



Research article

Potential for U sequestration with select minerals and sediments via base treatment

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ABSTRACT

Temporary base treatment is a potential remediation technique for heavy metals through adsorption, precipitation, and co-precipitation with minerals. Manipulation of pH with ammonia gas injection may be especially useful for vadose zone environments as it does not require addition of liquids that would increase the flux towards groundwater. In this research, we conducted laboratory batch experiments to evaluate the changes in uranium mobility and mineral dissolution with base treatments including sodium hydroxide, ammonium hydroxide, and ammonia gas. Our data show that partitioning of uranium to the solid phase increases by several orders of magnitude following base treatment in the presence of different minerals and natural sediments from the Hanford site. The presence of dissolved calcium and carbonate play an important role in precipitation and co-precipitation of uranium at elevated pH. In addition, significant incongruent dissolution of bulk mineral phases occurs and likely leads to precipitation of secondary mineral phases. These secondary phases may remove uranium via adsorption, precipitation, and co-precipitation processes and may coat uranium phases with low solubility minerals as the pH returns to natural conditions.

1. Introduction

Base injection via ammonia gas is a potential remediation technology for heavy metals including uranium (U). Gas injection has been previously described as a viable remediation technique for heavy metals and radionuclides via pH manipulation as they are highly affected by solution chemistry (Denham and Looney, 2005; Dresel et al., 2011). The injection of ammonia gas is designed to temporarily raise the pH of the aqueous phase to dissolve some natural minerals. When the system returns to a neutral pH as ammonia dissipates from the system, U is expected to be immobilized via the following phenomena (1) adsorption to mineral phases, (2) precipitation of U phases, and (3) co-precipitation as the aqueous phase is saturated with Si, Al, and similar ions followed by (4) coating of adsorbed and (co)precipitated U phases with low solubility precipitates.

The Department of Energy's (DOE) Hanford site located in Washington state represents an ideal case study for this technique as over 200,000 kg of uranium (U) have been released into its deep vadose zone (Corbin et al., 2005; McKinley et al., 2007). This release occurred as a result of improper disposal of waste from plutonium production during World War II and the Cold War. Moreover, U is highly mobile in the Hanford vadose zone due to oxidizing conditions and the presence

of carbonate creating aqueous uranyl ($U(VI)O_2^{2+}$) carbonate species. Partitioning coefficients, K_d 's, for U were previously measured in the range of 0.1–5 mL/g at pH 8 and retardation factors were measured at 1.43 for Hanford sediments and groundwater (Szecsody et al., 2013; Zachara et al., 2007). U concentrations have been measured as high as 660 mg/L in groundwater in this area making it one of the primary risk drivers at the site (Serne et al., 2004, 2008; Zachara et al., 2007).

Further, the Hanford vadose zone is up to 255 feet thick with contamination measured down to 170 feet below the ground surface (Serne et al., 2008). Therefore, there is a desire to create a remediation option that does not input additional liquid to the vadose zone as this would increase U flux towards the groundwater below. Of the remediation methods that the Department of Energy (DOE) is currently considering, ammonia gas injection is a favorable option that requires greater investigation. This potential treatment could also be applicable to other sites especially those with vadose zone contamination of heavy metals and radionuclides.

Based on preliminary laboratory-scale column experiments with Hanford sediments, the system may reach a pH of 11–13 depending on the amount of gas injection and will remain elevated for six months or more unless additional gases (e.g. air or CO_2) are injected after ammonia (Szecsody et al., 2010, 2012). For example, the pH was

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approximately 9.5 after three months in column experiments conducted previously (Szecsody et al., 2010). Therefore, it is imperative that we understand the changes to the aqueous and solid phases caused by mineral dissolution and precipitation with treatment. Some comparisons may be drawn with previous work characterizing vadose zone minerals impacted by highly basic (NaOH and NaNO₃ at pH > 13) tank wastes and laboratory column experiments investigating mineral dissolution following ammonia gas treatment. For example, silicates, feldspars, and micas are suggested to be the major dissolving phases in Hanford sediments under highly alkaline conditions based on previous work (Qafoku et al., 2003a; Szecsody et al., 2010, 2012; Wan et al., 2004).

Dissolution of minerals following gas treatment leads to an increase in aqueous Si⁴⁺ and Al³⁺ as well as small increases in Na⁺, K⁺, Fe^{2+/3+}, Cl⁻, F⁻ and SO₄²⁻ (Szecsody et al., 2012, 2013). Over time, the aqueous phase becomes saturated with respect to several different mineral phases. Some low solubility precipitates that are expected to form based on previous work with tank wastes and vadose zone sediments include cancrinite, sodalite, hydrobiotite, brucite, and goethite (Bickmore et al., 2001; Mashal et al., 2004; Qafoku et al., 2004; Qafoku and Icenhower, 2008; Zhao et al., 2004). Quartz was also demonstrated previously to dissolve and form the following secondary precipitates: brucite, calcite, cancrinite, and portlandite (Zheng et al., 2008). Mashal and team further reported nitrate-cancrinite and sodalite formation due to mineral dissolution and secondary product formation following reaction of Hanford sediments with basic simulated tank waste solutions (pH > 14) (Mashal et al., 2004).

