

Technical and Policy Challenges in Deep Vadose Zone Remediation of Metals and Radionuclides -12025

Dawn M. Wellman*¹, Michael J. Truex¹, Mark Freshley¹, P. Evan Dresel², and Kirk J. Cantrell¹

¹Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland, WA, 99352, USA

² Future Farming Systems Research Division, Department of Primary Industries, PO Box 3100, Bendigo Delivery Centre VIC 3554, Australia

ABSTRACT

Deep vadose zone contamination is a significant issue facing the U.S. Department of Energy's (DOE) Office of Environmental Management (EM). Contamination in the deep vadose zone is isolated from exposure such that direct contact is not a factor in risk to human health and the environment. Transport of deep vadose zone contamination and discharge to the groundwater creates the potential for exposure and risk to receptors, so limiting flux to groundwater is key for protection of groundwater resources. Remediation approaches for the deep vadose zone need to be considered within the regulatory context, targeted at mitigating the source of contamination and reducing contaminant flux to groundwater. Processes for deep vadose zone metal and radionuclide remediation are discussed, as well as challenges and opportunities for implementation.

INTRODUCTION

DOE EM manages the largest groundwater and soil cleanup program in the world. Although DOE EM has made substantial progress in its cleanup mission, significant challenges remain. The difficult subsurface remediation problems that remain are some of the most complex encountered, including extensive and challenging groundwater contamination and large quantities of contaminants that reside in the deep vadose zone that are difficult to access. The deep vadose zone is defined as the sediments below the zone of practicable excavation and removal, but above the water table. Implicit in this definition is an assumption that contamination in deep vadose zone environments is isolated from exposure such that direct contact is not a factor in its risk to human health and the environment. Transport of contamination from the deep vadose zone and discharge (flux) to the groundwater creates the potential for exposure and risk to receptors. The deep vadose zone represents a potential source of ongoing contamination to groundwater and downgradient receptors. Therefore, while the deep vadose zone is not considered a resource requiring restoration, limiting flux from the contaminated vadose zone is key for protection of water resources.

Remediation of the vadose zone is typically linked to meeting cleanup goals for groundwater. As such, the prospect for success of any deep vadose zone remediation technology needs to be considered within the regulatory context. Herein lies the challenge: applying vadose zone remediation to reach an acceptable rate of contaminant transport while effectively managing considerable uncertainties associated with estimating and measuring contaminant transport at the field scale. However, this construct affords the opportunity to view remediation strategies for the vadose zone as targeted to mitigate the source of contamination and reduce transport through the vadose zone to receptors, in contrast to meeting a specific concentration measured at some location within the vadose zone. However, this approach requires technology development, methods, and protocols to demonstrate that groundwater will remain

uncontaminated or that contamination will remain below levels of concern in the future, and achieve in situ remedial performance sufficient to support a remedial decision.

Technical challenges complicate the decision process for deep vadose zone remedial actions. Despite active research and development, few remediation technologies have been tested in the field and fewer have been successfully implemented as full remedial actions. Remediation options for the deep vadose zone are less developed than approaches for shallow soil or groundwater contamination. Included in the discussion is a review of how hydrogeologic and biogeochemical processes may operate in the deep vadose zone and be used to meet remediation objectives, the technical risks and challenges for consideration of a proposed remedial action, and policy implications for deep vadose zone remediation.

DISCUSSION

Vadose Zone Conceptual Models

Conceptual models of deep vadose zone metal and radionuclide contamination at DOE EM sites are typically complicated by heterogeneous contaminant distributions and preferential saturation-dependent flow in layered and heterogeneous sediments. Conceptual models are not static; rather, they are dynamic, becoming more refined as site characterization proceeds. Uncertainties in the conceptual model can impact prediction of long-term impacts from deep vadose zone contamination and the success or failure of remediation approaches.

