Scaling Gas-Phase Treatment of Vadose-Zone Contaminants for Field Application at the Hanford Site – 15133

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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 at the U.S. Department of Energy's Hanford site.   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.   Ammonia-vapor treatment of uranium relies on induced sediment dissolution and precipitation processes that decrease the amount of mobile uranium in the vadose zone.   Previous laboratory studies have demonstrated the decrease in uranium mobility caused by ammonia treatment.   As part of development efforts for the ammonia technology, scale-up issues were identified and have been addressed through a series of laboratory and modeling efforts. Key scale-up elements are scoping calculations to support treatment design and understanding ammonia transport.   Recent research has extended the concept of geochemical manipulation by ammonia to investigate a combined-gas treatment for sequestering Tc-99 in the vadose zone.   The technique uses a combination of geochemical Tc-99 reduction with hydrogen sulfide gas and induced sediment mineral dissolution and precipitation with ammonia vapor, creating conditions for deposition of stable precipitates that decrease the mobility of Tc-99.   Laboratory experiments have demonstrated the effectiveness of this treatment under a variety of operational and sediment conditions important to the scale-up and evaluation of potential addition field applications.

INTRODUCTION

Technetium-99 (Tc-99) and uranium are present in the vadose zone of the Hanford Central Plateau and are of concern with respect to the protection of groundwater [1].   Because Tc-99 is present as the pertechnetate anion in oxic systems such as the Hanford Site subsurface, it is highly mobile in the pore water of the vadose zone and in the groundwater.   Radioactive decay of Tc-99 has a long half-life (2.1×10^5 years) and does not functionally contribute to natural attenuation of Tc-99 plumes.   However, some Tc-99 physical and geochemical retention has been observed in oxic vadose zone sediments that have not been reduced [2,3] and may contribute to natural attenuation in the vadose zone.   The Tc(VII) valence state is dominant in oxic systems (e.g., as the pertechnetate anion) and can be geochemically reduced to less soluble Tc(IV) forms [e.g., 4].   However, geochemical reduction alone is not effective as a remedy for naturally oxic environments because Tc(IV) can be rapidly reoxidized [5].   Uranium geochemistry and migration in the Hanford Site subsurface is more complex than for Tc-99, though, in general, uranium migrates as carbonate complexes with moderate sorption behavior [6].   The magnitude of attenuation of uranium in the vadose zone may also be influenced by the chemistry of the disposed waste [7].   Uranium can be geochemically reduced to a low-solubility form, though like Tc-99, reduced uranium can be re-oxidized readily.   The persistence, limited natural attenuation mechanisms, and geochemical behavior of Tc-99 and uranium in oxic vadose zone environments must be considered when developing effective alternatives for remediation.

In 2008, the U.S. Department of Energy Richland Operations Office (DOE/RL) initiated a treatability test program to evaluate potential deep vadose zone remedies for protection of groundwater [1].   As part of this

effort, in situ vadose zone remediation approaches are being evaluated as potential options for mitigating the transport of Tc-99 and uranium from the vadose zone to the groundwater.   Delivery of aqueous-phase amendments to the vadose zone for remediation can be problematic [e.g., 8], whereas gas-phase amendment delivery may be advantageous [9,10] and has, therefore, been a focus of remediation technology development efforts.   Previous research conducted as part of the treatability test program developed geochemical manipulation to address uranium contamination using gas-phase delivery of amendments, in particular, use of ammonia vapor as the remediation amendment [3,11,12].   In this approach, if 5% ammonia vapor in a carrier gas is introduced to an unsaturated sediment, the pore water pH is temporarily increased above 11.5.   The ammonia-based remedy induces sediment mineral dissolution and formation of precipitates that decrease uranium mobility.   Recent research [13,14] has shown that, in laboratory studies, a combined-gas treatment can be effective for sequestering Tc-99 in the vadose zone. The technique uses a combination of geochemical Tc-99 reduction with hydrogen sulfide gas (3-20 vol% in a carrier gas has been tested) and induced sediment mineral dissolution and precipitation with ammonia vapor (nominally 5 vol% in a carrier gas), creating conditions for deposition of stable precipitates that decrease the mobility of Tc-99.   This result is consistent with previous research for saturated aqueous systems where geochemical manipulation with an alkaline amendment created alkaline and geochemically reducing conditions and effectively decreased Tc-99 mobility [4].

