brook University, Stony Brook

Title: Microbial Transformations of TRU and Mixed Wastes: Actinide Speciation and Waste Volume Reduction

SC Division: SC-23.4

Program Manager: Roland F. Hirsch 301-903-9009

Research Areas:

Final technical report

Research objectives:

In order to understand the susceptibility of transuranic and mixed waste to microbial degradation (as well as any mechanism which depends upon either complexation and/or redox of metal ions), it is essential to understand the association of metal ions with organic ligands present in mixed wastes. These ligands have been found in our previous EMSP study to limit electron transfer reactions and strongly affect transport and the eventual fate of radionuclides in the environment.^{1,2} As transuranic waste (and especially mixed waste) will be retained in burial sites and in legacy containment for (potentially) many years while awaiting treatment and removal (or remaining in place under stewardship agreements at government subsurface waste sites), it is also essential to understand the aging of mixed wastes and its implications for remediation and fate of radionuclides. The EMSP program described in this report is part of a joint program with the Environmental Sciences Department at Brookhaven National Laboratory. Researchers at BNL have submitted their own final report on this program approximately one year ago (the Stony Brook portion of this program has operated under a one year no cost extension).

The Stony Brook University portion of this award has focused on the association of uranium (U(VI)) and transuranic analogs (Ce(III) and Eu(III)) with cellulosic materials and related compounds, with development of implications for microbial transformation of mixed wastes. The elucidation of the chemical nature of mixed waste is essential for the formulation of remediation and encapsulation technologies, for understanding the fate of contaminant exposed to the environment, and for development of meaningful models for contaminant storage and recovery. Mixed waste containing actinides and organic

¹ A.J. Francis, C.J. Dodge, J.A. McDonald and G.P. Halada, Decontamination of Uranium-Contaminated Surfaces by Hydroxycarboxylic Acid with Uranium Recovery, *Environ. Sci. Technol.*, **39** (13), 5015 -5021, 2005.

² Eng, C.W.; G.P. Halada; A.J. Francis; and C.J. Dodge., "Spectroscopic study of decontaminated corroded carbon steel surfaces" *Surface and Interface Analysis*, vol. 36, pp. 1516-1522 (2004)

materials are especially complex and require extensive study.

Research methodology:

We have used quantum mechanical molecular modeling and synchrotron based IR microspectroscopy and chemical mapping to complement SEM/EDAX and laboratory FTIR and Raman microspectroscopy to determine the spatially-resolved chemical association of actinide analogs (Eu(III), Ce(III), dilute U(VI)) and other metals present in mixed waste (Fe, stainless steel components including oxyanions molybdate and tungstate) with fresh and aged cellulosic materials, chitosan, and simpler organic ligands including isosaccharinic acid and catechol.

Our work to date has involved a broad matrix of samples, including:

1. fresh cellulosic tissue (Kimwipes)
2. aged cellulosic tissue (Kimwipes and two other paper products stored in inoculated and uninoculated brine solutions at Brookhaven National Laboratory for 11 years)
3. isosaccharinic acid (ISA), a key cellulose breakdown product
4. cellulose-coated thin layer chromatography (TLC) plates, before and after surface oxidation
5. electrospun cellulose acetate nanofibers
6. electrospun oxidized cellulose nanofibers
7. low and high molecular weight chitosan
8. catechol ligands (to simulate aromatic phenol association with radionuclides over time)

Our matrix of materials has been carefully chosen to both simulate compounds found in mixed waste and also representative candidate materials for further development as chelating agents to limit mobility of radionuclides in the subsurface. In this way I hope to transition the work completed to date to new programs focused on groundwater remediation and long term waste site stewardship, areas of high importance to the ongoing DOE EM mission.

Electrospinning is a new technique which has been incorporated into this program due to its capability to produce extremely pure materials of high surface area (important for the study of surface chemical states). As noted below, we have used this in combination with chemical post-treatment to generate significant amounts of oxidized cellulose surface states.

As mentioned above, an understanding of the metal-organic association, including stability of complexes formed, is essential for optimizing waste storage and transport. In addition, creating an accurate model of this association is vital for understanding transport and fate of contaminants in the environment. Using recognized analogs and dilute U solutions with deuterated water, we prepared samples which were analyzed using both laboratory and synchrotron-based IR microspectroscopy to identify associations in areas rich in various ligands and structures (i.e. fibers). Initial analysis using scanning electron microscopy and EDAX has indicated that this association is heterogeneous and

hence needs further study. As stated above, the baseline knowledge developed in this work will aid in our understanding of organometallic complexes in biomacromolecular material, which has applications in other areas of remediation, materials development and biomass energy research.

