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HANFORD IFRC QUARTERLY REPORT ~ January 2012

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I. Management Statement

In this January 2012 Quarterly Report for the Hanford IFRC project, we briefly summarize activities performed during the first quarter of FY 2012. At the time of this reporting 23.9% of the FY has elapsed and 35% of our total FY 2012 IFRC budget (including carryover) has been spent. The project is ahead on spending because of costs incurred during our very active fall experimental campaign (October through December) where river conditions were excellent for field experimentation. Additionally, significant efforts were expended in the first part of the quarter to make our data base current in advance of the November 2011 IFRC data-base viewing.

II. First Quarter Research

A. High Uranium Injection Experiments

Three injection experiments were performed during October-December 2012 using 40,000 gallons of high U groundwater that was collected in the spring of 2011, and stored on site over the summer. The collected groundwater contained 1700 µg/L of U(VI) that was diluted approximately 3-fold for injection. Experiment 1 injected 45,000 gallon of groundwater containing 600 µg/L U(VI) and Br^- tracer into the upper aquifer. Experiment 2 injected 47,000 gallon of filtered river water containing 570 µg/L U(VI) and Cl^- tracer into the upper aquifer. Experiment 3 injected 21,000 gallon filtered river water containing 750 µg/L U(VI) and F^- tracer into the lower permeability, intermediate zone of the aquifer. Two primary hypotheses were evaluated: i.) U(VI) retardation would increase in the river water matrix because of the reduced effects of carbonate complexation, and ii.) mass transfer effects and retardation would increase in the lower permeability zone because of higher mud content.

All experiments experienced relatively stable, but oscillating river levels, and are expected to yield high quality data. Close to 4000 samples were collected that are currently under analysis for U(VI), tracer, and major anion and cation concentrations. The initial results are very encouraging and the project team anxiously awaits completion of the entire data-set.

B. Precipitation Recharge Monitoring System

A surface ERT line was installed across the IFRC site during the winter months of 2011 to evaluate the feasibility of monitoring precipitation infiltration and transport through the vadose zone. These measurements were highly successful during the wet 2011 winter, indicating that infiltration through the U-enriched vadose zone reached groundwater. However, results indicated that the analysis would be more robust, and publishable, if two surface lines were monitored rather than one. A two-line surface ERT system over the south eastern half of the IFRC site and a small weather station (temperature and precipitation) were consequently installed in November 2011 to monitor winter precipitation and infiltration. Previous groundwater monitoring studies during spring high water has indicated that vadose zone recharge of U(VI) occurs in this quadrant of the well field. The ERT monitoring will be supported by weekly cross-hole radar surveys and neutron logging in 6 wells. Unfortunately fall 2011 and early winter of 2012 have been exceedingly dry in Richland with minimal precipitation. Monitoring will continue through May 2012 with hopes that rain will fall.

C. Smear Zone Geochemical Model

Multi-investigator experiments using a smear zone composite sediment from the IFRC well field have been underway for over a year. Experiments have been performed at the USGS, Oregon State, and PNNL. The final experiments were recently completed, providing data sets for the quantification of surface complexation thermodynamic parameters and rates from the grain scale (mm) in stirred-flow reactors to larger columns with < 8mm materials under both water-saturated and unsaturated conditions.

An integrative modeling campaign was begun at the beginning of this quarter to fit parameters to populate our field-scale reactive transport models, beginning first with the analysis of grain scale parameters from USGS flow cell data of U(VI) desorption. The parameters include surface site concentration, surface complexation constants, and multi-rate kinetic constants. An interesting aspect of the modeling was that microbial respiration, denitrification specifically, had to be included to describe the experimental observed pH/HCO_3^- relationships. This work is now being readied for publication. Modeling has progressed to the description of a complicated series of column experiments that have run for close to one year, where mass transfer effects are much greater than observed at the grain scale. It is expected that the column parameters will be transferred to the field scale simulators taking account of the large in-situ mass fraction of gravel and cobble at the IFRC site.