Figure 1 depicts the three primary elements of uranium treatment by ammonia vapor.   When a gas containing ammonia vapor is injected into an unsaturated porous medium, a large percentage of the ammonia partitions into the pore water (Step 1, Figure 1).   For example, a 5 vol% ammonia vapor produces an equilibrium pore-water concentration of about 3 M ammonia.   Self-dissociation of ammonia at this concentration results in an increase in the pore water pH from initially around pH 8 to about pH 11.5 [3,11,12].   Ion exchange and mineral dissolution (including silicate dissolution) is caused by the caustic pH (Step 2, Figure 1) [3,11,12].   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, and hematite that could coat uranium already precipitated or adsorbed on the sediment surface (Step 3, Figure 1) [3,11,12].   The goal of the dissolution and re-precipitation process is to create uranium precipitates or coatings that render uranium less mobile than before treatment.   The combined-gas treatment of Tc-99 uses the same principle as for the ammonia treatment, but adds hydrogen sulfide as a reductant so that the Tc-99 is reduced and precipitates where it can be effectively sequestered by coating with stable precipitates of other minerals.
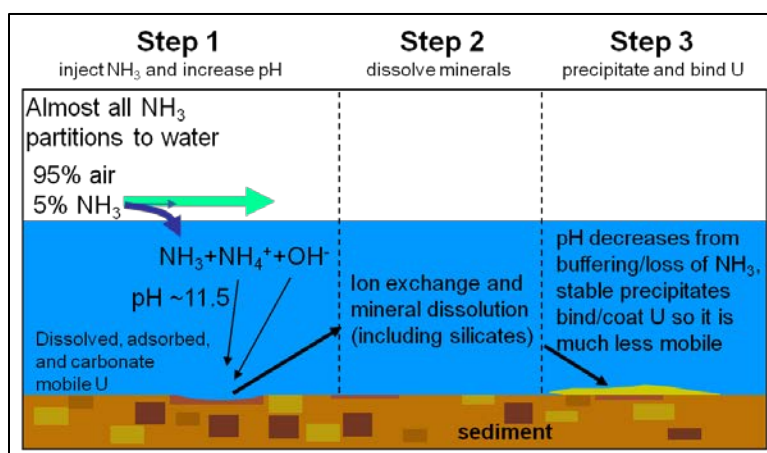
Figure 1. Overview of the processes that occur with injection of ammonia vapor into an unsaturated
uranium-contaminated Hanford sediment [15].

Understanding the robustness of gas-phase treatment approaches and scale-up to the field is an important
part of the technology development process. As part of development efforts for the ammonia technology,
scale-up issues were identified and have been addressed through a series of laboratory and modeling efforts.
Key scale-up elements are scoping calculations to support treatment design, ammonia transport
information, field application monitoring approaches, and information about processes affecting the fate of
ammonia in the subsurface [15,16]. For combined-gas treatment of Tc-99, laboratory experiments were
conducted to examine changes in Tc-99 mobility in vadose zone sediment samples and evaluate the
effectiveness of the treatment under a variety of operational and sediment conditions [13,14].

METHODS

Ammonia partitioning to pore water and unsaturated-zone transport were examined in batch and column
tests, as described in detail by Zhong et al. [16]. In summary, partitioning of ammonia between vapor and
water phases was studied in batch systems. Unsaturated soil columns up to 6 m in length were used to
evaluate ammonia advection with variations in injected gas flow rate and soil moisture content. Diffusion
of ammonia was studied using heterogeneously packed flow cells where advection was induced in
high-permeability layers and diffusion into surrounding low-permeability layers was quantified.

Experiments examining the combined-gas treatment for Tc-99 are described in detail by Szecsody et al.
[13]. In summary, experiments were conducted using 0.75-cm-diameter by 12-cm-long stainless steel
columns packed with sediment including treatments with variations in moisture content. The gas
amendment was injected at 50 mL/min for 18 minutes as the baseline injection approach. Amended soil
columns were then sealed and incubated for 3 weeks. For some cases, soil columns were then opened to
air for 3 weeks to allow for any re-oxidation processes. Each treatment included replicates so that
sediment samples could be used to determine the Tc-99 concentration for 1) pre-treatment, 2)
post-treatment, and 3) for selected treatments, after exposure of treated sediments to air for 3 weeks.
Sequential liquid extractions at a 2:1 solution:sediment ratio were used to evaluate the distribution of Tc-99
in functionally defined pore-water and sediment fractions ([13], Table 1). This type of sequential
extraction evaluation has previously been applied for investigation of uranium treatment [3,11,12]. Tc-99
concentration in the extraction solution was determined by scintillation counting.

