Addressing Technical and Policy Challenges for Remediation of Metals and Radionuclides within Complex Deep Vadose Zone Environments - 17028

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ABSTRACT

Deep vadose zone contamination is a significant issue in many regions of the world. Although remediation of deep vadose zone contamination is important, direct contact with the contamination does not threaten human health or the environment due to its depth in the vadose zone. Yet, movement of contamination from the deep vadose zone to the groundwater creates the potential for exposure and risk to receptors. Therefore, the challenge of deep vadose zone remediation is to maintain a minimal rate of contaminant transport such that flux from the contaminated vadose zone is limited to protect groundwater resources and downgradient receptors. We herein review major processes for viable remediation of deep vadose zone metal and radionuclides that form the practical constraints on remedial actions and provide an overview of how these principles are being practiced to address key contaminants at the U.S. Department of Energy Hanford Site.

INTRODUCTION

The deep vadose zone is defined as the sediments below the zone of practicable excavation and removal, but above the water table. This definition assumes 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, and therefore represents a potential source of ongoing contamination to water resources.

Remediation of the vadose zone is typically linked to 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.

The process for remedial action decisions is complicated by difficult technical issues. For example, remediation of metal and radionuclide contamination is complicated by heterogeneous contaminant distribution and the preferential saturation-dependent flow in heterogeneous sediments. These complications have generally rendered attempts to remove the contamination unsuccessful. As a result, the magnitude of contaminant discharge (mass per time) from the vadose zone to the groundwater must be kept low enough to meet the groundwater concentration goals, either by natural attenuation (e.g., adsorption processes or radioactive decay) or through remedial actions (e.g., contaminant mass or mobility reduction).

Regulatory considerations are also important. Remediation of deep vadose zone contamination typically is linked to regulatory cleanup goals for groundwater, and as such, remediation technologies need to be considered within the regulatory context. A key concept here is that contaminant transport mechanisms through the vadose zone can attenuate the overall contaminant flux to the groundwater, and vadose zone contamination may not necessarily require remediation if the natural flux results in sufficiently low contaminant concentrations in the groundwater. In other cases, however, remediation to control transport, enhance attenuation mechanisms, or remove contaminants may be needed to limit flux so that groundwater or surface water protection standards are maintained. 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.

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. Additionally, protocols are needed to demonstrate that groundwater will remain uncontaminated or that contamination will remain below levels of concern in the future, and will achieve in situ remedial performance sufficient to support a remedial decision. The following discusion includes a review of (1) how hydrogeologic and biogeocehmical procsses may operate in the deep vadose zone and be used to meet remediation objectives, (2) the technical risks and challenges for consideration of a proposed remedial action, and (3) policy implications for deep vadose zone remediation.