D. Data Assimilation for Geochemical Parameters

Recently we submitted results of the IFRC geochemical characterization for publication. That manuscript included a 3-D geostatistical model of sorbed U(VI) concentration. Since that submission, the project team has been working to establish petrophysical relationships between the high density spectral gamma logging (SGLS) data that was performed at the time of well installation, and sediment physical and chemical properties measured in characterization. The objective is to allow accurate prediction of geochemical properties as a function of depth and location in the well field.

Success has recently been achieved in this endeavour where ^{232}Th measured by SGLS has shown excellent correlation with % mud, while % mud has shown excellent correlation with ^{233}U-K_d measured in the chemical characterization activities. Details aside, these relationships support a robust approach to estimate adsorption site concentration in sediments from the vadose and saturated zones at scales of 0.15 m. This is a key parameter for modeling U(VI) adsorptive retardation, and the results (in various forms) are being integrated into our STOMP and PFLOTRAN site simulators.

E. Data Assimilation for Geophysical and Petro-physical Relationships

An extensive 3-D cross-hole electrical resistivity tomography (ERT) dataset was collected within the IFRC well field prior to vertical wellbore flow mitigation. This dataset has been analyzed by tomographic inversion to yield the 3D distribution of the direct-current electrical conductivity structure of the IFRC well-field from the surface to the Hanford/Ringold contact. Initial efforts to analyze these data using a standard smoothness-constrained imaging approach were only slightly successful, being highly influenced by borehole effects, sharp conductivity contrasts at the water table and Hanford/Ringold contact, and variable imaging resolution between boreholes. To address these issues, the imaging code was modified with a series of physical constraint improvements including sharp contrasts at conductivity boundaries, explicit modeling of boreholes, and the integration of core measurements and geostatistical information derived from logging data. The improvements were implemented with cluster computing capability allowing a single inversion of the entire dataset using high performance computing resources. The final imaging results display a significant improvement over the standard inversion.

Although subsurface electrical conductivity is governed by parameters that are important for predicting uranium behavior at the IFRC (e.g. clay content, ionic strength, porosity, saturation), quantitatively extracting these parameters from the ERT imaging results using a petro-physical relationship is problematic. The imaging approach developed here aims to identify ‘electrofacies’, or spatially continuous and geostatistically accurate electrical conductivity structures that have been defined by the analysis of intact cores in the laboratory. These parameters can then be mapped to the well field through the corresponding ERT-derived electrofacies, assuming the spatial correlation structure of each derived parameter is consistent with the corresponding spatial correlation of electrical conductivity. This mapping is made possible by constraining the imaging inversion to honor known conductivity values derived from core measurements, and fixing the spatial covariance structure to be equal to that determined by other characterization activities. The imaging results produced by this approach were driven by complex resistivity measurements performed by Rutgers University on six well-field cores taken from strategic locations, and with spatial covariance structure derived from borehole logging measurements. The final results for the saturated zone showed good correlation with borehole flow-meter logging data of hydraulic conductivity, suggesting promise in the use of ERT data to further condition the IFRC permeability field.

F. Modeling the March 2011 Injection Experiment

Significant efforts are underway to model the March 2011 desorption injection experiment. This experiment was a slow (10 gpm), long-term (353 h) injection experiment with low U(VI) groundwater (6.2 μg/L) intended to create an extended zone of desorbed U(VI) through the central domain of the IFRC well field. The experiment encountered very dynamic groundwater flow conditions as a result of unusual weather conditions. The low U injection plume was pushed up into the smear zone several times during the injection experiment leading to multiple events of vadose zone U(VI) mobilization.

Modeling has used the PFLOTRAN code and its multi-realization capability to assess the influence of hydrologic and geochemical uncertainty on the ability to describe the complex tracer and U(VI) breakthrough curves that were obtained from the experiment. The hydrologic uncertainties evaluated were flow boundary conditions and the permeability field; and the geochemical uncertainties were initial U(VI) groundwater concentrations, sorbed U(VI) distribution in the vadose zone, and adsorption site concentrations and distribution. The geochemical uncertainties were evaluated using realizations of the permeability field that best reproduced the non-reactive tracer data.

The model simulations were performed on the Jaguar supercomputer. They were indeed massive as they included multiple 3D realizations of both the permeability field and U(VI) distribution in a 432,000 cell grid. It is the first time that our 3D geostatistical model of sorbed U(VI) distribution has been included in reactive transport calculations. The results affirmed the critical role of sorbed U(VI) distribution and release rate on U(VI) concentrations in this injection experiment that entered the smear zone.