Results and discussion (summary):

1. Laboratory FTIR study of aged cellulosic materials:

Note: This part of the overall study was conducted while the EMSP activities were operated as a subcontract from Brookhaven National Laboratory. Hence the information below is summarized from the progress report on this program submitted by BNL.

Aged cellulosic materials have been prepared at BNL since 1992. Initial analysis of these samples was conducted in order to identify the nature of any chemical transformation brought about by solution chemistry (including pH and the presence of ions or growth media) as well as by the presence of microbial activity in the samples as noted below.

Cellosic samples were prepared 1/29/92 from various sources, including white and brown paper towel, and Kimwipes. The mixed cellulose samples were cut into 1 cm x 1 cm squares and transferred to glass serum bottles and various treatments were conducted: unamended (U) samples were filled with nitrogen-purged brine from G-Seep (4.1 M Na⁺ and 5.1 Cl⁻ with minor amounts of Mg, K, and Ca and 0.3 M sulfate (Brush, 1990)); unamended/inoculated (UI) samples were filled with bacteria-containing surface lake water, sediment, and halite from the underground at the WIPP site; amended/inoculated (AI) samples were inoculated in this fashion and amended with nutrients; and amended/inoculated/excess nitrate (AINO3) samples were inoculated with excess nitrate in the form of KNO₃ (5 g L⁻¹ (49.5 mM)). Further information on sample preparation is available. All samples were analyzed by Fourier transform infrared spectroscopy (FTIR) at SBU to identify any transformations in cellulosic material which may have occurred during treatment and storage.

FTIR spectra were obtained using a Nicolet 760 infrared spectrometer modified to collect data in both mid- and far infrared regions and equipped with a Continuum microscope (Spectra-Tech, Inc., Shelton, CT) to collect data in reflection mode from features down to tens of microns. Additional equipment information and details of data analysis are available. All wavenumbers used in this study and not specified to be obtained from standards were obtained from the Spectral AtlasTM database (Academic Press, version 1.0, 1998).

In general, spectra were found to contain features associated with carbonyl from xylose or glucuronic acid, carbonyl associated with aromatic ring structures, lignin, carboxylic acid, aliphatic ligands, hydroxyl groups, and some features normally associated with alkali-treated paper. These features were identified during preliminary analysis of the data. The samples have degraded heterogeneously as observed by the slight differences in spectra obtained from various spots on the same sample. While some differences have

been noted between samples, these are only on the order of differences found within a single sample. For statistical purposes, we have averaged a series of spectra obtained from the same sample. This averaging has undermined the intensity of degradation, and indicated that degradation is very heterogeneous. The following studies have been conducted to determine the effect of these chemical changes in relation to chemical and physical association with radionuclides.

Note: Activities 2 – 7 are reported as supported through direct EMSP support at Stony Brook University

2. Laboratory FTIR and Raman study of uranium and oxyanion association with fresh and aged cellulosic materials:

Studies using fresh cellulosic material showed primarily physical adsorption of metals, which left large crystalline deposits following aqueous exposure. No strong evidence of chemical reaction was found. This is not entirely surprising, since the cellulosic polymer contains only hydroxyl groups and CH_2OH as possible binding sites for metal ions. Accelrys™ density functional software was used to calculate a molecular model, including the highest occupied molecular orbital (likely metal binding site) for the three glycosic ligand long segment of cellulose.

Aged cellulosic materials (Kimwipes as described above) provided a somewhat more active substrate for adsorption. More dispersed deposits could be noted in SEM micrographs. This was found to be true in the case of exposure to 0.1 M to 1 M solutions of sodium molybdate and sodium tungstate, using deuterated water as the medium (in order to shift the water-generated interference lines in the FTIR spectrum). Increasing the pH of the solution increased metal deposition (to be expected), but even acidic solutions showed significant and well-dispersed attachment of oxyanions to cellulosic fibers. This was somewhat enhanced in the case of the aged fibers. Attachment at elevated pH (near WIPP site values - 8.5 - 9) showed significant changes in the C-OH bonding states, indicating attachment at hydroxyl groups.

Energy optimized molecular models provide clear evidence that the oxyanions associate with terminal hydroxyl groups and serve as sites for further metal ion deposition.