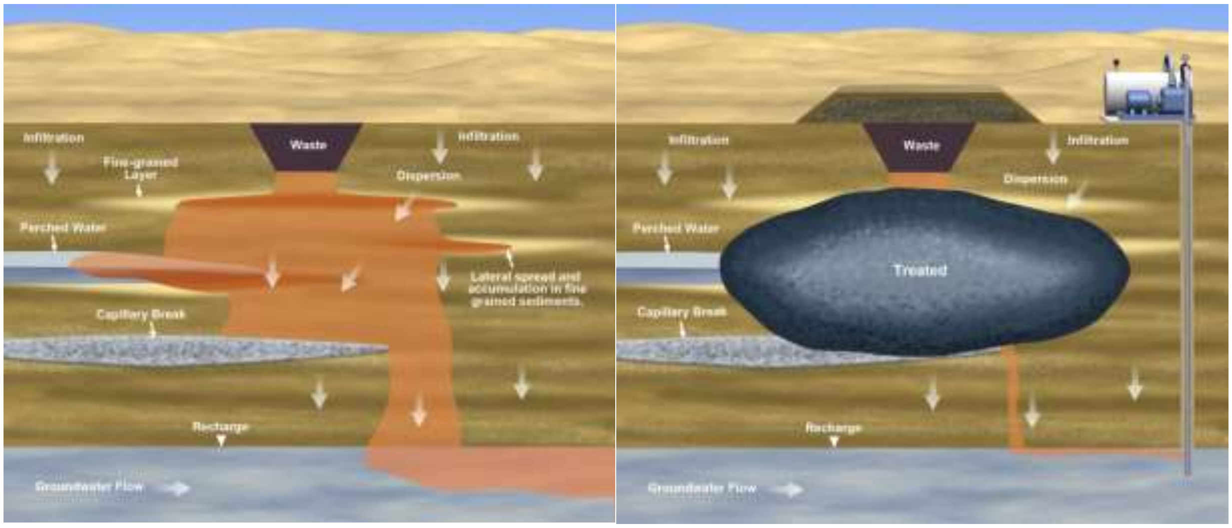
DISCUSSION

Vadose Zone Cencpetual Models

Conceptual models of deep vadose zone metal and radionuclide contamination 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 affect 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 impede flow and thus can resist vertical transport [1]. This resistance can cause lateral spreading and accumulation in finer-grained layers until water saturation and associated pressure increase 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 affect the hydraulic gradient and relative permeability of the sediments, which vary nonlinearly under unsaturated conditions. The physical processes of dispersion and diffusion can also affect pore water contaminant concentrations and associated flux to groundwater. Figure 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—which include sorption, precipitation, or dissolution reactions and microbial interactions—affect 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 an important influence on water chemistry with respect to the constituents present and associated precipitation or dissolution processes, as described for uranium [2, 3].



(a) (b)

Figure 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. The following factors should be considered for evaluating vadose zone remediation approaches:

- Incremental enhancements to contaminant attenuation in the vadose zone may meet remediation goals, given typically slow unsaturated flow conditions.
- Because of slow transport rates, interactions with sediments, contaminants, and remediation amendments that occur over long timeframes may be viable to use in addressing contaminants (in contrast to groundwater systems).
- Capillary forces resist movement in some cases and hold contaminants in fine-grained units that can be targeted for remediation.
- The driving force for water flow, 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 affect 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 contamimants 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 technically feasible or economically viable.

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 affect both aspects of contaminant flux and improve groundwater protection. Contaminant mass can be reduced 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 contamination 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 U.S. Department of Energy (DOE) Office of Environmental Management (EM) sites will have residual contamination following completion of remedial actions [7].

When complete removal by excavation is not feasible, contaminant mass reduction must be achieved by either migrating the contaminants to a point of collection within the vadose zone or 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 tenet 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 by adding amendments to reduce chemical solubility, mobility, or toxicity of contaminants. Solidification involves changing the physical form of contaminants such that they are 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 appproaches 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 [17]. 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 surface barriers impact vadose zone flow as a function of areal extent and their ability to reduce infiltration [18]. Surface barriers and caps are being evaluated by DOE EM.

Portions of the vadose zone can be desiccated or dried to remove water and significantly decrease permeability [19]. Even with preferential drying of high-permeability layers, the reduced permeability and induced capillary breaks may significnatly 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.

Materials can be introduced to the vadose zone to reduce permeability. Permeability can be reduced through application of grout or polymers [17], or through precipitation of mineral phases to divert water and contaminants [20].

Vadose Zone Remediation Challenges

There are several technical challenges for remediation of metals and radionuclides in the deep vadose zone. These challenges affect implementation and success of possible remediation technologies and strategies. Effective methods for delivery of reagents are problematic for in situ deep vadose remediation [21]. 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. Introduction of water may create conditions that tend to accelerate downward contaminant movement.

Current understanding of the movement and distribution of fluids in the subsurface is far from complete [22]. 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 effect 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 complicate the 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, and active biological and biochemical processes, along with 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 compared with surface or groundwater environments. Remediation chemistry must also consider the pesence of the gas phase (e.g., carbon dioxide, oxygen) and low ratios of water content to soil matrix.