Table 1.   Sequential extraction solutions [15].

| Extraction Solution	Hypothesized Targeted Sediment Components	Interpreted Tc-99 Mobility of Extracted Fraction	Color Code
1. Aqueous: uncontaminated Hanford groundwater	Tc-99 in pore water and a portion of sorbed uranium	Mobile phase	🟥
2. Ion Exch.: 0.5M $Mg(NO_3)_2$ (1 h)	Readily desorbed Tc-99	Readily mobile through equilibrium partitioning	🟫
3. Acetate pH5: 1 hour in pH 5 sodium acetate solution	Tc-99 associated with surface exposed carbonate precipitates or other readily dissolved precipitates	Moderately mobile through rapid dissolution processes	🟧
4. Acetate pH 2.3: 5 days in pH 2.3 acetic acid	Dissolution of most carbonate compounds that may coat Tc-99	Slow dissolution processes for Tc-99 release from this fraction; mobility is moderate to low with respect to impacting groundwater	🟨
5. Oxalic acid 0.1M ammonium oxalate, 0.1M oxalic acid (1 h)	Dissolution of iron oxides	Slow dissolution processes for Tc-99 release from this fraction; mobility is low with respect to impacting groundwater	🟩
6. 8M HNO_3: 2 hours in 8M nitric acid at 95°C	Considered to represent total Tc-99 extraction for this study	Very slow dissolution processes are associated with Tc-99 release; functionally immobile	🟩

RESULTS AND DISCUSSION

Ammonia Treatment Scale-up

Ammonia partitioning from gas to water phases significantly controls ammonia movement in unsaturated sediment.   Scoping calculations can be made using Henry's Law and the dissociation of ammonia in the pore water.   Details of these calculations are provided by Zhong et al. [16].   Figure 2 shows the comparison of calculated and measured water pH after partitioning into the water phase as a function of ammonia vapor concentration.   For ideal equilibrium partitioning, ammonia gas injected into the sediment would partition into the pore water to reach equilibrium concentration before the ammonia gas front (i.e., the front behind which the gas is at the ammonia concentration of the influent) would move downgradient. A sharp front of pore-water ammonia concentration and associated pore-water pH would also be observed under ideal equilibrium conditions.
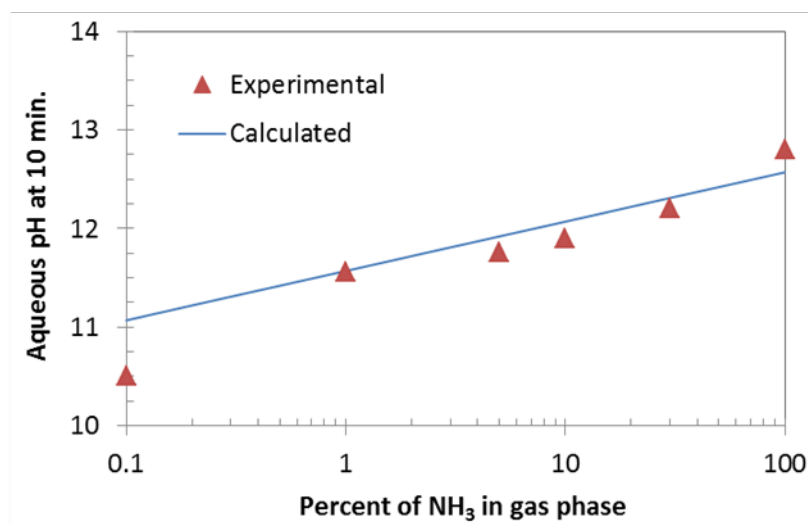
Figure 2. Comparison of calculated and measured pH from partitioning of ammonia (NH_3) from the gas phase to the water phase. Ammonia vapor at concentrations from 0.1 to 100 vol% were bubbled into 100 mL of deionized water at a flow rate of 20 mL/min. for 10 min to obtain the experimental pH values [16].