In summary, this work indicated that metal oxyanions, such as molybdate and tungstate, which are known as oxidation agents, associate with aged cellulosic materials, primarily at terminal hydroxyl groups. These metal oxyanions, especially at pH closer to WIPP site values and higher concentrations, associate with hydroxyl and glycosic sites, affecting cellulose structure (as indicated by increasing disorder and changes to vibrational states of the glycosic linkage). In addition, it was found that the nature of metal and pH have a strong effect on the surface chemistry, which would be reflected in the susceptibility to breakdown by microorganisms.

3. Cellulosic Materials reacted with depleted uranium (D.U.) substrates

From a previous study, my laboratory has maintained several depleted uranium “coins”, used to monitor ongoing atmospheric corrosion of U (and methods for corrosion protection). In a set of carefully monitored experiments, a number of cellulosic samples (both fresh Kimwipe-type tissues and cellulosic TLC plates (as described in (3) below) were placed in contact with the DU coins following immersion in various pH buffer solutions. The samples included:

- (i) 0.05 M NaNO_3 , pH \sim 6.6 , pH adjusted with NaOH, packed with coin
- (ii) 0.05 M NaNO_3 , pH \sim 9.3 , pH adjusted with NaOH, packed with coin
- (iii) 0.05 M NaNO_3 , pH \sim 5.5 , natural pH, packed with coin
- (iv) 0.05 M EuCl_3 , pH \sim 4.8 , natural pH, packed with coin
- (v), (vi) two DU coins placed on cellulose TLC plates, one of which had been oxidized in nitric acid prior to exposure

All six samples were allowed to age in a sealed glove box for approximately 11 months, following which the cellulosic materials were removed, rinsed in equivalent pH (5.5 – 9.3) solutions in the case of the Kimwipe materials, allowed to dry, and analyzed using optical and FTIR/Raman microscopy. Key results from this study are: (a) reactions in the low pH solutions (both 4.8 and 5.5) resulted in large amounts of uranium degradation product (primarily uranyl hydroxides) which became physically and chemically sorbed by the cellulosic material; (b) the sample maintained at neutral pH as well as the sample maintained at pH 9.3 both showed migration of uranyl ions to the cellulosic matrix, and (c) the dry cellulose TLC plates showed no detectable chemical change with time. While results (a) and (c) are expected, (b) is surprising in that even at a pH at which no migration should have occurred, the presence of moisture alone is enough to allow some limited complexation with aged cellulosic materials. This result has important implications for the remediation of stored mixed wastes.

These results are currently in preparation for publication.³ In addition, the continually aged and exposed TLC plates, while not showing any appreciable accumulation of uranyl ions, may still show some surface chemical change with further exposure. In a second set of experiments we will analyze the TLC plates a number of times over the next year. Again, we will be using vibrational and electron spectroscopies (X-ray photoelectron spectroscopy) to analyze the effect of irradiation on cellulose surface states, and then expose the surface to U, Eu and Ce solutions to study the effect on immobilization of metal ions. This work will involve a current undergraduate student who is conducting independent research in the P.I.’s laboratory.

4. Synchrotron-based Infrared Microspectroscopy of cellulosic TLC plates

A proposal to the National Synchrotron Light Source at Brookhaven National Laboratory for Infrared microspectroscopy was submitted, entitled "IR Microspectroscopy of Metallic Binding to Lignocellulosic Materials" and granted. Analysis was conducted for two sessions so far (of two days each) at beamline U10B, and one follow up session was

³ M. Cuiiffo, D. Roeper and G. Halada, “Aging and Transformation in Cellulosic Materials in Contact with Depleted Uranium”, in preparation for publication.

conducted during the the January-April, 2007 experimental period.

Analysis was conducted using thin layer chromatography (TLC) Al plates coated with cellulose (100 micron layers, Sorbent Technologies). Plates were compared both prior to and following oxidation by exposure to a sodium hydroxide solution and acidified by acetic acid. In order to create more accurate molecular models, we collaborated with James Kubicki at Penn State University to use Gaussian software on a Linux cluster processor at his facility. This enabled us to create highly accurate models of the oxidized cellulose (OC) surface, showing the carboxyl binding sites now made available for metal ions. This was confirmed through comparison with experimental analysis. FTIR and complementary molecular modeling using Gaussian indicated that energy optimized models developed for oxidized cellulose (having multiple carboxyl groups) are accurate.

Analysis of the OC-TLC plates, exposed to U(VI), Ce(III) and Eu(III) solutions, provided the following conclusions:

- (a) OC surfaces provide strong binding sites for radionuclides, including transuranics.
- (b) The carboxyl group is involved in the bonding.
- (c) The heterocyclic glycosic structure is intact following exposure to metal ion solutions.
- (d) Metal ions are well distributed along OC fibers.

