



Ammonia gas transport and reactions in unsaturated sediments: Implications for use as an amendment to immobilize inorganic contaminants



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HIGHLIGHTS

- Ammonia transport can be predicted from gas movement and equilibrium partitioning.
- Ammonia diffusion rate in unsaturated sediment is a function of water contents.
- High pH induced by ammonia causes mineral dissolution and sequential precipitation.
- Ammonia treatment effectively immobilized uranium from contaminated sediments.

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ABSTRACT

Use of gas-phase amendments for in situ remediation of inorganic contaminants in unsaturated sediments of the vadose zone may be advantageous, but there has been limited development and testing of gas remediation technologies. Treatment with ammonia gas has a potential for use in treating inorganic contaminants (such as uranium) because it induces a high pore-water pH, causing mineral dissolution and subsequent formation of stable precipitates that decrease the mobility of some contaminants. For field application of this treatment, further knowledge of ammonia transport in porous media and the geochemical reactions induced by ammonia treatment is needed. Laboratory studies were conducted to support calculations needed for field treatment design, to quantify advective and diffusive ammonia transport in unsaturated sediments, to evaluate inter-phase (gas/sediment/pore water) reactions, and to study reaction-induced pore-water chemistry changes as a function of ammonia delivery conditions, such as flow rate, gas concentration, and water content. Uranium-contaminated sediment was treated with ammonia gas to demonstrate U immobilization. Ammonia gas quickly partitions into sediment pore water and increases the pH up to 13.2. Injected ammonia gas advection front movement can be reasonably predicted by gas flow rate and equilibrium partitioning. The ammonia gas diffusion rate is a function of the water content in the sediment. Sodium, aluminum, and silica pore-water concentrations increase upon exposure to ammonia and then decline as aluminosilicates precipitate when the pH declines due to buffering. Up to 85% of the water-leachable U was immobilized by ammonia treatment.

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1. Introduction

In situ remediation of inorganic contaminants in unsaturated sediments of the vadose zone is still in an emerging stage of development [1]. Delivery of aqueous-phase amendments to the vadose zone can be problematic due to mobilization of untreated contaminants and limited distribution e.g. [2,3]. Use of gas-phase delivery

may be advantageous in the vadose zone, but there has been limited development and testing of gas treatment technologies e.g. [4,1]. Treatment with ammonia (NH_3) gas has a potential for use in treating inorganic contaminants (such as uranium) by creating stable precipitates that limit the mobility of inorganic contaminants [5]. Using uranium as a specific example, Fig. 1 depicts the three primary elements of treatment by ammonia gas. When a 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 6.5×10^{-4}) of ammonia (Step 1, Fig. 1). For example, a

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Table 1
Sediment grain size and mineralogy characterization.

Sample location		Hanford formation sand	Cold Creek unit silty sand ^a
Depth (m)		6.1	45
Grain size	Gravel, sand (%)	94.8	63.9
	Silt (%)	3.8	36.1
	Clay (%)	1.4	–
Mineralogy (for the <2 mm particle size fraction)	Quartz (%)	34	52
	Plagioclase (%)	27	25
	Mica (%)	17	–
	K-feldspar (%)	13	15
	Amphibole (%)	6	–
	Chlorite (%)	4	–
	Calcite (%)	–	8

^a Silty sand data from Ref. [11].

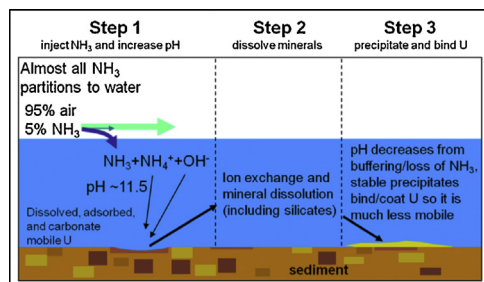


Fig. 1. Overview of the processes that occur with injection of ammonia vapor into an unsaturated, uranium-contaminated sediment.

