



# INTEGRATED FIELD CHALLENGE SITE Hanford 300 Area

U.S. Department of Energy Office of Science  
Environmental Remediation Sciences Program



## Multi-Scale Mass Transfer Processes Controlling Natural Attenuation and Engineered Remediation: An IFC Focused on Hanford's 300 Area Uranium Plume

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### SCIENCE THEMES

**Overall**  
Multiscale, multi-rate mass transfer influencing field-scale contaminant migration and remediation

**Secondary**

- Physical, chemical, and microbiologic factors controlling field-scale mass transfer
- Transferring laboratory kinetic data to field
- Kinetic effects of transients in water chemistry
- Microbiologic stability of remediation products
- Process evolution along flow paths
- Characterization and modeling approaches for mass-transfer dominated field systems
- Fundamental to applied science transfer

**Anticipated Outcomes**

- Outstanding, multidisciplinary collaborative effort that significantly advances science
  - Characterization, experiment design, interpretation
  - Basic underpinnings of EM-20 activities
  - Enduring and accessible field experiment data sets for hypothesis and model testing
- Improved linked multi-scale mass transfer/biochemical models for reactive contaminants
  - New conceptual understanding of mass transfer processes at different scales influencing field behavior
    - Desorption, dissolution, dissipation
    - Effective reaction kinetics
    - Contaminant immobilization

### EXPERIMENTAL SITE, MONITORING, AND CHARACTERIZATION

**Field Site Location in WMA 300-FF-5**

**The IFC Injection/Monitoring Array**

**Monitoring/Injection Wells**

**IFC Hanford Formation Cores**

| South Process Pond Excavation | Matrix-supported | Open-framework | Coarse-sand |
|-------------------------------|------------------|----------------|-------------|
|                               |                  |                |             |

**Experimental Site, Monitoring, and Characterization**

- A geostatistical hydrostratigraphic model will be established from geophysical logging, geophysical measurements, and analysis of borehole samples.
- Injection experiments of approximately 75,000 gallons will be performed in the 6 m saturated zone under different seasonal head gradients and associated flowpaths (see Experimental Program, right)
- Passive experiments will exploit natural gradients in aqueous chemistry resulting from river water infiltration.
- Continual water level monitoring at 12 locations will provide necessary hydrologic linkages.

**Monitoring/Injection Wells**

- The monitoring system will include 25, 4" monitoring and injection wells screened through the saturated Hanford interval.
- There will be three additional multi-level well clusters; with each screened over 2 m of the saturated zone.

### PLANNED EXPERIMENTAL PROGRAM

- U(VI) concentration dynamics within the groundwater plume (FY09 – FY10)
  - Scale-dependent mass transfer involved in forward (adsorption), backward (desorption), and steady-state (isotopic exchange) reaction processes in flow paths with different trajectories and residence times.
  - Injection experiments with varying  $\text{HCO}_3^-$  and U(VI) concentrations, and U(VI) isotopic ratios
  - Passive experiments follow vadose zone pulses, or inland riverwater – groundwater gradients
- U(VI) fluxes from the vadose zone (FY10 – FY11)
  - Scale-dependent mass transfer, geochemical kinetics (adsorption/desorption) and water pathway effects on U(VI) fluxes to groundwater.
  - Infiltration experiments with varying water application rates, volumes, and composition (pH,  $\text{HCO}_3^-$ , NaCl)
  - Passive experiments to explore rising and falling water table effects on U(VI) solubilization and release from lower vadose zone
- Optimized and sustained remediation strategies (FY11 – FY12)
  - Evaluate role of mass transfer and microbiological processes on different forms of phosphate used to precipitate and immobilize U
  - Injection experiments with polyphosphate, Ca-citrate/ $\text{PO}_4^{3-}$ , organic P with  $\text{HCO}_3^-$
  - Collaborate with EM-22 and team if timing allows.

### BACKGROUND

**History**

- Site received effluents from REDOX and PUREX process development (1944-1954) and N-reactor fuels fabrication (1976 – 1986)
- Neutralized U(VI)-Cu(II) nitric acid solutions were primary waste stream
- 37,000 – 65,000 kg of U and 265,000 – 300,000 kg of Cu
- Wastes disposed to North (NPP) and South (SPP) Process Ponds

**Hydrology**

- Linked groundwater – river system
- Groundwater trajectory and composition shifts between fall/winter and spring/summer
- Sediments vary from open-framework to matrix-supported gravels to coarse sands
- Upper portion (Hanford formation) of aquifer (~3-7 m) carries U(VI) contamination
- Generally high hydraulic conductivity (> 1000 mD)
- Sorbed U(VI) in capillary fringe an assumed, long-term source

**Science**

- Significant ERSP (EMSP), EM-30, and EM-20 research
- Hydrology, U(VI) speciation, and microscopic mass transfer characterization studies performed. Slow kinetic desorption
- Initial hydrologic and reactive transport models developed
- Limited microbiologic information, *Shewanella* in the hypoxic zone

**Remediation**

- MNA IROD issued 12 years ago, but U(VI) concentrations have not decreased as predicted
- EM-20 is testing a polyphosphate remediation strategy at the site (see left) in response to regulatory (EPA) demands

### Groundwater Monitoring and Sampling

The monitoring wells have downhole instrumentation for temperature and electrical resistance tomography (ERT). Remotely activated pumps allow for timed sampling of individual wells for plume capture. Pumped waters pass through a manifold system to flow cells in the field laboratory for ion selective electrode (ISE) measurement and additional sampling for lab analysis. ISE clusters in each well continuously monitor select analytes (pH, Br, EC, etc.). ISE are changeable for experiment adaptation. Well monitoring equipment are under central control where continuous or timed logging occurs.