In order to analyze the metal-OC association further, we began a study of electrospun OC fibers.

5. Development of electrospun oxidized cellulose fibers:

The technique of electrospinning was utilized in order to fabricate cellulose non-woven mats to be used as the bulk material for further oxidizing treatment. This technique introduces more extensive and porous configurations into the polymeric mats, which may be potentially beneficial for sequestering a larger percentage of available ions. The electrospinning setup for cellulosic fibers was optimized for a number of critical factors, including source fluid viscosity, voltage between the spinning tip and the target, flow rate of solvent, and physical parameters (distances) in the setup.

An electrospun 'mat' of cellulose acetate nanofibers was formed. This material was then deacetylated using a KOH treatment, followed by oxidation using a preparation of nitric acid and phosphoric acid/sodium nitrate. At each stage, FTIR and Raman vibrational spectra were collected to track the chemical transformation of surface states. The final surface showed evidence of carboxyl states which can act as strong binding sites for metal ions.

OC was successfully produced through electrospinning. IR and Raman spectroscopic data demonstrate the formation of characteristic carboxylic groups in the structure of the final products. However, the use of NaOH/Acetic acid did not fabricate targeted materials, which may be due to the insufficient exposure time to NaOH and acetic acid. OC

represents a strong and effective matrix to bind heavy metal ions such as Ce(III), Eu(III) and U(VI) to form complexes due to its two major ligands, carboxylic and hydroxide groups. Low pH (pH 3) of solutions favors these reactions. High pH cause the metal to precipitate before it is exposed to OC. Molecular modeling provides the theoretical support to the formation of metal-polymer structure. The comparison of the experimental and predicted data shows good agreement.

6. Studies of isosaccharinic acid (ISA)-metal ion complexes:

Another matrix material which acts as an “immobilizer” for uranyl and other metal ions is the alkaline degradation product of cellulose, isosaccharinic acid (ISA). ISA was used, in this research, in the form of Na-ISA, which was obtained from Ca-ISA treated in an aqueous sodium carbonate solution (pH>10) and by subsequent acidifying procedures.

FTIR analysis of Na-ISA associated with uranyl ions revealed ISA comprises primary, secondary and tertiary alcohols as well as carboxylic groups, which certainly shows the potential to bind metal ions. However, perhaps due its short chain length (much smaller than OC), it dissolves in metal ion solutions in low pH. Although this may not be beneficial for use as a stand-alone chelator or filtration substrate, it does not prevent further study of its complexation with metals, which may be useful in combination with bacterial methods for uranium reduction and immobilization.

7. Sorbtion/leaching studies with polysaccharides

We have incorporated electrospun OC and high and low molecular weight chitosan in a polyacrylamide hydrogel matrix for in situ tests of metal chelation in a contaminant plume (containing 60 ppm U) at the Field Research Center at Oak Ridge National Laboratory. Samples were analyzed in the field using X-ray Fluorescence, and re-solubilization of any metal ions sequestered were analyzed through a second immersion.

This has allowed us to collect data on real-world interactions to complement laboratory experiments and provide a clearer understanding of practical applications of these materials.

Sample holders, permeable environmental leaching capsules (PELCAPs), were molded from polyacrylamide gels to encapsulate two types of OC and were immersed in the contaminated wells, FW106 and SS5, to allow the interaction between matrices and contaminant metals, such as U and thorium (Th), to take place. Preliminary data shows that OC and E-OC adsorbed a considerably larger amount of U and Th than equal weights of their counterparts (cellulose, CA, electrospun CA, and neat polymers, which are the encapsulation materials by themselves) in a given time. After some 1300 hours of deployment, samples were transferred to a non-contaminated well to test for leaching of complexed metal ions. It is of interest to note that while sorption of U was more rapid, retention of Th is greater over time. Also, an equal mass of E-OC sorbed over three times more U ions as compared to non-electrospun OC. Encapsulated OC and E-OC samples

are currently being analyzed spectroscopically to further characterize of sorption and retention of both U and Th by OC.