As an example of ammonia transport behavior, experiments conducted using 6-m-long soil columns at varying gas injection rates all resulted in a pH profile within the column that was indicative of reaching near-equilibrium pH up to the ammonia gas front, after which the pH was sharply lower (Figure 3). Ammonia gas-front retardation relative to the carrier gas flow rate was 202 ±31 in these experiments [11]. High gas velocities may overcome the partitioning-controlled behavior. For instance, ammonia gas-front retardation relative to the carrier gas flow rate was 363 in a similar column test with a measured ammonia gas-front advection rate of 2200 cm/min [11]. Ammonia gas-front retardation estimates are very sensitive to the sediment moisture content and porosity. For instance, the computed retardation for sediment moisture content values of 2, 4, and 6 wt% are 220, 510, and 910, respectively, assuming a porosity of 30%. Retardation estimates for a 4% sediment moisture content and 25, 30, and 35% porosity are 720, 510, and 380, respectively. Thus, an approximate ammonia gas-front retardation factor (ratio of unimpeded movement to retarded movement) can be estimated for field applications. However, variations of the actual retardation factor in the targeted treatment zone should be expected due to variations in moisture content and porosity.
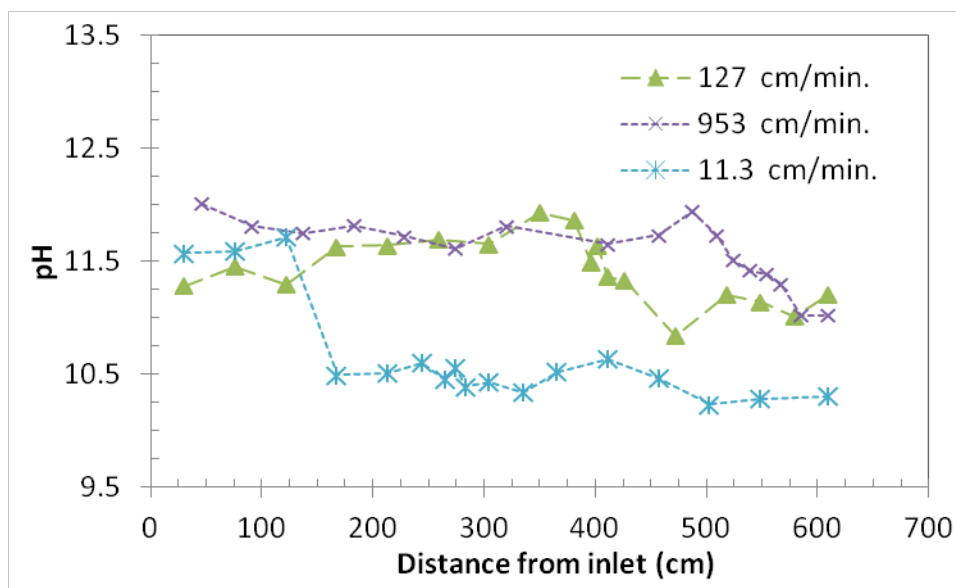
Figure 3. Resulting pH profile for 5 vol% ammonia gas injection into 6-m-long columns at different gas flow rates and associated ammonia velocities within the columns.   Stable, high pH occurs behind the ammonia gas front, which is shown by a sharp drop in pH.   Values shown in the legend are the computed ammonia gas-front advection rate for the experiment [11].

Advective ammonia distribution largely occurs in the high-permeability and lower moisture-content zones. Thus, ammonia diffusion may be important for evaluating the extent of field-scale treatment that can be expected in low-permeability portions of the subsurface, which would be bypassed by advection. Upgradient of the ammonia injection front, gas concentrations in the primary advective distribution pathways would be expected to be near the injected ammonia gas concentration.   Under these conditions, ammonia could diffuse into lower permeability zones.   If layers of contrasting permeability and moisture content are present, the relative rates of diffusion and advection are important for evaluating the overall distribution of ammonia in the targeted treatment zone.   Ammonia distribution by diffusion into lower permeability, higher moisture-content zones was qualitatively observed in flow cells with heterogeneous packing [11].