Aqueous wastes discharged to the ground are acted on by gravitational and capillary forces in the unsaturated flow conditions of the deep vadose zone. Gravity drives moisture and associated contaminants downward. Capillary forces preferably attract moisture to finer sediments. Coarse sediments act as impediments to flow and thus can provide resistance to vertical transport [1]. This resistance can cause lateral spreading and accumulation in finer-grained layers until water saturation and associated pressure increases sufficiently to allow vertical flow into the coarser sediments. Hysteresis causes additional variation in flow, depending on whether the system is in a wetting or drying phase. After waste discharges cease, continued movement of water and contaminants through the vadose zone is a function of moisture distribution—typically elevated compared to the natural state—and the net rate of recharge (i.e., water that moves beyond the zone of evapotranspiration at the land surface). The rate of water movement through the vadose zone to groundwater is a function of the recharge rate and water saturation in the vadose zone. These factors in turn impact the hydraulic gradient and relative permeability of the sediments, which vary nonlinearly under unsaturated conditions. The physical processes of dispersion and diffusion can also impact pore water contaminant concentrations and associated flux to groundwater. Fig. 1 is a conceptual diagram of a contaminated vadose zone after waste discharge and moisture redistribution depicting conditions that are the target of deep vadose zone remediation.

Vadose zone metal and radionuclide contaminants may interact with sediments or other pore water solutes, in addition to being transported by the complex, nonlinear processes described above. These interactions include sorption, precipitation or dissolution reactions and microbial interactions, impact the overall transport of contaminants in the vadose zone, and are important attenuation mechanisms that can limit the flux of contaminants to the groundwater. The presence of a gas phase in the vadose zone also needs to be considered with respect to pore-water chemistry. Under ambient conditions, oxygen and carbon dioxide in the gas phase may have important impacts on water chemistry with respect to the constituents present and

associated precipitation or dissolution processes, as described for uranium [2, 3].

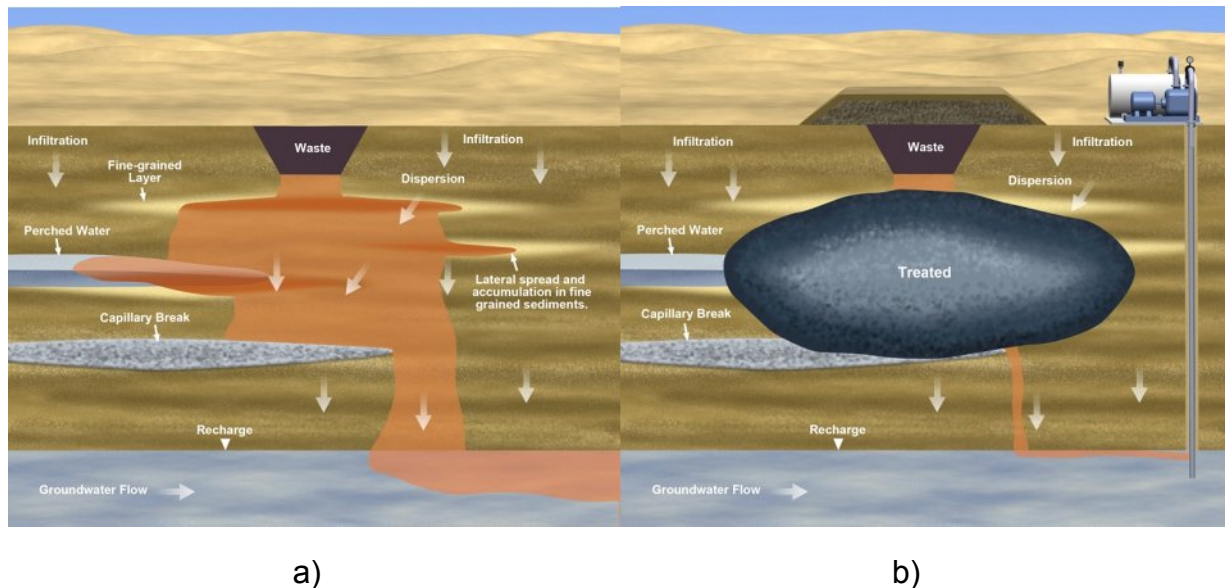


Fig 1. Conceptual diagram of a) contaminated vadose zone after waste discharge and moisture redistribution depicting the type of contaminant conditions that are the target of deep vadose zone remediation, and b) the impact of remediation efforts to control contaminant flux.

