

**"Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling":
Annual Report for Johns Hopkins University (Contract No. DE-FG07-02ER63498)
William P. Ball, Principal Investigator
Submitted June 12, 2003**

Forward: Project Context

This project is a part of a collaborative effort being undertaken with other investigators at the Pacific Northwest National Laboratory (Dr. John M. Zachara, Dr. Chongxuan Liu, and Dr. Zheming Wang), the Los Alamos National Laboratory (Dr. Peter Lichtner), and Stanford University (Dr. Gordon E. Brown) to undertake research as described in a March, 2002 proposal to the FY-02 Environmental Management Science Program, entitled "Characterization of U(VI) Sorption-Desorption Processes and Model Upscaling," under the direction of Dr. John M. Zachara, Principal Investigator.

The project being reported here is under the direction of Principal Investigator William P. Ball, and has been specifically designed to better understand the coupled adsorption, diffusion, and transport of adsorbing U(VI) species in pristine subsurface materials from the Hanford site. The results from this project will ultimately be compared and integrated with those from other institutions to meet the objectives of the overall collaborative project.

1. Research Objectives

The objectives of the overall collaborative EMSP effort (with which this project is associated) are to characterize sorption and desorption processes of U(VI) on pristine and contaminated Hanford sediments over a range of sediment facies and materials properties. The research is intended to provide new insights on the mechanisms of U(VI) retardation at Hanford, and to develop approaches by which laboratory-characterized geochemical models can be upscaled for defensible predictions of uranium transport in field.

Within this context, the objectives of the JHU-based project are to test hypotheses regarding the coupled roles of adsorption and diffusion in controlling the fate and transport of U(VI) species under conditions of short-term exposure. In particular, this work will contribute toward the testing of the following hypotheses: (1) the primary adsorption process in the Hanford sediment over the pH range of 8 to 10 are surface complexation reactions between aqueous U(VI) hydroxycarbonate and carbonate complexes with amphoteric edge sites on detrital phyllosilicates in the silt/clay size fraction; and (2) macroscopic adsorption intensity (at given aqueous conditions) will scale in proportion to clay content (phyllosilicate surface area); and (3) equilibrium desorption will be observed in short-term, laboratory-spiked pristine sediments. Focus of the work is on developing and applying both models and experiments to test the applicability of "local equilibrium" assumptions in interparticle diffusion, as relevant to processes of U(VI) diffusion in silt/clay layers. In addition, the role of diffusion-limited transport on solute advection in coarser (sandy) materials will be explored through advection-based column experiments and associated computer modeling of results.

2. Research Progress and Implications

This report summarizes work completed as of May, 2003, for a project nominally begun in October, 2002. However, substantial progress on the work did not begin until after January, 2003, owing to delays in funding and start-up for our collaborative partners, culminating in an overall project "kick-off meeting" that was held on January 15-16, 2003.

Progress to date has comprised hiring project personnel, initial project planning and development of some of the experimental methods to be employed, and the receipt and initial processing of composite sediment samples obtained and prepared by our PNNL collaborators from the subsurface environment at the Hanford site. Each of these activities is briefly discussed in the paragraphs that follow.

Hiring of project personnel

Dr. Wenming Dong has been hired as the post-doctoral associate for this project, and began effort on 1 March, 2003. Dr. Dong worked 50% time on the project in the months of March and April, and, since 1 May, 2003, has devoted 100% of his effort to this project. Dr. Dong has an excellent research background in the sorption and transport of radionuclides in soils and minerals, including work conducted as part of his MS and Ph.D. degrees in radiochemistry and atomic nuclear physics, respectively, from Lanzhou University (Lanzhou, Gansu province, PRC), teaching experience at Lanzhou University, post-doctoral experience at the Institute de Physique Nucleaire (Université de Paris XI, France), and, most recently, post-doctoral experience at Johns Hopkins University, where he worked under the guidance of Professors Edward Bower (project P.I.), Alan Stone, and William Ball on batch and column experiments related to the sorption, desorption, transport and biotic reduction of depleted uranium at sites associated with Aberdeen Proving Ground, Maryland.

Ms. Jing Bai has been selected as a graduate student Research Assistant for the project. She will be coming to Baltimore in August of 2003, at which time she will begin both her R.A. responsibilities and her academic studies toward the Ph.D. degree. Ms. Bai is currently completing an M.S. degree in the Department of Chemical & Environmental Engineering at the University of California at Riverside and has a Bachelor of Engineering degree from the Department of Environmental Science and Engineering at Tsinghua University (PRC).