More quantitative examination of ammonia diffusion was recently evaluated by Zhong et al. [16].   In summary, Zhong et al. [16] conducted a 2D diffusion study using a 7.62-cm-internal-diameter, 10.16-cm-long soil column with two types of heterogeneous sediment packing (Figure 4).   A flow distribution plate was emplaced in each end of the vessel to evenly distribute the gas injection and collect the gas effluent.   For the experiments, 26 L of 5 vol% ammonia gas was pumped through the soil column at flow rate of 2.5 mL/min over a 1-week period.   The soil column was then disassembled and sediment samples were taken at selected distances from the injection end and multiple lateral locations to measure the concentrations of dissolved ammonia in pore water.
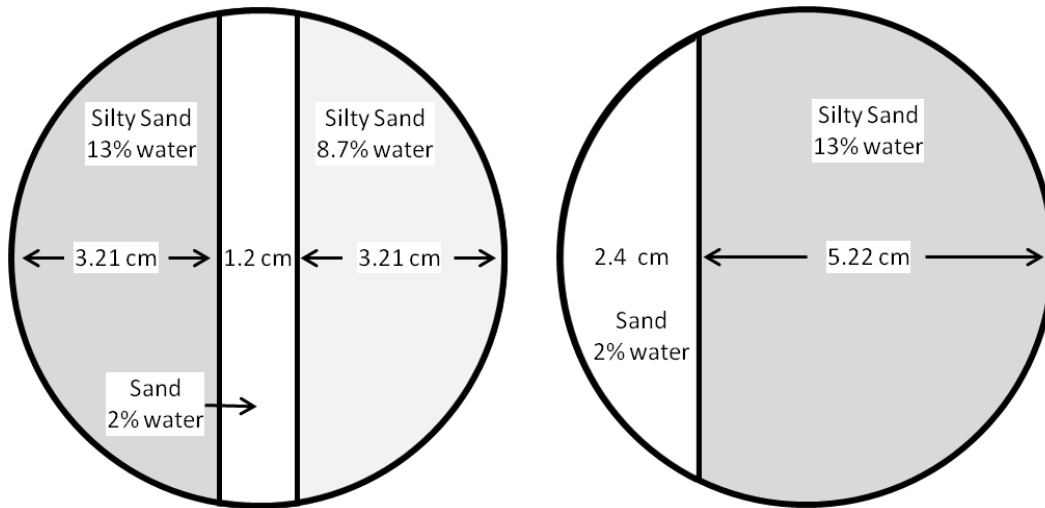
Figure 4.   Cross section view of heterogeneous sediment packing for 2D diffusion studies with a central high-permeability layer (left) or a side high-permeability layer (right).   This packing extended the full length of the soil column [16].