Potential Remediation Approaches

The inherently challenging properties of deep vadose zone environments also provide opportunities for remediation, including the following:

- Incremental enhancements may meet remediation goals given typically slow unsaturated flow conditions
- Long periods enhance opportunities for interactions with sediments and remediation amendments because of slow transport rates
- Capillary forces resist movement in some cases and hold contaminants in fine-grained units
- The driving force for water flow and recharge from surface infiltration can be controlled and reduced by surface structures (e.g., infiltration barriers)
- Gas-phase advection for distribution of remediation amendments can potentially be effective over large zones of influence
- Water added in relatively small quantities, although increasing the downward driving force, will only minimally impact the overall rate of movement.

Within the context of the vadose zone conceptual model described above, the approaches for deep vadose zone remediation can be categorized as controlling the flux of metal and radionuclide contaminants to groundwater through three different alternatives [4]: 1) contaminant mass reduction; 2) stabilization of contaminants to slow movement; or 3) manipulation to slow movement of pore water carrying contaminants. These approaches for flux reduction are based on the premise that excavation of deep vadose zone contamination is likely not a technically feasible or economically viable approach.

Contaminant Mass Reduction

Contaminant mass directly influences the magnitude and duration of contaminant flux from the vadose zone to the groundwater. Reducing the mass can directly impact both aspects of contaminant flux and improve groundwater protection. Contaminant mass reduction can be achieved by complete removal, collection, or flushing to groundwater. Complete removal of contaminants dispersed in the deep vadose zone is generally unattainable because of complexities of contaminant distribution and subsurface heterogeneities [5, 6]. Thus, some residual will remain and control mass flux over time. The need to understand and predict contaminant transport behavior over long periods is reinforced by the fact that many DOE EM sites will have residual contamination following completion of remedial actions [7].

When complete removal by excavation is not feasible, contaminant mass reduction must either be achieved by migrating the contaminants to a point of collection within the vadose zone or by applying sufficient water to drive contaminants to the groundwater for collection. Possible approaches for contaminant collection in the vadose zone include electrokinetic methods [8]. Electrokinetic methods work in unsaturated conditions using a low-level direct current to mobilize ions and migrate them to a positive charged anode. A number of reviews of the technology and its approach to DOE have been published [9, 10] and ongoing research is being conducted.

Soil flushing can be applied to purposely accelerate movement of contaminants from the vadose zone to groundwater where they are then captured by pump and treat systems. Soil flushing methods come from other applications such as mining, heap leaching, and limited in situ flushing development [11, 12]. Challenges for this method include the potential for lateral flow in the vadose zone that must be managed or preferential flow in paths that may not facilitate contaminant extraction.

Stabilization and Solidification

The basic tenant of stabilization and solidification is to limit interaction of contaminants with vadose zone pore water and thereby decrease contaminant flux to groundwater. Stabilization is accomplished through chemical modification via addition of amendments to reduce chemical solubility, mobility, or toxicity of contaminants. Solidification involves changing the physical form of contaminants such that it is mechanically trapped in a solid structure. Many stabilization and solidification processes overlap and the term stabilization is therefore generally applied. Stabilization can be achieved by methods such as biogeochemical manipulation. Biogeochemical manipulation is based on processes that occur naturally in the vadose zone, including surface complexation (sorption), precipitation of end member constituents, or co-precipitation with other constituents into solids. These manipulations either occur geochemically or are enhanced by microbial interactions. One category of stabilization remediation processes is based on the introduction of amendments that enhance these natural processes. Potential remediation approaches in this category include manipulating surface complexation by altering the pH of pore water, introducing compounds that enhance sorption, and altering pore water chemistry to favor sorption. Additionally, precipitates or minerals with low solubility can be formed to either incorporate or shield contaminants from pore water [13, 14]. Pore water chemistry can be manipulated by pH to dissolve and reprecipitate compounds that may decrease solubility/availability of contaminants; calcite chemistry can be manipulated [15]; and phosphate-precipitating agents can help form low-solubility precipitates [16]. Injection grouting and soil vitrification are stabilization methods applied for shallow wastes. These techniques could be extended to the deep vadose zone using the same or similar approaches