Measurements of the Hanford site's 300 Area Process Ponds has reported extremely slow rates of U adsorption and desorption following interaction with highly basic aqueous waste which has been hypothesized to be due to the creation of unique microporous domains following exposure to pH extremes from waste streams (Zachara et al., 2007). Wan and team also reported that this net precipitation of solids may decrease porosity and permeability of sediments leading to a decrease in U desorption with time (Tokunaga et al., 2004). Szecsody et al. reported that as much as 93% less U mass may be leached with 5% ammonia gas injection versus untreated sediments after 100 pore volumes in column experiments with contaminated sediments from the Hanford 200 area (Szecsody et al., 2010). Similar work by Zhong et al. reported that 85% less U is mobilized for columns treated with 5 and 15% v/v ammonia gas (Zhong et al., 2015). Nonetheless, there is a lack of understanding of the dominant processes controlling the fate of U and the major precipitates forming under the transient conditions caused by ammonia gas injection. Further, for this technology to be effective for remediation of U, it is important to demonstrate enhanced removal of U from the aqueous phase for a variety of conditions with a decreased release of U in the long-term.

In order to understand the dominant processes, it is necessary to design controlled, laboratory-scale experiments with a well-defined U source term. Szecsody et al. have shown that U release from field-contaminated sediments decreased with ammonia gas treatment and that the hard-to-extract U phases (8 M HNO₃ extraction solution) increased following treatment (Szecsody et al., 2010). Research also indicates that U initially in the solid phase associated with carbonates and boltwoodites is not significantly altered with treatment (Szecsody et al., 2012). However, the effect of ammonia gas treatment on U initially in the aqueous phase is still unknown. Enhancement of U removal from the aqueous phase with ammonia gas injection must be confirmed under controlled conditions and associated solid phases must be identified to demonstrate the long-term success of this remediation process. The objective of this work is to quantify partitioning of U and mineral dissolution caused by injection of ammonia in simplified experiments with relevant minerals and sediments. Further, batch samples were prepared with a baseline (a neutral pH representative of natural conditions) and several base treatments including NaOH, NH₄OH, or NH₃ gas to allow for a comparison of ammonia gas injection with additional base

injection techniques and natural conditions at the Hanford site.

2. Methods and materials

2.1. Materials

The following minerals were chosen for experiments based on the mineralogy of the site as summarized in Table S1 in the *Supplementary Materials* with data from Serne et al. (2008), discussions with PNNL collaborators Drs. Jim Szecsody and Nik Qafoku, and previous work (Qafoku et al., 2004; Szecsody et al., 2010; Zheng et al., 2008; Zhong et al., 2015). However, these minerals are also applicable to potential sites worldwide as they represent some of the most common minerals on the Earth's surface. The minerals chosen for experiments include: quartz (Ottawa Sand Standard passed through 20–30 mesh, Fisher), kaolinite (Alfa Aesar), montmorillonite (SWy-2, Crook County, Wyoming, Clay Minerals Society), illite (Imt-2, Silver Hill, Montana, Clay Minerals Society), muscovite (Ward Scientific, < 2 mm size fraction), calcite (Alfa Aesar, 0.06–0.19" diameter) and Hanford bulk sediments. Each of these minerals are within the 11 most commonly identified minerals in the Hanford formation and were previously identified as potentially dissolving with base treatment (Szecsody et al., 2010, 2012). Hanford sediment samples were received from Dr. Jim Szecsody at PNNL from the ERDF pit in the 200 Area at a depth of 6.1 meters. Further characterization of this sediment has been published previously (Szecsody et al., 2013). BET surface area measurements were collected for each of the minerals investigated with the exception of calcite and are shown in Table 1. Minerals were washed based on methods outlined in Table 2 prior to batch experiments. However, Hanford sediments, muscovite, and calcite were used as received without a washing procedure.

Two solutions were formulated as background electrolytes for these experiments, (1) a simplified synthetic groundwater (SGW) as described in Table 3 and (2) NaCl solution of similar ionic strength for comparison. The simplified SGW is based on correspondence with Dr. Szecsody and previous measurements (Szecsody et al., 1998) to describe the average groundwater composition of the Hanford site. All salts used to prepare background electrolyte solutions were ACS purity or better.

2.2. Experimental methodology

2.2.1. Batch experimental protocols

Batch experiments were conducted in triplicate at pH 7.5 in the presence of minerals and either synthetic groundwater (Table 3) or NaCl at similar ionic strength (7.2 mM) to represent natural conditions in a subsurface in equilibrium with calcite. Experiments were also conducted at elevated pH to mimic those following base treatment with adjustment via 2.5 M NaClO₄ + 0.025 M NaOH, 2.5 M NH₄OH, or 5% NH₃/95% N₂ gas. All samples were initially prepared at pH 7.5 in the presence of 500 ppb U (2.1 × 10⁻⁶ M, Spex Certiprep, New Jersey) and background electrolytes as either SGW or NaCl. This initial U concentration is consistent with concentrations of U measured previously at 487 ppb in leaching experiments for contaminated sediments

Table 1
BET surface area for relevant minerals and Hanford sediment.

Mineral ID	m ² /g
Montmorillonite	23.8
Illite	19.1
Kaolinite	17.9
Hanford Sediment	17.4
Muscovite	0.096
Calcite	0.068
Quartz	0.046

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