Although more than enough ammonia to fully saturate the high-permeability, lower moisture-content layer was used in the experiments, ammonia concentrations decrease with distance from the inlet within this high-permeability layer (Figure 5).   Lateral ammonia movement into the surrounding low-permeability, higher moisture-content layers is evident in the observed pattern of ammonia concentrations, with highest concentrations in the layer nearest the inlet and nearest the high-permeability layer.   These results demonstrate the slow advection of ammonia due to partitioning into the pore water and the associated significant diffusion into surrounding low-permeability zones.   Due to the configuration of the 2D experiments, some advection of ammonia into the low-permeability zones could also have occurred. However, the observed distribution of ammonia in the low permeability zones is consistent with diffusion rates determined by Zhong et al. [16] in 1D soil columns using the same materials and at the same moisture contents as were used for packing the 2D experiments shown in Figure 5.
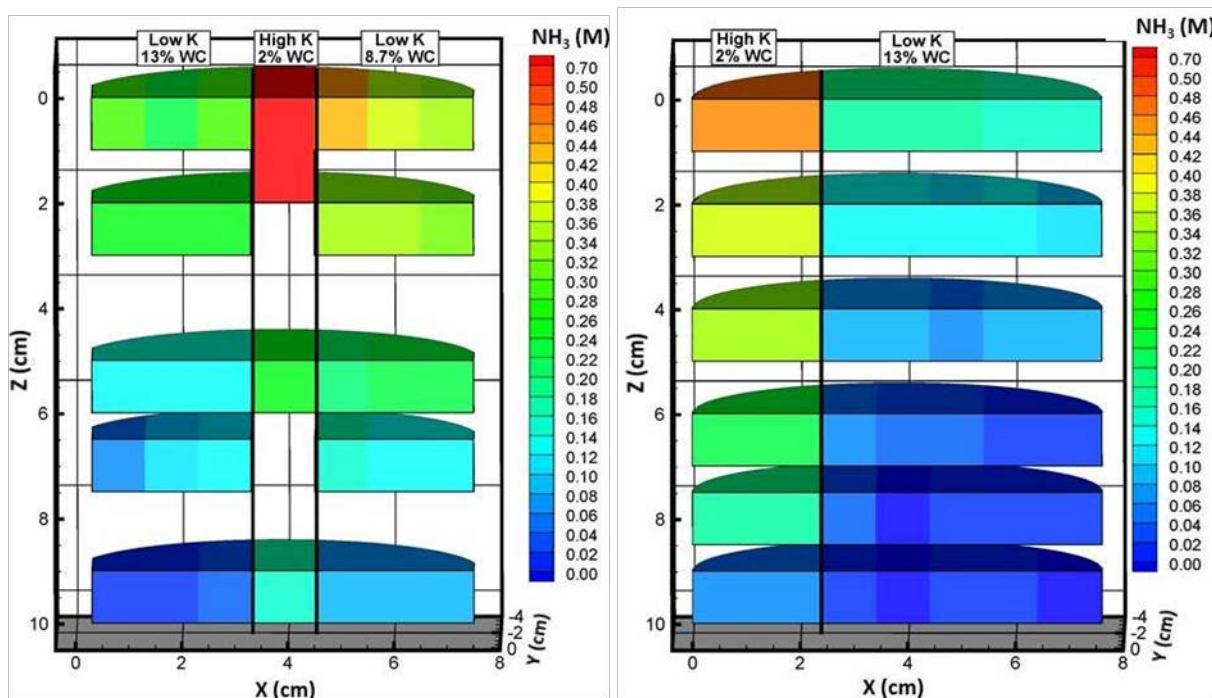
Figure 5. Ammonia pore-water concentration distribution in heterogeneous systems with a central high-permeability layer (left) and a side high-permeability layer (right). Distributions are after one week of ammonia gas injection [16].
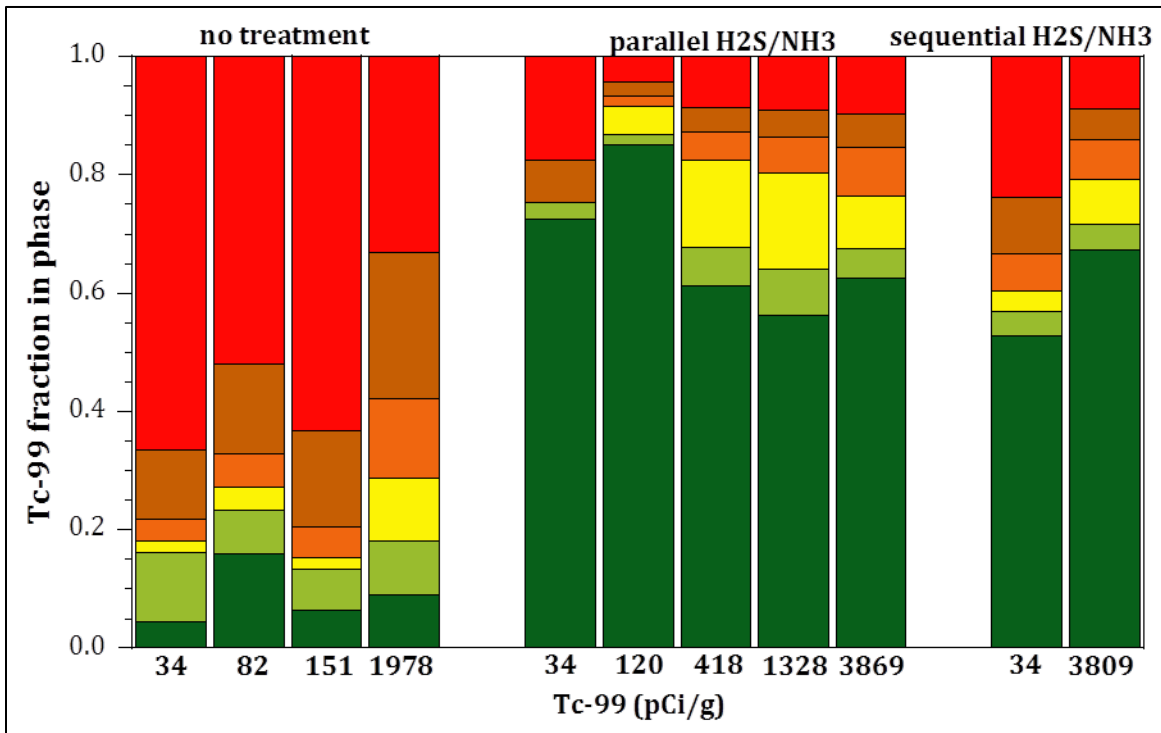
Combined-Gas Treatment Robustness