**Linked Characterization/Modeling Strategy**

- A linked characterization and modeling strategy will allow rigorous field experimental interpretation and simulation.
- A field-scale reactive transport model for U(VI) will be developed with kinetic adsorption and desorption controlled by complexation to mineral surface sites (SOH) and mass transfer between mobile and immobile fluid domains at different scales.
- The physical transport model will be established from:
  - Correlations between down-hole geophysical measurements and facies-scale laboratory hydrophysical measurements of particle size distribution (PSD), particle volume distribution (PVD), and hydraulic conductivity (K) (below right).
  - Downhole measurements of localized groundwater velocities using an electromagnetic borehole flow-meter (EBF).
  - Nonreactive tracer experiments (temperature, Br, PFSA, and other tracers) over different flow-paths.
- The U(VI) reaction model will be established from:
  - Facies-scale measurements of total contaminant U ( $U_{\text{total}}$ ) and equilibrium ( $P_{\text{eq}}$ ) and kinetic ( $P_{\text{kin}}$ ) reaction parameters of U(VI) as a function of aqueous chemistry (AC) (below left).
  - Measurements of localized U(VI) groundwater concentrations and composition using a multi-level well water sampler (MLS).
  - Laboratory column or meter-scale flow-cell experiments where groundwaters with higher (+U) or lower (-U) U(VI) concentrations, or those with different aqueous chemistry (AAC) are advected through contaminated sediment.
  - Up-scaled representations of equilibrium and/or kinetic reaction parameters based on relationships to grain size, porosity, or other primary properties.

**Extrapolative Property Correlations**

Field experiments will perturb aqueous (C) and adsorbed (q) U(VI) in pore or groundwater, influencing adsorption extent (C) to surface sites (SOH, M) along different flowpaths. Scientific questions examine the rate (q) of response (adsorption or desorption), effects of sediment properties (porosity,  $\theta$ , site concentration,  $M_0$ ), local groundwater velocity (v, distance (x), and scale), and best ways to model. Reaction parameters describe equilibrium ( $P_{\text{eq}}$ ) and kinetic ( $P_{\text{kin}}$ ) behavior of U(VI).

**Basic for Characterization**

**U Transport Experiments**

$$+U \quad X \rightarrow Y \rightarrow Z$$

$$-U \quad X \rightarrow Y \rightarrow Z$$

$$\Delta AC \quad X \rightarrow Y \rightarrow Z$$

$$\theta \frac{\partial C}{\partial t} + (1-\theta)\rho_s \frac{\partial q}{\partial t} = \theta \frac{\partial^2 C}{\partial x^2} + \theta \frac{\partial^2 q}{\partial x^2}, \quad i=1, 2, \dots, N$$

$$\rho_s \frac{\partial q}{\partial t} = a_i \rho_s (S_i^* - q_i), \quad i=1, 2, \dots, N; \quad k=1, 2, \dots, M$$

$$-SOH + UO_2^{2+} + H_2O = >SO_2UO_2OH + 2H^+$$

$$-SOH + UO_2^{2+} + CO_3^{2-} = >SO_2UO_2CO_3 + 2H^+$$

**Geochemistry**

$$U_{\text{total}} = P_{\text{eq}}(a) + P_{\text{kin}}(a) + AC(a) \quad PSD(K) \quad PVD(K) \quad K(v) \quad H \quad I$$

$$L \quad L \quad F \quad F \quad L \quad L \quad F \quad F \quad F \quad F \quad F$$

P = reaction parameter; L = laboratory; F = field; AC = aqueous chemistry; PSD = particle size distribution; PVD = porosity; K = hydraulic conductivity; H = head; I = infiltration

### MODELS AND MODELING STRATEGY

- STOMP as the primary project model that integrates site-wide hydrogeological results of different types and newly developed process models for 3-D, reaction-based reactive transport calculations used in experiment planning, interpretation, and evaluation of future remediation actions.
- Other codes developed by project participants with different and/or special capabilities for individual experiment interpretation, hypothesis testing, and inter-model comparisons (e.g., FLOTTRAN for multi-continuum, mass-transfer limited geochemical calculations, and MODFLOW for multi-scale mass transfer).
- Stochastic modeling of hydraulic conductivity, sorption, mass transfer rate, and sorbed U(VI) distributions (e.g., hydro- and chemo-facies) by project experts, as well as spatial moment analyses of plumes resulting from different subsurface manipulations.

### EXAMPLE OPPORTUNITIES FOR COLLABORATIVE RESEARCH

- In-situ adsorption/desorption experiments of various types
- Laboratory to field comparisons
- Evaluation of geophysical methods and inversion techniques
- Mass transfer processes of different types at different scales
- Microbiology of linked groundwater-river systems of low to high transmissibility
- Geologic, hydrologic, geochemical, and biogeochemical modeling of different types
- Microbiology and geochemistry of phosphate amended systems

### MATERIALS AVAILABLE TO EXTERNAL INVESTIGATORS

- Historic U(VI)-contaminated source term materials (limited)
- Contaminated U(VI) vadose zone material whose geochemical speciation and mass transfer properties have been determined (limited)
- Uncontaminated vadose zone and aquifer sediments from various locations
- Circumneutral site groundwaters with variable U(VI),  $\text{HCO}_3^-$ , and Ca concentrations
- Core materials and grab samples from vadose zone and aquifer experimental plots
- Aseptic samples of vadose zone and Hanford and Ringold formation aquifer sediments (for microbiological studies TBC, limited)
- TBC = to be collected, see website for details: <http://efhanford.pnl.gov>