as for shallow applications. For the deep vadose zone, cost and infrastructure (access) requirements may become impractical or costs may become prohibitive as depth and contaminated volume increase.

Decrease Contaminated Pore Water Movement

Slowing contaminated pore water movement will decrease the flux of metal and radionuclide contaminants from the deep vadose zone to groundwater. Deep vadose zone flow through movement of pore water is controlled by the recharge rate, hydraulic gradient, and unsaturated (relative) permeability. Vadose zone flow can be slowed by manipulating these parameters and limiting the flux of dissolved or soluble contaminant. This control can be done by limiting infiltration (thus recharge) at the land surface, removing soil water (drying or desiccation), or reducing permeability of the sediments.

Surface barriers or caps are a well-established technology for reducing infiltration and recharge. Surface barriers may provide significant isolation, even for deep vadose zone contamination, but success is subject to site-specific design. Questions remain regarding the depth to which they impact vadose zone flow as a function of areal extent and ability to reduce infiltration [17]. Surface barriers or caps are being evaluated by DOE EM.

Portions of the vadose zone can be desiccated or dried to remove water and significantly decrease permeability [18]. Even with preferential drying of high permeability layers, the reduced permeability and induced capillary breaks may significantly slow pore water movement and reduce contaminant flux to groundwater. Desiccation or drying of vadose zone sediments is temporary in that the moisture will re-equilibrate over time. However, removal of water, along with control of infiltration and recharge, will render an overall decrease in movement. A specific case study of desiccation at the Hanford Site is also presented.

Materials can be introduced to the vadose zone to reduce permeability. Permeability reduction can be done through application of grout or polymers, or through precipitation of mineral phases to divert water and contaminants [19].

Vadose Zone Remediation Challenges

There are several technical challenges for remediation of metals and radionuclides in the deep vadose zone. These challenges impact implementation and success of possible remediation technologies and strategies. Effective methods for delivery of reagents are problematic for in situ deep vadose remediation [20]. Successful application of a remedy depends on the ability to deliver an amendment to the subsurface or induce an active process. Unlike groundwater environments, the nonlinear unsaturated characteristics of deep vadose zone environments add considerable complexity. Any introduction of water creates conditions that tend to accelerate downward contaminant movement.

Current understanding of the movement and distribution of fluids in the subsurface is far from complete [21]. The transport path of a contaminant in the vadose zone depends on the conditions of initial liquid contaminant release and subsequent recharge. The subsurface environment is physically, chemically, and biologically heterogeneous across a multitude of scales. Physical heterogeneity, in particular, has a profound impact on fluid flow, and thus on the retention and distribution of metals and radionuclides in the deep vadose zone. Field-scale heterogeneity, reflected in the unsaturated permeability distribution, greatly influences the configuration and distribution of contaminants within the vadose zone. The nonlinear variability of hydraulic properties with water saturation (moisture content) leads to heterogeneous

contaminant distributions, with contaminants residing in either fine or coarse sediments, depending on the source term history and subsequent contaminant transport. Physical heterogeneity may result in complications in application of vadose zone remediation methods because of processes such as lateral flow in a layered system, or the presence of vertical preferential flow features that may be difficult to target with treatments.

The presence of a gas phase, biogeochemical heterogeneities, active biological and biochemical processes, and the relatively large surface area of unsaturated soils results in significantly greater complexity of physical and chemical processes controlling contaminant mobility in vadose zone environments than in surface or groundwater environments. Remediation chemistry must also consider the presence of the gas phase (e.g., CO₂, oxygen) and low ratios of water content to soil matrix.