We have also performed some in-laboratory assessment of sorption of radionuclides under laboratory conditions to compare to the results of field research. This study focused on assessing the ability with which selected polysaccharides, both modified (electrospun and non-electrospun oxidized cellulose) and natural (low and high molecular weight chitosan), removed heavy metal from acidic metal ion solutions (U, Ce and Eu) of pH ranging from 1 to 6 under different reaction times, and analyzing the reaction mechanisms occurring between targeted functional groups of polymers, carboxylic group in oxidized cellulose and amino group in chitosan, and metal ions in the solution. Direct-coupled plasma (DCP) spectroscopy was used to determine the amount of metal that polymeric matrices adsorbed, and FTIR and Raman spectroscopy facilitated the investigation on the mechanism of the reaction. Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDAX) were used to study the morphology and compositions of polymeric matrices and polymer-metal complexes. The experimental results suggests that both oxidized cellulose and chitosan possess the capability of immobilizing heavy metals to a certain degree and have the potential of being used as inexpensive PRB filler alternatives.

The results have proved to be extremely promising, and have suggested a number of new proposed experiments for which we will seek additional funding. An industrial partner in the remediation field has shown some interest in helping to further develop these materials for remediation of heavy metal-contaminated groundwater. Discussions are currently underway to develop a university/industry collaboration to further these ends.

Information Dissemination:

Published:

1. Vasko, Stephanie, E; Eng, Charlotte; Halada, Gary, "The Degradation, Complexation, and Chemistry Of Cellulose With Transuranic Analogues: A Study Of The Interaction Of Cellulose With $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ AND $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ", in Proceedings, Sixteenth (16th) Annual Argonne Symposium For Undergraduates In Science, Engineering And Mathematics November 4-5, 2005, Argonne National Laboratory
2. Halada, Gary P., "Complementary Spectroscopic Techniques to Model the Association of Contaminant Uranium with Structural Surfaces", *Journal of Electron Spectroscopy and Related Phenomena*, vol. 150, no. 2-3, pp. 185-194, (2006)
3. Francis, A.J., C.J. Dodge, J.A. McDonald and G.P. Halada, "Decontamination of Uranium-Contaminated Surfaces by Hydroxycarboxylic Acid with Uranium Recovery", *Environ. Sci. Technol.*, 39 (13), pp. 5015 -5021 (2005). (*partially supported through EMSP*)

4. Roeper, Donald F., Devicharan Chidambaram, Clive R. Clayton, Gary P. Halada and J. Derek Demaree, Development of an environmentally friendly protective coating for the depleted uranium–0.75 wt% titanium alloy Part III: Surface analysis of the coating, *Electrochimica Acta* _Volume 51, Issue 19 , 20 May 2006, Pages 3895-3903 (*partially supported through EMSP*)
5. Roeper, Donald F., Devicharan Chidambaram, Clive R. Clayton and Gary P. Halada, Development of an environmentally friendly protective coating for the depleted uranium–0.75 wt.% titanium alloy Part V. Electrochemical impedance spectroscopy of the coating, *Electrochimica Acta*, Volume 53, Issue 5, 1, pp. 2130-2134 (2008). (*partially supported through EMSP*)
6. Gary P. Halada and Clive R. Clayton, “The Intersection of Design, Manufacturing and Surface Engineering”, in Handbook of Environmental Degradation of Materials, Myer Kutz, editor, John Wiley and Sons, New York (2005) (*partially supported through EMSP*)

Submitted and in review:

1. G. Halada, C. Eng and P. Jha, “Electrochemistry of Uranium-Organic Complexes”, submitted to *Electrochimica Acta* (in review).
2. Dong Han, Gary P. Halada, Brian Spalding and Scott C. Brooks. “Electrospun and Oxidized Cellulosic Materials for Environmental Remediation of Heavy Metals in Groundwater”. Model Cellulosic Surfaces, Cellulose and Renewable Materials Division, ACS Symposium Series Book (in review).
3. Dong Han, Scott M. McLennan, and Gary P. Halada, “Potentially low-cost engineered and natural polymeric materials, oxidized cellulose and chitosan, for heavy metal removal from acidic solutions (pH 1-6)”, submitted to Environmental Science and Technology (in review).

In preparation:

1. Cuiffo, M., D. Roeper and G. Halada, “Aging and Transformation in Cellulosic Materials in Contact with Depleted Uranium”, in preparation for publication.
2. Eng, C., P. Jha and G. Halada, “Complexation of Uranium by Organic Ligands: Implications for Bioreduction and Stability”, in preparation for publication
3. Han, Dong; Ph.D. Thesis, department of Materials Science and Engineering, Stony Brook University (2008).