Heterogeneities in contaminant distribution make it difficult to deliver chemical amendments to the same contaminated horizons. For instance, heterogeneities affect the ability of 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 by introducing 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 [23]. However, gas phase delivery of amendments may still be impacted by lithologically controlled preferential flow that bypasses contaminated zones. 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 if implementation and performance risks can be appropriately addressed by considering 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 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.

At relatively “simple” or shallow sites, remediating the vadose zone to essentially eliminate vadose zone contamination may be a reasonable 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 level 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 in southeastern Washington state, significant amounts of contaminants reside in the vadose zone, the result of past waste discharges associated with plutonium production.

Primary mobile contaminants of concern in the deep vadose zone include technetium-99 (Tc-99), uranium, iodine-129 (I-129), nitrate, and chromium. In 2008, DOE initiated a treatability test to evaluate potential deep vadose zone remedies [24]. Soil desiccation was selected for field testing at a site with significant Tc-99 contamination in the deep vadose zone. The field testing demonstrated effective drying of soil and provided scale-up information to support design of systems for remediation use [25-27]. Post-desiccation monitoring confirmed the expected rate of rewetting tied to the intensity of desiccation and the recharge rate [28]. These results showed that manipulating the moisture conditions in the vadose zone by desiccation can reduce the flux of contaminants to groundwater, but desiccation must be applied in conjunction with a surface infiltration barrier. The value of desiccation is in its ability to more rapidly reach the moisture conditions in the deep vadose zone associated with the low recharge conditions imposed by the surface barrier. In this way, desiccation improves the performance of a surface infilration barrier for deep vadose zone contaminants.

The treatability test plan also identified field testing of gas-phase reactants to sequester contaminants in the vadose zone. Preparatory laboratory experiments have shown that ammonia delivered in the gas-phase effectively induces a cycle of increased pore-water pH and associated sediment dissolution, followed by precipitation and buffering reactions as the pH level decreases [29-31]. This cycle of dissolution and precipitation causes formation of uranium precipitates and other mineral precipitates (e.g., silicates) that reduce the mobility of uranium. This reduced moblity decreases the flux of uranium to the groundwater. Scaling experiments have confirmed the viability of distributing ammonia to targeted areas of the vadose zone [32, 33]. A field test has been initiated in a uranium-contaminated zone at the Hanford Site to evaluate the field-scale performance of this technique, which has been shown highly effective in the laboratory experiments [34]. Laboratory experiments have also shown that use of reactive gases may also be effective at reducing Tc-99 moblity in the vadose zone [35].

While active remedies are important to evaluate, natural attenuation processes for contaminants in the vadose zone contribute to protection of groundwater. Thus, natural attenuation can be considered alone or in conjunction with targeted active treatment to meet remediation objectives. However, to apply natural attenuation and effectivley evaluate contaminant transport in the vadose zone, information is needed to identify attenuation processes and quantify the site-specific contaminant transport parameters that are used in models to predict the flux of contaminants to the groundwter under the site-specific conditions. Vadose zone characterization activities at the Hanford Site are underway and samples are being collected and analyzed for attenuation processes and to quantify transport parameters. These analyses are following the approaches outlined in U.S. Environmental Protection Agency (EPA) guidance for evaluating natural attenuation of inorganic and radionuclide contaminants (e.g., [36] and references therein). By using these EPA approaches, the site is developing a technically defensible set of information to support predictions of contaminant flux and to define the extent to which natural attenuation can be applied as a remedy for vadose zone contamination. Technical approaches for incorporating this type of information into vadose zone transport analyses have been developed to facilitate these evaluations (e.g., [37, 38]).

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, EPA and the Washington State Department of Ecology formally requested that DOE evaluate and test technologies for deep vadose zone contamination [21]. 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 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 associated 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.

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