Heterogeneities in contaminant distribution create difficulty in delivering chemical amendments to the same contaminated horizons. For instance, heterogeneities affect the ability for amendments to react and stabilize vadose zone metal and radionuclide contaminants within an infiltration front without further mobilization of the contaminants towards the water table. Slurry emplacement, soil mixing, high-energy emplacement (e.g., jetting of nanoparticles or solutes with mist or nanoparticles in air), and liquid injection are techniques for amendment delivery that offer potential solutions, but work against or attempt to overcome vadose zone conditions.

Mass reduction methods generally work against the dominant processes in the vadose zone that retain contaminants in finer-grained materials and maintain relatively slow water and contaminant migration. Redistributing contaminants through introduction of large quantities of water or other materials changes the vadose zone in ways that favor migration of contaminants to the groundwater at a greater rate than ambient conditions. Soil flushing intentionally increases moisture content and contaminant transport in the vadose zone. Increased moisture content may increase post-treatment flux of contaminants to the groundwater and result in longer than planned groundwater treatment. Introduction and movement of vadose zone moisture results in pore-water chemistry changes that may be more favorable for contaminant migration. Therefore, while these methods add value because they reduce the mass of contaminants in the vadose zone, they need to be evaluated and the implementation risks appropriately addressed on a site-specific basis.

Remedial amendment distribution methods that work in concert with vadose zone properties have also been proposed and are in various stages of development. These include advection in the gas phase and foam delivery methods. Gas-phase amendments containing reactants or nutrients are attractive for unsaturated sediments in that the gravitational effects on flow are minimal and the gas permeability of the subsurface is often relatively high [22]. However, gas phase delivery of amendments may still be impacted by lithologically controlled preferential flow that bypasses contaminated zones. Foam-based amendment delivery is a topic of research for in situ remediation. As with gas-phase amendments, foam transport is also less subject to gravitational effects, increasing the uniformity of distribution and reducing (but not eliminating) the effects of heterogeneities [23]. Foam-based remediation is largely untested at the field-scale, but laboratory development efforts are the subject of current investigations. Issues to be considered include limitations on the mass of reactant that can be carried with the foam, and the increase in liquid saturation that will occur at the periphery of a foam injection where foam integrity breaks down, possibly resulting in undesired gravitational transport. Foam may include gaseous and/or liquid reactants, and surfactants in the foam may allow emplacement of nano-sized solids. As previously mentioned, electrokinetic methods can move water and solute in

unsaturated soils, and therefore could offer the potential to also move amendments within the vadose zone after reactants are in place.

All the remediation approaches described above may be appropriate to use if implementation and performance risks can be appropriately addressed through consideration of the site conceptual model and fundamental processes. The application of a site conceptual model to remediation of metal and radionuclide contamination is an iterative process; the model is updated as characterization and remediation processes proceed.

Policy Challenges

The prospect of using any deep vadose zone remediation technology for metals and radionuclides needs to be considered within a regulatory context. Remediation of the vadose zone is typically linked to meeting remediation goals for groundwater. As such, remediation in the vadose zone can be viewed as targeted for mitigating the source of contamination and reducing transport through the vadose zone to these receptors in contrast to meeting a specific concentration measured at some location within the vadose zone. Herein lies the challenge: applying vadose zone remediation to reach an acceptable rate of contaminant transport while realizing there are considerable uncertainties associated with estimating and measuring contaminant transport at the field scale.

At relatively “simple” or shallow sites, remediating the vadose zone to essentially eliminate vadose zone contamination may be a reasonably obtainable goal. At complex sites, residual contamination will likely remain after remediation is considered complete. An alternative approach is to determine the acceptable contaminant flux from the vadose zone to the groundwater and devise a means to implement and monitor a flux reduction technology until the vadose zone contamination is reduced to below levels that require control. There is a regulatory basis for leaving contamination in place in the vadose zone, provided flux to the groundwater is shown to be limited.

