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Coupled Geochemical and Hydrological Processes Governing the Fate and Transport of Radionuclides and Toxic Metals Beneath the Hanford Tank Farms

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This project addresses the goals of the Environmental Management Sciences Program (EMSP) that seeks innovative basic research to benefit cleanup technologies and decision-making strategies for contaminated environments. Our proposal specifically addresses Hanford research needs in subsurface science by contributing to the objectives of the Tank Farm Vadose Characterization Project and the 200 Area Remedial Action Project (<http://www.bhi-erc.com/projects/vadose/sandt/stdocs/subneeds.pdf>) which are components of the Hanford Site Groundwater/Vadose Zone Integration Project (Integration Project). The work described in this proposal will advance the technological and scientific needs associated with the long-term management of the enormous in-ground inventories of $^{235/238}\text{U}$, ^{99}Tc , ^{60}Co , and Cr(VI) present at the Hanford site. We believe that scientifically defensible predictions of contaminant transport and strategies for remediation must be based upon a field-relevant understanding of coupled hydrological and geochemical processes that control subsurface contaminant fate and transport. This research project investigates the migration of $^{235/238}\text{U}$, ^{99}Tc , ^{60}Co , and Cr(VI) in undisturbed sediments from the Hanford site using realistic experimental protocols designed to delineate complex hydrological and geochemical processes controlling contaminant movement. The work complements and builds upon our current EMSP project 70219, which is scheduled to end this year, and our Hanford S&T project

with PNNL (John Zachara as PI) that focuses on ^{90}Sr transport beneath the BX tanks. The specific research goals of the following proposal are:

! to provide an improved understanding of how preferential vertical and lateral flow, and the formation of immobile water influence the transport of radionuclides and toxic metals in heterogeneous, laminated sediments.

! to quantify the rates and mechanisms of radionuclide and toxic metal interaction with the solid phase under various hydrologic conditions.

! provide new insights into how physical and mineralogical heterogeneities (e.g. stratification, pore regime connectivity, mineral composition along flowpaths) influence contaminant retardation and the degree of geochemical nonequilibrium during transport.

The overall research products will be (1) knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for Tank Farm restoration; and (2) improved predictive strategies for assessing the transport rate and fate of $^{235/238}\text{U}$, ^{99}Tc , ^{60}Co , and Cr(VI) beneath the Hanford Tank Farms. Since this project will unravel fundamental contaminant transport mechanisms in complex porous media, the results will assist in improving our overall conceptual understanding and predictive capability of a variety of vadose zone issues within the DOE system (e.g. INEEL and Sandia).

Significant findings regarding hydrologic processes in sediments beneath the tanks:

- (1) The saturated and unsaturated hydraulic conductivity of cores acquired parallel to lithological layering was an order of magnitude more rapid than the conductivity of cores acquired perpendicular to lithological layering. Thus, lateral flow beneath the tank farms is a strong contributor to the spread of contaminants. Also, the conductivity of fine grained cores were an order of magnitude slower than core acquired in sandy media.
- (2) The transport of the three nonreactive tracers at different degrees of unsaturation showed essentially no difference in breakthrough patterns when flow remained unrestricted along continuous lithological features as is the case for the horizontal cores. This suggested that physical nonequilibrium conditions were not occurring during lateral flow in these sediments. Thus matrix diffusion processes are not contributing to the attenuation of waste being released from the Hanford tanks allowing for more rapid transport rates beneath the tank farms.
- (3) However, when flow is partially restricted by lithologic discontinuities as is the case for the vertical cores (e.g. alternating coarse and fine layers), perched water tables develop resulting in unstable wetting fronts and the prevalence of preferential flow. The early breakthrough and significant separation of tracer in the effluent suggest that large pockets of immobile water develop creating a

condition of physical nonequilibrium between flowing domains and immobile domains. From a contaminant transport perspective this process is advantageous since the presence of large pockets of immobile water will significantly impede the vertical migration of waste being released from the Hanford tanks.

Significant findings regarding geochemical processes in sediments beneath the tanks:

- (1) Batch and repacked column studies have shown that U, Cs, and Sr can be strongly bound to the various sediments beneath the tank farms even under conditions where the solid phase pH is as high as 8.4. However, when U-CO₃ species dominant the system, sorption reactions become increasingly less important and U remains highly mobile. Sediment samples from the Ringold formation (White Bluffs) and Hanford formation (ERDF and ILAW sites) have been shown to effectively dissociate Sr-EDTA complexes and reduce mobile Cr(VI) to sparingly soluble Cr(III). These findings are important since they show geochemical reactions can help impede the migration of Sr and Cr through the Hanford vadose zone. However, the Ringold and Hanford sediments were also found to effectively oxidize Co(II)EDTA to Co(III)EDTA. The adverse environmental implications of this reaction is that Co(III)EDTA is an extremely stable complex that enhances its mobility in subsurface environments.
- (2) X-ray Absorption Spectroscopy (XAS) suggested that inner-sphere ternary carbonate complexes formed on Fe-oxides in sandy Ringold sediments while sorption of sheet silicates was the primary sorption mechanism in silty Ringold sediments. These data underscore the importance of understanding the sediment mineralogy to accurately assess the fate and transport of uranium in the environment. The implications of the sorption reactions are that the downward vertical migration of U beneath the tank farms will be significantly slowed by interfacial geochemical sorption reactions. We are currently performing Cr XAS where we are trying to (1) map the distribution of Cr and relate it to that of Fe, (2) determine the valence state of Cr, and (3) if localized areas of Cr are noted, and are proximal to an Fe phase, determine the structure of the presumed Fe reductant.
- (3) Reactive transport of Sr, U, and Co(II)EDTA in undisturbed Hanford cores and U in undisturbed consolidated material of the Plio-Pleistocene unit have also been conducted. The Plio-Pleistocene unit was not conducive to either preferential vertical finger flow or to lateral flow, as no tracer separation (Br/PFBA/PIPES) was observed under our experimental conditions. The absence of distinct sedimentary bedding in the Plio-Pleistocene probably accounts for this observation. Our results therefore suggest that physical nonequilibrium processes will be minimal in the Plio-Pleistocene unit. Reactive transport of ^{235/238}U through the Plio-Pleistocene unit exhibited evidence of nonequilibrium, possibly influenced by kinetics or multi-site/multi-species reactivity. Sorption of ^{235/238}U was significantly enhanced under equilibrium conditions when compared to transport or flowing conditions, which suggests kinetic effects on sorption. Transport experiments were conducted in an atmosphere representative of

subsurface conditions (1% CO₂), which resulted in the formation of a stable uranyl-carbonate complex. Therefore, it is also likely that the large complex may have different affinities for subsurface sorption sites. Transport through the Plio-Pleistocene unit has demonstrated the presence of geochemical nonequilibrium while physical nonequilibrium processes were minimal, thus resulting in a greater understanding of the relevant mechanisms governing contaminant interactions in the Hanford subsurface.

The transport of Sr and U-CO₃ in the Hanford core shows strong and moderate reactivity, respectively which is consistent with batch and repack column studies and the transport of Co(II)EDTA shows complete oxidation to Co(III)EDTA.

Implications:

The experimental and numerical results from this research will provide knowledge and information in previously unexplored areas of vadose zone fate and transport to support EM's performance/risk assessment and decision-making process for Tank Farm restoration. By unraveling fundamental contaminant transport mechanisms in complex porous media, we will provide an improved conceptual understanding and predictive capability of a variety of vadose issues within the DOE system.