Initial Planning and Development of Experimental Methods

Following our attendance of the project "kick-off" meeting in January, 2003, (including presentation of work) we began to plan future activities (see "Planned Activities") and develop experimental methods needed for the work. In particular, we have purchased some of the materials needed for laboratory batch and column experiments, we have undertaken literature study of past laboratory methods to estimate adsorbing contaminant diffusion coefficients in porous media, we have researched appropriate methods for extracting and measuring adsorbed phase uranium concentrations in soils and sediments, and we have further developed the analytical method to be used in measuring aqueous phase uranium concentrations.

Our literature study of laboratory methods for measuring diffusion coefficients has included study (by our post-doctoral researcher) of a "macropore" method previously used in our laboratory (Young and Ball, 1998; Young and Ball, 2000) as well as other methods based on diffusion cell experimental set-ups (Cormenzana et al., 2003; Mungall and Dingwell, 1997; Pike et al., 2002; Smith and Giletti, 1997). A key aspect of such experiments is to keep the reservoir mixed thoroughly and also to extract U accurately from post-experiment "slices" of the porous medium studied within the diffusion cells. In the latter regard, Dr. Dong has had good success in accomplishing the extrusion, slicing, and extraction of soil columns in his prior work with APG soil materials. In the upcoming work, however, we envision that modifications to the extraction procedure may be required, given that the material to be studied (*i.e.*, the Hanford Silt Composite, described subsequently) has substantial carbonate content and that the initial

solution will be at much higher pH. For this material, the U profile distribution in our extruded and sliced material will be obtained using a sequential extraction procedure taken on the basis of our literature review (Clark et al., 1996; Tessier et al., 1979). Although our main interest for such extractions will be total uranium, the sequential extraction approach will allow for at least a nominal quantification of the particulate U amount that is considered as "exchangeable", "bound to carbonate", "bound to iron and manganese oxides", "bound to organic matter", and "residual." Further work will be needed to select a most appropriate method for our studies, based on modeling expectations and experimental detection limits for the extraction procedures. These latter limits still need to be determined.

Work has also been continuing to develop and apply our method for aqueous U(VI) analysis, as to be used for batch sorption studies and solute transport experiments in columns. In this regard, we are using a kinematic phosphorescence analysis based on a KPA-11 analyzer (Chemchek Instruments, Inc., Richland, WA) that has been generously made available for our use by colleagues at JHU's School of Public Health. Since U(VI) measurement using KPA-11 is sensitive to aqueous organic matter and chloride ions, the analysis needs to be conducted under weakly acidic conditions. Therefore, a pretreatment procedure for U(VI) samples has been developed: (1) All experimental vessels are washed by a mixture of 30% H₂O₂ and 4 mol/L HNO₃ solutions to remove contamination of trace organic matter and U(VI); (2) to negate the effect of organic matter and chloride present in U(VI) solution, concentrated HNO₃ and 30% H₂O₂ solution are added, samples dried on a hot plate, and the ash residual dissolved in 0.1 mol/L HNO₃ solution for measurement of U(VI) concentration. For U(VI) present in weakly alkaline solution (pH>7) and low ionic strength, the procedure may be less complex, with need only that the solution be acidified to pH = 1, using 4 mol/L HNO₃ solution. The detection limit for the method is reported to be 0.01 µg/L from the KPA-11 manual, but the effective detection limit for environmental samples is more on the order of 0.5 µg/L, based on our past experiences. We also intend to conduct preliminary control experiments to ensure that our sample preparation techniques (in combination with careful baseline calibrations under similar conditions of aquatic chemistry) are adequate to control for interference of analysis by other cations or anions in solution (Sowder et al., 1998). If not, alternative analytical methods may need to be sought.

Receipt and Initial Processing of Hanford Samples

We received samples of materials designated as Hanford fine sand composite (HFSC, 3 kg) on April 12 and Hanford silt composite (HSC, 2kg) on May 23. Both samples are non-contaminated soils and were collected and initially processed by collaborators within the Environmental Dynamics and Simulation group at PNNL. The HFSC was collected from several sand layers, and was initially reported to consist of mostly fine sand with about 5-10% silt. Our own wet sieve analysis of this material has indicated roughly 17% of the material to be in the silt/clay fraction (< 53 µm). The HSC was collected from a 40-inch diameter core from the depth interval between 140.0 ft and 143.5 ft below ground surface. Our wet sieve analysis of this material has revealed that roughly 31% of this material is actually in the "sand" size fraction (i.e., > 53 µm). As noted under "Planned Activities," our intent is to use these materials for our studies of sorption, diffusion, and transport under a range of aqueous conditions and using several experimental techniques (batch studies, diffusion cells, and column transport studies). In this context, an important early task of upcoming research will be to consider which additional "fractions" of these materials are also appropriate for study, and to create these fractions.