Determining the acceptable level of residual metal and radionuclide contamination to meet goals for groundwater remediation and how to appropriately measure when this residual has been obtained is a key challenge for establishing remediation objectives in the vadose zone. This approach, however, requires computational monitoring or other methods to calculate flux. Often, use of modeling within a regulatory framework is challenging, particularly with respect to making predictions of in situ remedial performance sufficient to support a remedial decision. While this effort may seem daunting, acceptance of monitored natural attenuation as a remedy for a wide range of contaminants and site settings provides a good example of how predictions of long-term remedy performance can be structured and used to support remedy selection. Methods suitable for monitoring and managing the long-term presence of contaminants in the vadose zone will be key components of implementation for a flux-control remedy for the vadose zone. It is relatively straightforward to measure contaminant concentrations in groundwater, but it is difficult to demonstrate and provide monitoring information showing that a flux-based remedy for the vadose zone impacting groundwater will remain below levels of concern over the long term.

Vadose Zone Remediation Example at the Hanford Site

At the DOE Hanford Site, significant amounts of contaminants reside in the vadose zone, the result of past waste discharges associated with plutonium production. One of the principal contaminants of concern in the deep vadose zone is technetium-99 (Tc-99); a large fraction of its inventory resides at the BC cribs and trenches waste site. This waste site contains 26 cribs and trenches that received about 110 million liters of liquid waste during the 1950s, containing about 410 curies of Tc-99 [24] and nitrate. The cribs and trenches were operated for specific retention of wastes, meaning the intent was to minimize breakthrough to groundwater. There is no evidence of Tc-99 having reached groundwater. Site characterization efforts demonstrate that most of Tc-99 inventory is located in the deep vadose zone, about 30 to 50 m depth. However, the contamination poses a risk as it is predicted to impact groundwater in the future.

In 2008, DOE initiated a treatability test to evaluate potential deep vadose zone remedies. A field test of a new and innovative technology, soil desiccation, was conducted in a shallower portion of the vadose zone beneath the BC cribs contaminated with both Tc-99 and nitrate. The shallower depth was used during the treatability test to reduce infrastructure costs (well drilling) associated with deep vadose zone contamination. In the treatability test, dry gas (relative humidity less than 100% at the same temperature as the contaminated sediment) was injected into the subsurface. The dry gas evaporated water from the porous medium until the gas reached 100% humidity, and then it was extracted from the subsurface. The vaporization process removed the pore water and resulted in very low moisture content in the desiccated zone [25]. The desiccation significantly decreased the unsaturated permeability of the treated zone, slowing the future movement of water and contaminants. Laboratory and modeling studies [26, 27] were done to design the treatability test. Previous efforts proposed desiccation as a potential treatment technology [28] and others [29] proposed that inclusion of a layer dried by evaporation within a multilayer surface barrier could enhance barrier performance, but the BC cribs and trenches treatability test appears to be the first time a field test has been reported.

Remediation of deep vadose zone contamination at the Hanford Site is being done as part of the *Comprehensive Environmental Response, Compensation, and Liability Act* (CERCLA) process under a federal facility agreement. In the CERCLA process, treatability studies are used to fill in critical gaps needed for detailed analysis of alternatives during the feasibility study. At the Hanford Site, the U.S. Environmental Protection Agency (EPA) and Washington State Department of Ecology formally requested that DOE evaluate and test technologies for deep vadose zone contamination [20]. These federal agencies requested that DOE develop a strategy to improve the understanding of the nature and extent of vadose zone contamination and develop remedial alternatives, specifically for Tc-99. The approach included a comprehensive evaluation of treatment technologies and conducting two technical workshops with panels of outside experts to recommend characterization and remediation technologies that could be deployed. Throughout development of the plan, informal meetings were held with regulators, stakeholders, Tribal Nations, and the State of Oregon Department of Energy to solicit input on the approach. DOE, EPA, and the Washington State Department of Ecology have formed a working group to address regulatory and decision-making challenges and develop a recommended approach for deep vadose zone investigations and decision making. These steps were taken to overcome the policy challenges associated with deep vadose zone remediation.

