

**Technical Basis for Gas-Phase Vadose Zone Remediation Technologies  
at Hanford: A Review – 12186**

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**ABSTRACT**

In situ vadose zone remediation approaches are being evaluated as potential options to mitigate the transport of inorganic and radionuclide contaminants from the vadose zone to the groundwater. Some of the candidate approaches are based on changing the contaminant or subsurface conditions in a way that slows downward migration of the contaminants through the vadose zone using amendments delivered in the gas-phase. Two promising approaches that have undergone testing at Hanford include soil desiccation to address technetium-99 contamination and ammonia-induced sequestration of uranium. For soil desiccation, a dry gas is injected to desiccate a targeted portion of the subsurface and thereby decrease contaminant movement by removing moisture and decreasing the hydraulic conductivity of the desiccated zone. Ammonia-induced sequestration of uranium relies on changing the pore water chemistry, primarily through pH changes, to induce dissolution and precipitation processes that decrease the amount of mobile uranium in the vadose zone.

**INTRODUCTION**

Inorganic and radionuclide contaminants in the deep vadose zone are at depths below the limit of direct exposure pathways, but may need to be remediated to protect groundwater [1]. The groundwater contaminant concentrations that result from vadose zone contamination are a function of the rate of contaminant movement through the vadose zone. For remediation, the magnitude of contaminant discharge from the vadose zone to the groundwater must be maintained low enough to achieve groundwater protection goals.

The Department of Energy Hanford Site contains a significant amount of contamination that resides in a 60-to-100-m-thick vadose zone due to past discharges associated with plutonium production operations. Much of this contamination is deep in the vadose zone where remediation options are limited by the physical and hydrogeologic properties of the vadose zone. There are several distinct categories of deep vadose zone problems at Hanford. The two principal deep vadose zone contaminants of concern are technetium-99 and uranium [2]. Other contaminants such as iodine-129 and nitrate are also prevalent in the deep vadose zone and groundwater. The BC cribs and trenches waste site at Hanford is an example of vadose zone contamination issues. This waste site contains 26 cribs and trenches that received about 110 million liters of liquid waste, primarily in the mid 1950s. The waste contained about 410 curies of technetium-99 [3]. There is no evidence that the contamination has reached

groundwater, located about 100 m below ground surface (bgs) in this area. Initial characterization efforts indicate that the technetium-99 inventory is located mostly at a depth in the vadose zone of between about 30 and 50 m bgs. Transport model predictions, however, indicate the potential for this contamination to adversely impact groundwater in the future [4].

In 2008, the Department of Energy initiated a treatability test program to evaluate potential deep vadose zone remedies for protection of groundwater [2]. As part of this effort, in situ vadose zone remediation approaches are being evaluated as potential options to mitigate the transport of inorganic and radionuclide contaminants from the vadose zone to the groundwater. Some of the candidate approaches are based on changing the contaminant or subsurface conditions in a way that slows downward transport of the contaminants through the vadose zone using amendments delivered in the gas-phase. Two promising approaches that have undergone testing at Hanford include soil desiccation to address technetium-99 contamination and ammonia-induced sequestration of uranium.

### **SUMMARY OF SOIL DESICCATION**

Desiccation of a portion of the vadose zone, in conjunction with a surface infiltration barrier, has the potential of minimizing migration of deep vadose zone contaminants towards the water table [5]. To apply desiccation, a dry gas (relative humidity less than 100% at the in situ temperature) is injected into the subsurface. The dry gas evaporates water from the porous medium until the gas reaches 100% relative humidity. The evaporation process can remove pore water and result in very low moisture content in the desiccated zone [5, 6, 7]. The desiccation process removes previously disposed water from the vadose zone and significantly decreases the aqueous-phase permeability of the desiccated zone. Through these mechanisms, the future rate of movement of moisture and contaminants through the desiccated zone is decreased.