III. Plans for Next Quarter

- Complete numeric analysis of field hydrologic characterization measurements of the upper aquifer and release data package to project team.
- Complete chemical analyses of the Fall 2012 injection experiments, and release data package to the project team.
- Complete geochemical kinetic modeling of multi-investigator laboratory experiments of the smear zone composite to determine effective parameters for the field scale model.
- Continue reactive transport modeling of the March 2011 low-U injection experiment where high river stage pushed the plume into the U-enriched smear zone.
- Continue data assimilation activities to develop a petro-physical model for interpretation of site ERT measurements, begin manuscript preparation.
- Continue surface and downhole geophysical monitoring of the vadose zone to assess the extent of winter precipitation infiltration and transport through the vadose zone.

IV. First Quarter Presentation and Publication Activity

Presentations

Chen, X., G.E. Hammond, P.C. Lichtner and M.L. Rockhold. 2011. Impacts of hydrologic and geochemical uncertainty on predicting uranium migration at the Hanford

300 Area. Poster presentation, AGU Fall Meeting, December 5-9, 2011, San Francisco, CA.

Hammond, G.E. 2011. *A Benchmark for Physical and Chemical Processes at the Hanford 300 Area*, PNNL-SA-84358, 2011 Subsurface Environmental Simulation Workshop, Berkeley, CA.

Rockhold, M.L., X. Chen, R. Ramanathan, V.R. Vermeul, T.C. Johnson, and C.J. Murray. 2011. Facies delineation using core, wireline log, electrical resistance tomography, and electromagnetic borehole flowmeter data. Poster presentation, AGU Fall Meeting, December 5-9, 2011, San Francisco, CA.

Thai, J., M.L. Rockhold, V.R. Vermeul, T.C. Johnson, J.M. Zachara, and Y. Rubin. 2011. Prediction of lithology types at the Hanford 300 Area using a cluster analysis. Poster presentation, AGU Fall Meeting, December 5-9, 2011, San Francisco, CA.

Publications

Barros, F., S. Ezzedine and Y. Rubin. 2012. Impact of hydrogeological data on measures of uncertainty, site characterization and environmental performance metrics. *Advances in Water Resources*, 36: 51-63.

Chen, X., H. Murakami, M.S. Hahn, G.E. Hammond, M. Rockhold, J.M. Zachara, and Y. Rubin. 2012. Three-dimensional bayesian geostatistical aquifer characterization at the Hanford 300 Area using tracer test data. *Water Resources Research* (Accepted).

Hay, M.B., D.L. Stoliker, J.A. Davis, and J.M. Zachara. 2011. Characterization of the intragranular water regime within subsurface sediments: Pore volume, surface area, and mass transfer limitations. *Water Resources Research*: 47, W10531, doi:10.1029/2010WR010303.

Lin, X., D. Kennedy, J. Fredrickson, B. Bjornstad, and A. Konopka. 2011. Vertical stratification of subsurface microbial community composition across geological formations at the Hanford site. *Environmental Microbiology* doi:10.1111/j.1462-2920.2011.02659.x

Lin, X., D. Kennedy, A. Peacock, J. McKinley, C.T. Resch, J. Fredrickson, and A. Konopka. 2012. Distribution of microbial biomass and potential for anaerobic respiration in Hanford site 300 A sediment. *Applied and Environmental Microbiology* (Accepted).

Liu, C., J. Shang, and J.M. Zachara. 2011. Multispecies diffusion models: A study of uranyl diffusion. *Water Resources Research*: 47, W12514, doi:10.1029/2011WR010575.

Murray, C.M., J.M. Zachara, J.P. McKinley, A. Ward, K. Draper, and D. Moore. 2012. Establishing a geochemical model for a contaminated vadose zone – aquifer system. *Journal of Contaminant Hydrology* (Accepted).

Nowak, W., Y. Rubin, and F.P.J. de Barros. 2012. A hypothesis-driven approach to optimal site investigation. *Water Resources Research* (Accepted).