5% by volume 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 [5,6]. Ion exchange and mineral dissolution (including silicate dissolution) is caused by the caustic pH (Step 2, Fig. 1) [5,6]. 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., forming sodium boltwoodite) or may form compounds, such as quartz, chrysotile, calcite, diaspor, and hematite that could coat uranium already precipitated or adsorbed on the sediment surface (Step 3, Fig. 1) [5–7]. The goal of the dissolution and re-precipitation process is to create uranium precipitates or coatings that render uranium less mobile than before treatment. These mineral dissolution and precipitation principles are also applicable to other inorganic contaminants in the vadose zone.

Studies on several fundamental aspects of uranium treatment using ammonia gas [5] and the application of ammonia gas for technetium immobilization [8] have been reported. When ammonia gas was injected into vadose zone sediments, a series of geochemical reactions, including mineral dissolution and precipitation, were observed. These reactions resulted in an electrical resistivity response in the pore water, which can be utilized to monitor the spreading of the gas [5]. Treatment using ammonia gas in combination with hydrogen sulfide (H_2S) gas has been shown to effectively immobilize technetium in vadose zone sediments [8]. Other studies have shown that treatment of water-saturated sediments with alkaline solutions induced similar mineral dissolution reactions. In two studies using the same sediments used in this study, montmorillonite, muscovite, kaolinite, biotite, and magnetite were partially dissolved, resulting in high silica, aluminum, sodium, and iron concentrations [9,10].

However, deploying the ammonia technology in the field for treatment of uranium or other inorganic contaminants requires further knowledge about ammonia transport and the geochemical reactions induced by ammonia treatment. Laboratory studies were conducted to support calculations needed for field treatment

design, to quantify advective and diffusive ammonia transport in unsaturated sediments, and to evaluate pore-water chemistry changes as a function of ammonia delivery conditions. Batch tests were carried out to evaluate ammonia partitioning into bulk water or pore water, and to provide baseline data for pore-water chemistry changes induced by ammonia addition. Gas injection and flow tests were carried out in soil columns and radial wedge flow cell configurations to study the ammonia advection and resulting reactions under differing sediment water content values, ammonia gas concentrations, gas injection flow rates, and variations in physical heterogeneities. Column and pseudo two-dimensional (2D) flow cell tests were also conducted to evaluate ammonia diffusion as a function of sediment water content and sediment heterogeneity.

2. Materials and methodology

2.1. Materials

Liquefied anhydrous pure ammonia was used as the gas source to prepare ammonia-in-nitrogen gas mixtures at NH_3 concentrations ranging from 0.1% to 100%. Ultrapure nitrogen gas was used for dilution. Uncontaminated sediments collected from the Hanford formation (sand) and from the Cold Creek unit (silty sand) at the U.S. Department of Energy's Hanford Site (Washington, USA) were used as the porous media. Hereafter, the Hanford formation and Cold Creek unit sediments are referred as "sand" and "silty sand", respectively. These sediments have low natural uranium concentration levels (<2 $\mu g/g$). Sediments were sieved to remove pebbles with grain size larger than 4 mm. The grain size and mineralogy determined using X-ray diffraction of the sediments are listed in Table 1.

Sediments were prepared for batch, column, and 2D wedge experiments with specific water contents to either approximate field conditions (averaging 4% by weight) or to evaluate NH_3 gas partitioning (at various water content percentages). Hanford Site groundwater with 0.08 $\mu g/L$ uranium was mixed with the natural sediment to achieve the desired water contents. This groundwater generally has high carbonate concentrations [12].

2.2. Experimental setup and procedures

2.2.1. Batch tests

To quantify the rate and extent of ammonia gas partitioning into bulk water, NH_3 at concentrations of 0.1%, 1.0%, 5%, 10%, 30%, and 100% v/v was bubbled into a 100 mL aliquot of deionized water (DIW) at a gas flow rate of 20 mL/min., while the container holding the water was open to the atmosphere. The pH and electrical conductivity (EC) of the water was monitored over time.

To study the ammonia-pore water interaction, 3 g of the sand sediments with water contents of 1, 4, 8, and 16 wt% were each placed into separate 50-mL vials. A 250 mL quantity of ammonia gas

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