Laboratory and modeling studies have been conducted to study desiccation and provide a technical basis for its use as a potential remedy [5, 6, 7]. In these studies, the overall performance of desiccation in limiting water and contaminant flux to the groundwater was shown to be a function of the final moisture content, contaminant concentration, sediment properties, size of the desiccated zone, the hydraulic properties and conditions in surrounding subsurface zones, and the net surface recharge rate. Desiccation was shown to be capable of reducing the moisture content to below the residual moisture content of the porous medium [5, 6, 7]. Under these conditions, the relative aqueous-phase permeability is near zero and subsequent moisture movement is significantly hindered [8]. Truex et al. [5] demonstrated through numerical modeling that combinations of a surface infiltration barrier and subsurface desiccation enhanced protection of groundwater compared to no-treatment or surface-barrier-only scenarios. The effectiveness of desiccation was related to the thickness and vertical location of the imposed desiccated zone in relation to the location of the elevated moisture and contaminant conditions. While the concentration of solutes increased in the desiccated zone in these simulations, this effect did not lead to a significant high-concentration pulse to the groundwater.

After a targeted portion of the vadose zone is desiccated, rewetting of this zone can occur by vapor- and aqueous-phase moisture transport. The timescale of rewetting is related to the overall performance of desiccation in minimizing contaminant flux to the groundwater. Truex et

al. [5] examined rewetting of desiccated zones in the laboratory and found that vapor-phase rewetting from adjacent humid soil gas, in the absence of advective soil gas movement, occurs slowly by diffusion of water vapor and increases the moisture content of desiccated porous medium to a limited extent, nominally to near the residual moisture content for the porous medium. The aqueous-phase rewetting rate was found to be a function of the relative aqueous-phase permeability of the porous medium.

Key factors that impact applying desiccation are the initial moisture content, permeability contrasts between adjacent sediment layers, and temperature and relative humidity of the injected gas. Laboratory studies [5, 6, 7] and field testing [8] have shown that the rate of desiccation is directly related to the water-holding capacity of the injected dry gas, the initial moisture content, and the number of pore volumes of dry gas transported through the porous medium. Because the transport of dry gas is directly related to the permeability of the porous medium, higher permeability zones in soil columns and flow cells packed with heterogeneous media dried more quickly than lower permeability zones [7]. Modeling studies [5, 6] demonstrated that the desiccation rate is increased with higher temperature and lower relative humidity of the injected dry gas, consistent with laboratory studies where the thermodynamic factors controlling the water-holding capacity of the injected dry gas were correlated with the desiccation rate [5, 6, 7]. Laboratory studies have also demonstrated that the concentration of solutes in the pore water does not significantly affect the desiccation rate for solute concentration ranging up to 5.8M of sodium nitrate [5]. Field test data were consistent with expectations based on these laboratory and modeling efforts [8].

## **SUMMARY OF AMMONIA TREATMENT FOR URANIUM CONTAMINATION**

The subsurface geochemistry can be altered to sequester uranium by injecting vapor-phase ammonia. Ammonia-induced sequestration of uranium relies on changing the pore water chemistry, primarily through pH changes, to induce dissolution and precipitation processes that decrease the amount of mobile uranium in the vadose zone. Figure 1 depicts the three primary elements of uranium treatment by ammonia vapor. When a mixed gas containing ammonia vapor is injected into an unsaturated porous medium, a large percentage of the ammonia partitions into the pore water due to the low Henry's Law constant (a dimensionless value of about  $6.5E10^{-4}$ ) of ammonia (Step 1, Figure 1). For instance, a 5% by volume ammonia vapor produces an equilibrium pore water concentration of about 3 M ammonia. Through dissociation, this ammonia concentration results in the pore water, starting at around pH 8, rising to about pH 11.5 [9, 10, 11]. Ion exchange and mineral dissolution (including silicate dissolution) is caused by the caustic pH (Step 2, Figure 1) [9, 10, 11]. With high total dissolved solids, precipitates start to form, especially as the pH is buffered back toward neutral. The precipitates may incorporate uranium (e.g., sodium boltwoodite) or may be compounds such as quartz, chrysotile, calcite, diaspore, hematite that could coat uranium already precipitated or adsorbed on the sediment surface (Step 3, Figure 1) [9, 10, 11]. The goal of the dissolution and re-precipitation process is to create uranium precipitates or coatings that render uranium less mobile than before treatment. Note that chemical reduction of the uranium is not a component of these processes; thus, the oxidation state of the vadose zone does not directly impact the longevity of precipitates that incorporate or coat uranium.