Szecsody et al. [13] examined sequential (hydrogen sulfide, then ammonia) and parallel addition of hydrogen sulfide and ammonia gases for a range of treatment gas concentrations (1 to 20 vol% hydrogen sulfide and 5 to 10 vol% ammonia). Consistent results for decreasing Tc-99 mobility were obtained when the hydrogen sulfide gas concentration was above 1% (Figure 6). These tests are not comprehensive in determining the best gas mixture for field application, but demonstrate robust treatment for a variety of gas concentration and delivery options. Parallel gas addition may be a more easily managed approach for injection of gases for a field application. Szecsody et al. [13] also demonstrated that use of hydrogen sulfide or ammonia individually is not effective at reducing Tc-99 mobility. Reduction of Tc-99 by hydrogen sulfide is readily reversed and, in an oxic vadose zone, would not be effective. Ammonia treatment is only marginally effective for decreasing Tc-99 mobility. The poor effectiveness is likely because most of the Tc-99 is not associated with sediment surfaces and is therefore not readily coated when precipitates form. For the combined treatment, reducing the Tc-99 with hydrogen sulfide causes it to precipitate and subsequent precipitates from the ammonia treatment can effectively coat the Tc-99. Note that, in most of the combined-gas tests, a large fraction of the Tc-99 in treated samples can only be extracted from the sample using a hot nitric acid solution (i.e., the Tc-99 is significantly sequestered) (Table 1).
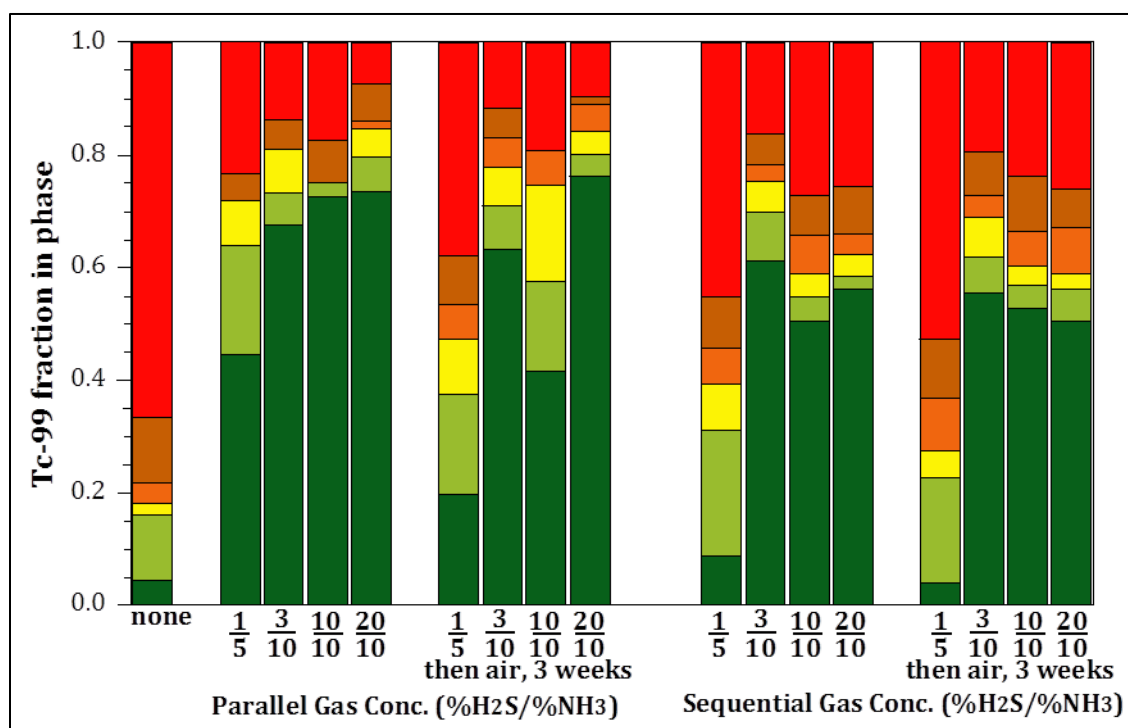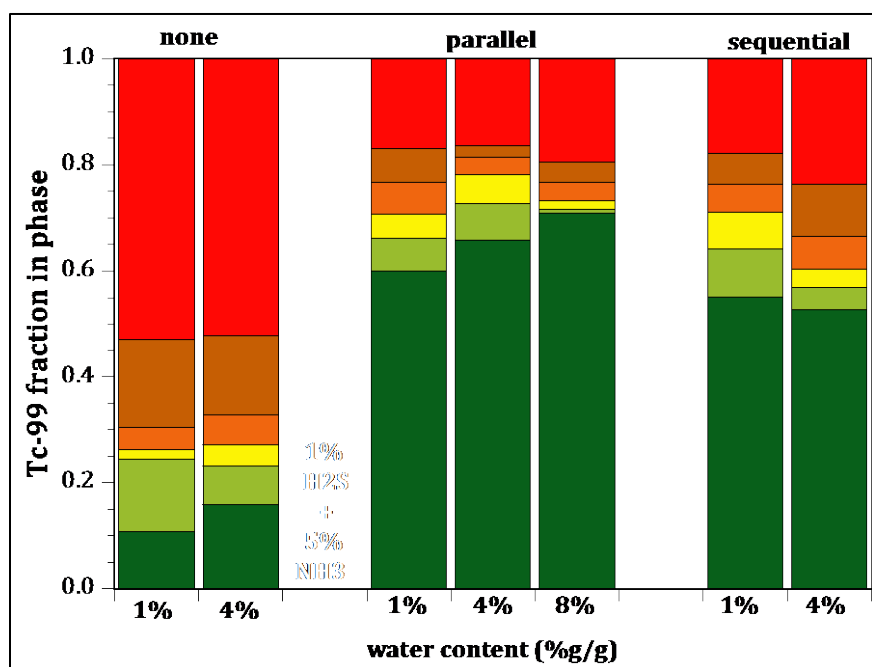
Figure 6. Sequential extraction data (see Table 1 for color codes) for combined-gas treatment using sequential (hydrogen sulfide, then ammonia) or parallel gas addition over a range of gas concentrations [13].   Results show data before treatment, after treatment, and after treatment plus oxidation by air addition for 3 weeks.   The sediment Tc-99 concentration was 82 pCi/g.