3. Planned Activities

Planned activities for the coming year are to use the above two samples (and selected fractions thereof) in both batch studies of U(VI) sorption and diffusion-cell studies of coupled sorption and transport. Our initial focus will be on the HSC material, and on the investigation of the coupled effects of surface complexation and diffusion in diffusion-cell experiments. The design and implementation of the diffusion cell studies will be our major emphasis in the coming months, and will be guided both by continued assessment of the literature as well as additional preliminary experiments to better understand both the magnitude of sorption in our intended systems (see batch sorption discussion below) as well as the limitations of our analytical methods (see prior section).

In order to support the numerical modeling of results in the aforementioned studies, we will also be: (1) conducting batch U(VI) sorption experiments under a range of potentially relevant aqueous conditions, and (2) developing, in collaboration with Dr. C. Liu of PNNL, numerical models of diffusion and transport that include appropriate formulations for accounting the effects of U(VI) speciation and surface complexation. We currently envision the batch work to involve study with up to four fractions of solid sample (at one selected pH and one CO₂ partial pressure), as well as additional studies with a single selected material (e.g., the silt/clay fraction of the HSC) to study the effect of pH at fixed P_{CO2} and ionic strength, and the effect of ionic strength and P_{CO2} at fixed pH. A subset of these sorbent/water systems will then be used in the various diffusion and transport experiments.

On the basis of diffusion-cell results, batch sorption experiments, and the initial modeling of these results, subsequent work will then be designed for possible further investigation with both types of material (HSC and HFSC). Such efforts are likely to include the study of combined sorption and mass transfer effects on advective transport in columns, including study of transport through the more coarser material (HFSC) and transport through either this material or a more idealized medium (e.g., glass or plastic bead medium) under conditions that are influenced by diffusion to and from a surrounding medium of the HSC. These latter studies are referred to as "macropore" studies, and have been previously applied in our laboratory for the study of coupled sorption and diffusion of organic contaminants (Young and Ball, 1998; Young and Ball, 2000).

4. Information Access

There are currently no publications or other means of accessing the research from this work. We do not envision journal or report publication until near completion of the project, although intermediate results may be published as abstracts in conference proceedings. Web page publication is currently not intended.

5. Optional Additional Information

No additional information is being posted.

6. Proprietary Information

No proprietary information is being generated from this work.

References Cited

Clark, S.B., Johnson, W.H., Malek, M., A., Serkiz, S.M. and Hinton, T.G., 1996. A comparison of sequential extraction techniques to estimate geochemical controls on the mobility of

- fission product, actinide, and heavy metal contaminations in soils. *Radiochim. Acta*, 74: 131-179.
- Cormenzana, J.L., Gutierrez, M.G., Missana, T. and Junghanns, A., 2003. Simultaneous estimation of effective and apparent diffusion coefficients in compacted bentonite. *J. Contam. Hydrol.*, 61: 63-72.
- Mungall, J.E. and Dingwell, D.B., 1997. Actinide diffusion in a haplogranitic melt: effects of temperature, water content, and pressure. *Geochim. Cosmochim. Acta*, 61: 2237-2246.
- Pike, A.W.G., Hedges, R.E.M. and Calsteren, P.V., 2002. U-series dating of bone using the diffusion-adsorption model. *Geochim. Cosmochim. Acta*, 66: 4273-4286.
- Smith, H.A. and Giletti, B.J., 1997. Lead diffusion in monazite. *Geochim. Cosmochim. Acta*, 61: 1047-1055.
- Sowder, A.G., Clark, S.B. and Fjeld, R.A., 1998. The effect of sample matrix quenching on the measurement of trace uranium concentrations in aqueous solutions using kinetic phosphorimetry. *J. Radionucl. Nucl. Chem.*, 234: 257-260.
- Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, 51: 844-851.
- Young, D.F. and Ball, W.P., 1998. Estimating diffusion coefficients in low-permeability porous media using a macropore column. *Environ. Sci. Technol.*, 32: 2578-2584.
- Young, D.F. and Ball, W.P., 2000. Column experimental design requirements for estimating model parameters from temporal moments under nonequilibrium conditions. *Adv. Water Resour.*, 23: 449-460.