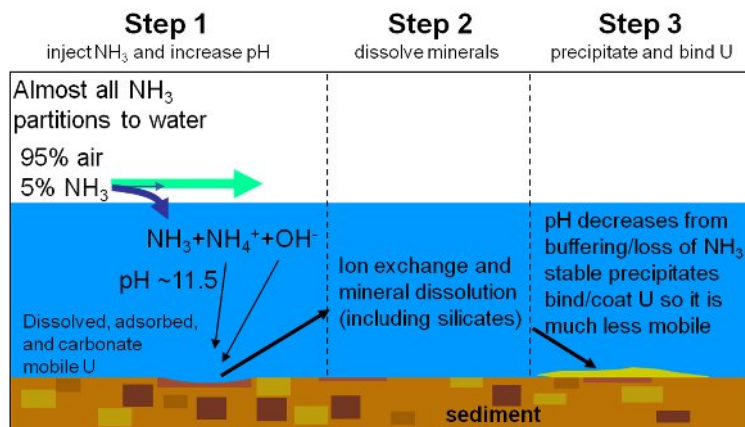




Figure 1. Overview of the processes that occur with injection of ammonia vapor into an unsaturated contaminated Hanford sediment.

The ammonia process targets uranium contaminants in the vadose zone that were the result of past disposal processes. Vadose zone contamination at the Hanford Site results from past uranium and plutonium enrichment activities and the intended or unintended release of 202,703 kg of uranium to the ground surface [12] in a variety of aqueous solutions (i.e., acidic, basic, with organic complexants [citrate, ethylenediaminetetraacetic acid]) and inorganic ligands (CO<sub>3</sub>, PO<sub>4</sub>). Uranium contamination exists in multiple forms in the subsurface as a result of these waste discharges. In addition to dissolved uranium and associated adsorbed uranium [9, 10, 13], the uranium contamination in Hanford sediments from the Central Plateau area have been found as a uranium-silicate (Na-boltwoodite; Na(UO<sub>2</sub>)(SiO<sub>4</sub>)\*1.5H<sub>2</sub>O), uranophane [Ca(UO<sub>2</sub>)<sub>2</sub>(SiO<sub>3</sub>OH)<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>], and as uranium-calcite co-precipitates [14, 15].

Recent laboratory investigations of the ammonia treatment process used a sequential extraction process to operationally define the initial distribution of uranium within different phases in the sediment and to then determine the impact of ammonia treatment on this distribution. Sequential liquid extractions at a 2:1 solution:sediment ratio have been used as shown in Table 1 [9, 10]. Uranium content in the extraction solution was determined by kinetic phosphorescence analysis [16] with a detection limit of 0.1 µg/L.

Table I. Sequential Extraction Solutions

Extraction Solution	Hypothesized targeted sediment components	Interpreted uranium mobility of extracted fraction	Color Code
1. Aqueous: uncontaminated Hanford groundwater	Uranium in pore water and a portion of sorbed uranium	Mobile phase	<span style="display: inline-block; width: 15px; height: 15px; background-color: red; vertical-align: middle;"></span>
2. Ion Exch.: 1M Mg-nitrate	Readily desorbed uranium	Readily mobile through equilibrium partitioning	<span style="display: inline-block; width: 15px; height: 15px; background-color: red; vertical-align: middle;"></span>
3. Acetate pH5: 1 hour in pH 5 sodium acetate	Uranium associated with surface exposed carbonate	Moderately mobile through rapid dissolution processes	<span style="display: inline-block; width: 15px; height: 15px; background-color: orange; vertical-align: middle;"></span>