4. P. Jha and G. Halada, "Polycondensation of Catechol Ligands in the Presence of Uranyl Ion", in preparation.

Additional abstracts/presentations:

1. Gary P. Halada, Brian Spalding and Scott C. Brooks, "Comparison of electrospun and non-electrospun oxidized cellulose and chitosan fibrous mats serving as matrices for adsorption of heavy metal ions", Dong Han, , abstract ENVR 208, 234th National American Chemical Society meeting, August 19th-24th, 2007, Boston, MA
2. P. Jha, Gary Halada, J. Kubicki, and A. Ceballos (undergraduate), "Combined spectroscopic and electrochemical analysis of Uranium-Organic interactions", abstract NUCL 139, 234th National American Chemical Society meeting, August 19th-24th, 2007, Boston, MA
3. P. Jha, Gary P. Halada, B. Phillips, J. D. Kubicki and A. Ceballos (undergraduate), Complexation and polymerization: interactions of uranium with organic molecules, abstract NUCL 119, Symposium on Understanding Radionuclide Transport in the Environment: Remediation, Nuclear Waste Disposal, and Long-term Stewardship, Division of Nuclear Chemistry and Technology, The 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007
4. Gary P. Halada, Michael Cuiffo, A. J. Francis, and Cleveland J. Dodge, Effect of uranium complexation on aging of iron oxyhydroxides, abstract ENVR 43 (also extended abstract published), Symposium on Abiotic and Biotic Factors Affecting Contaminant Transformation at Iron Oxide Surfaces, Division of Environmental Chemistry, The 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007
5. Dong Han, Gary P. Halada, , and James Kubicki, Oxidized cellulose fibers used for metal chelation, abstract CELL 13, Symposium on Model Cellulose Surfaces, Division of Cellulose & Renewable Materials, The 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007
6. P. Jha, G. Halada and B. Phillips, Effect of Uranyl on Organic Polymerization, CEMS Fall 2006 Graduate Student Conference and the CEMS Fall Meeting, Center for Environmental Molecular Science, Stony Brook University, November 2-3, 2006
7. D. Han, G. Halada and J. Kubicki, Cellulose Degradation Products used as Matrices for Uranium Remediation, CEMS Fall 2006 Graduate Student Conference and the CEMS Fall Meeting, Center for Environmental Molecular Science, Stony Brook University, November 2-3, 2006
8. G. Halada, C. Eng, P. Jha, A. Ceballos, M. Schoonen, A.J. Francis, C. Dodge, J. Kubicki and A. Turner, Effect of Electron transfer on Structure and Fate of

Uranium-Organic Complexes, Annual meeting, Center for Environmental Molecular Sciences, March 1, 2006

9. D. Han, D.R. Roeper, G. Halada and J. Kubicki, A Spectroscopic and Modeling Study of Metal Sequestration by Cellulose and its Breakdown Product Isosaccharinic Acid, Annual meeting, Center for Environmental Molecular Sciences, March 1, 2006
10. Halada, Gary P.; Eng, Charlotte W.; Phillips, Brian L. Multi-disciplinary approach to integration of complementary spectroscopies and molecular modeling for analysis of uranium-organic complexes. Abstracts of Papers, 230th ACS National Meeting, Washington, DC, United States, Aug. 28-Sept. 1, 2005 (2005)
11. Halada, Gary P.; Eng, Charlotte W.; Phillips, Brian L. Understanding the charge transfer-induced molecular transformation of uranium-organic complexes using molecular and synchrotron spectroscopies combined with electrochemistry. Abstracts of Papers, 229th ACS National Meeting, San Diego, CA, United States, March 13-17, 2005 (2005)

Educational impact:

As a direct result of this EMSP program support, one graduate student has developed a Ph.D. thesis on the nature of the association of radionuclides with polysaccharides and related cellulosic materials. This student will be defending their dissertation during the summer of 2008. Partial support has been provided for a second graduate student who will be defending their thesis (on uranium organic interactions) later in 2008. Several other graduate students in the Department of Materials Science and Engineering have assisted in experiments related to and supported by this work, and they have gained valuable experience in radiochemistry, vibrational spectroscopy, synchrotron techniques and environmental engineering. This is especially important considering the crucial and growing needs for investment in human capital development for areas related to the environmental management mission of the Department of Energy. Furthermore, three visiting undergraduate students and two Stony Brook University undergraduates have conducted research in the P.I.'s laboratory in cellulosic interactions and chemical transformation during the years of this project. They too have gained valuable experience in surface chemistry and remediation, chemical synthesis and molecular modeling related to this study. Several of these students have presented their work at national conferences, and all have had their education greatly enriched by their experiences.