The combined-gas treatment was also shown to be robust across a wide range of Tc-99 concentrations [13]. Experiments with existing and spiked Tc-99 concentrations ranging from 34 to 3800 pCi/g showed only small variations in the ability of the applied gas treatment to decrease Tc-99 mobility, even after oxidation of the post-treatment samples (Figure 7).   In addition, experiments examining soil moisture contents of 1, 4, and 8 wt% showed only minor variation in the ability of the combined-gas treatment to decrease Tc-99 mobility, even after oxidation of the post-treatment samples (Figure 8, [13]).

Figure 7. Sequential extraction data (see Table 1 for color codes) for combined-gas treatment using sequential (hydrogen sulfide, then ammonia) or parallel gas addition over a range of Tc-99 sediment concentrations [13].   Results show data before treatment and after treatment plus oxidation by air addition for 3 weeks.   A 10% concentration was used for both hydrogen sulfide and ammonia gases.

Figure 8. Sequential extraction data (see Table 1 for color codes) for combined-gas treatment using sequential (hydrogen sulfide, then ammonia) or parallel gas addition for different soil moisture content values [13]. Results show data before treatment and after treatment plus oxidation by air addition for 3 weeks. A 10% concentration was used for both hydrogen sulfide and ammonia gases. The sediment Tc-99 concentration was 82 pCi/g.

CONCLUSIONS

Gas-phase treatment may offer a means to sequester uranium and Tc-99 in the vadose zone, reducing the flux of these contaminants through the vadose zone and, thereby, protecting groundwater. Geochemical manipulation is one type of gas-phase treatment and laboratory tests have demonstrated that contaminant mobility can be decreased by creating conditions where contaminants are bound by or coated in stable mineral precipitates. Scale-up from the laboratory to field application is an important part of technology development. Key elements of scale-up involve providing information to support field-scale engineering calculations, determining the operational parameters that will provide acceptable performance, and understanding amendment transport to support design of amendment delivery to the targeted treatment zone.

Ammonia technology information described herein, and in detail by Truex et al. [15] and Zhong et al. [16], is being applied in the design of an upcoming field test of the technology in the vadose zone at the DOE Hanford Site. Information on ammonia partitioning enables calculation of the required ammonia mass to achieve treatment within the targeted treatment volume. Ammonia transport was shown to be well described by advection and equilibrium partitioning behavior and is supporting design of the injection system. Data also suggest that within the core of the ammonia vapor distribution zone, ammonia will penetrate into small- to moderate-sized silt lenses. Field testing will be used to verify this expected diffusion-driven treatment for silt lenses.

The combined-gas treatment of Tc-99 is in the initial stage of technology development.   However, as described herein and, and in detail by Szecsody et al. [13] and Truex et al. [14], scale-up elements are being considered from the onset of the development effort.   A key concern was the robustness of the treatment with respect to the gas concentrations, Tc-99 concentrations, and moisture content.   If the technology had required a very narrow set of conditions to be effective, it would more difficult to apply in the field.   Fortunately, the treatment is effective over a wide range of conditions.   Future development can include moderate optimization of the gas concentrations.   However, the focus of future efforts can be on other factors such as hydrogen sulfide gas fate and transport in the subsurface associated with obtaining the desired distribution of the amendment and on operational safety.

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