CONCLUSIONS

It may be useful to consider the risk and challenges with leaving contaminants in place as part of a flux-control remedy in comparison with risks associated with contaminant removal and final disposition elsewhere. Understanding and quantifying the ramifications of contaminant removal and disposition options are therefore warranted. While this review suggests that some additional development work is needed for deep vadose zone remediation techniques, the benefits of applying vadose zone remediation for groundwater protection are compelling and worthy of continued development.

REFERENCES

- [1] Hillel D. 1971. *Soil and Water Physical Principles and Processes*. Academic Press, New York.
- [2] McKinley JP, JM Zachara, J Wan, DE McCready, SM Heald. 2007. "Geochemical Controls on Contaminant Uranium in Vadose Hanford Formation Sediments at the 200 Area and 300 Area, Hanford Site, Washington." *Vadose Zone J.*, 6:1004–1017. DOI:10.2136/vzj2006.0184.
- [3] Langmuir D. 1997. "Aqueous Geochemistry of Uranium." In *Aqueous Environmental Chemistry*, R McConnin, Ed., pp. 494–512. Prentice-Hall, New Jersey.
- [4] Dresel PE, DM Wellman, K Cantrell, and MJ Truex. "Review: Technical and Policy Challenges in Deep Vadose Zone Remediation of Metals and Radionuclides." *Environ. Sci. Technol.* 45:4207–4216.
- [5] National Research Council. 1999. *Groundwater Soil Cleanup. Improving Management of Persistent Contaminants*. Natl. Acad. Press, Washington, D.C., pp. 182–188.
- [6] National Research Council. 2005. *Contaminants in the Subsurface: Source Zone Assessment and Remediation*. Natl. Acad. Press, Washington, D.C.
- [7] U.S. Department of Energy (DOE). 2001. *A Report to Congress on Long-Term Stewardship*. DOE Office of Environmental Management, Washington, DC.
- [8] U.S. Environmental Protection Agency. 1997. *Electrokinetic Laboratory and Field Processes Applicable to Radioactive and Hazardous Mixed Waste in Soil and Groundwater*. EPA/402/R-97/006, U.S. Environmental Protection Agency, Office of Research and Development, Washington D.C.
- [9] U.S. Environmental Protection Agency. 1997. Engineering Bulletin: *Technology Alternatives for the Remediation of Soils Contaminated with As, Cd, Cr, Hg, and Pb*. EPA/540/S-97/500, U.S. Environmental Protection Agency, Ohio.
- [10] U.S. Environmental Protection Agency. 1993. *Handbook: Approaches for the Remediation of Federal Facilities Sites Contaminated with Explosive or Radioactive Wastes*. EPA/625/R-93/013, U.S. Environmental Protection Agency, Office of Research and Development, Ohio.
- [11] Truex MJ, M Oostrom, F Zhang, KC Carroll, J Schramke, TW Wietsma, GD Tartakovsky, K Gordon. 2010. *Evaluation of Soil Flushing for Application to the Deep Vadose Zone in the*

WM2012 Conference, February 26 – March 1, 2012, Phoenix, Arizona, USA

Hanford Central Plateau. PNNL-19938, Pacific Northwest National Laboratory, Richland, Washington.

[12] Bartlett RW. 1998. *Solution Mining: Leaching and Fluid Recovery of Materials*. 2nd Ed., Gordon and Breach Science Publishers, Amsterdam, Netherlands.

[13] Szecsody JE, MJ Truex, L Zhong, MD Williams, CT Resch, and JP McKinley. 2010. *Remediation of Uranium in the Hanford Vadose Zone Using Gas-Transported Reactants: Laboratory Scale Experiments*. PNNL-18879, Pacific Northwest National Laboratory, Richland, Washington.