solution	precipitates, including uranium carbonates, or other readily dissolved precipitates		
4. Acetate pH 2.3: 1 week in pH 2.3 acetic acid	Dissolution of most carbonate compounds, including uranium carbonates, and sodium boltwoodite	Slow dissolution processes are associated with uranium release from this fraction such that uranium mobility is low with respect to impacting groundwater	
5. 8M HNO <sub>3</sub> : 2 hours in 8M nitric acid at 95°C	Dissolution of most minerals expected to contain uranium, considered to represent total uranium extraction for this study <sup>1</sup>	Very slow dissolution processes are associated with uranium release from this fraction such that uranium mobility is very low with respect to impacting groundwater	

<sup>1</sup>some sediment digestion techniques may release more uranium from a given sample

The data from extraction solutions are not necessarily representative of a single uranium surface phase [10]. For example, a uranium-carbonate sample (no sediment) subjected to the 5 sequential extractions showed that 84% was dissolved by extraction solution #3, 15% by extraction solution #4, and 1% in the extraction #5. In contrast, the Na-boltwoodite sample subjected to the 5 sequential extractions showed that 13% was dissolved by extraction solution #3 and 84% by extraction solution #4, with the remainder in extraction #5.

Laboratory efforts to evaluate the ammonia treatment processes have used a range of contaminated sediments from the Hanford site that contain the above forms of uranium [9, 10]. Figure 2 shows a set of sediment samples collected from the 241-U tank farm area at Hanford [10]. For these samples, both the overall concentration and amount of uranium in the different extraction solutions changed with depth. With ammonia treatment, the dissolved uranium and associated adsorbed uranium (extraction solutions #1 and #2) decreased in all but two of the samples, uranium in extraction solutions #3 and #4 (Table 1) showed a mixture of increases and decreases, and the uranium in extraction solution #5 increased in 79% of the samples [10]. Qualitatively, these results suggest that ammonia treatment shifts the uranium within most samples from this Hanford location to phases or physical locations (e.g., under mineral coatings) that would be less mobile than prior to treatment.

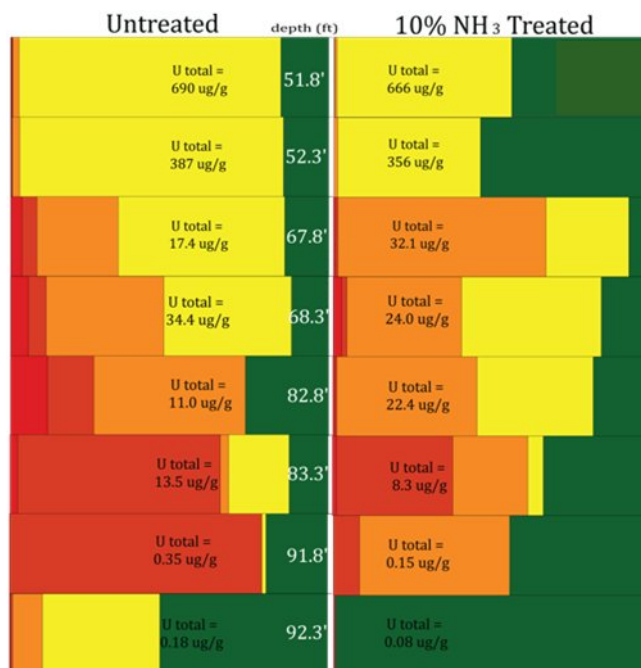


Figure 2. Fraction of the total uranium extracted using the solutions defined in Table 1 from sediment samples at the 241-U tank farm area of Hanford for a) untreated sediments and b) sediments contacted with 10% ammonia vapor for one month (after [10]). Color coding of the extraction solutions is shown in Table 1.

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