[14] Szecsody JE, MJ Truex, L Zhong, NP Qafoku, MD Williams, JP McKinley, CT Resch, JL Phillips, D Faurie, J Bargar. 2010 *Remediation of Uranium in the Hanford Vadose Zone Using Ammonia Gas: FY10 Laboratory-Scale Experiments*. PNNL-20004, Pacific Northwest National Laboratory, Richland, Washington.

[15] Kelly SD, MG Newville, L Cheng, KM Kemner, SR Sutton, P Fenter, NC Sturchio, C Spotl. 2003. "Uranyl Incorporation in Natural Calcite." *Environmental Science & Technology*, 37(7):1284-1287.

[16] Wellman DM, JN Glovack, K Parker, EL Richards, EM Pierce. 2008. "Sequestration and Retention of Uranium(VI) in the Presence of Hydroxylapatite Under Dynamic Geochemical Conditions." *Environmental Chemistry* 5(1):40-50.

[17] Fayer MJ, AL Ward, and VL Freedman. 2010. *Technical Basis for Evaluating Surface Barriers to Protect Groundwater from Deep Vadose Zone Contamination*. PNNL-18661, Pacific Northwest National Laboratory, Richland, Washington.

[18] Oostrom M, TW Wietsma, JH Dane, MJ Truex, AL Ward. 2009. "Desiccation of Unsaturated Porous Media: Intermediate-Scale Experiments and Numerical Simulation." *Vadose Zone J.* 8:643–650.

[19] Wellman DM, JP Icenhower, AT Owen. 2006. "Comparative Analysis of Soluble Phosphate Amendments for the Remediation of Heavy Metal Contaminants: Effect on Sediment Hydraulic Conductivity." *Environmental Chemistry* 3:219-224.

[20] U.S. Department of Energy. 2008. *Deep Vadose Zone Treatability Test Plan for the Hanford Central Plateau*. DOE/RL-2007-56, Revision 0, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

[21] National Research Council. 2001. *Conceptual Models of Flow and Transport in the Fractured Vadose Zone*. Natl. Acad. Press, Washington, D.C.

[22] Denham ME, BB Looney. 2007. "Gas: A Neglected Phase in Remediation of Metals and Radionuclides." *Environmental Science & Technology* 41(12):4193-4198.

[23] Zhong L, JE Szecsody, F Zhang, SV Mattigod. 2010. "Foam Delivery of Amendments for Vadose Zone Remediation: Propagation Performance in Unsaturated Sediments." *Vadose Zone Journal* 9 (3):757-767.

WM2012 Conference, February 26 – March 1, 2012, Phoenix, Arizona, USA

[24] Corbin RA, BC Simpson, MJ Anderson, WF Danielson II, JG Field, TE Jones, CT Kincaid. 2005. *Hanford Soil Inventory Model, Rev. 1*. RPP-26744, Rev. 1, CH2M HILL, Hanford Group, Inc., Richland, Washington.

[25] Truex MJ, M Oostrom, CE Strickland, GB Chronister, MW Benecke, and CD Johnson. 2011. "Field-Scale Assessment of Desiccation Implementation for Deep Vadose Zone Contaminants." *Vadose Zone J.* Submitted October 2011.

[26] Ward AL, M Oostrom, and DH Bacon. 2008. *Experimental and Numerical Investigations of Soil Desiccation for Vadose Zone Remediation: Report for Fiscal Year 2007*. PNNL-17274, Pacific Northwest National Laboratory, Richland, Washington.

[27] Oostrom M, TW Wietsma, JH Dane, MJ Truex, AL Ward. 2009. "Desiccation of Unsaturated Porous Media: Intermediate-Scale Experiments and Numerical Simulation." *Vadose Zone J.* 8:643–650

[28] Raimondi P, WP Acheson, and WK Overbey, Jr. 1997. *Barrier for Blocking Movement of Contaminants within an Aggregate Particulate Substrate*. U.S. Patent 5,591,115. Date issued: 7 Jan. 1997.

[29] Ankeny M and ME Burhard. 1995. *Means and Method for Hydraulically Isolating Unsaturated Zones in Soil*. U.S. Patent 5,421,672. Date issued: 6 June 1995.