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Assessment of calcium addition on the removal of U(VI) in the alkaline conditions created by NH_3 gas

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ABSTRACT

Remediation of uranium (U) contamination in the deep vadose zone (VZ) sediments abundant in calcite mineral is a challenging task considering the formation of highly stable and mobile uranyl complexes with carbonate and calcium in pore water composition. There is a concern that uranium contamination in the VZ can serve as a continued source for groundwater pollution, creating a risk to human health and the environment through the groundwater pathway. This requires in-situ remediation of the radionuclide-contaminated VZ to convert soluble U species to low solubility precipitates that are stable in the natural environment.

Injection of reactive gasses (e.g., NH_3) is a promising technology to decrease U mobility in the unsaturated zone without the addition of liquid amendments. The NH_3 injection creates alkaline conditions that can alter the sediment pore water composition due to a release of elements from minerals (via desorption and dissolution) that are present in the sediment. However, it is not known how VZ pore water constituents (Si, Al^{3+}, HCO_3^-, and Ca_2^+) would affect U(VI) removal/precipitation in alkaline conditions.

This study quantified the role of major pore water constituents typically present in the arid and semi-arid environments of the western regions of the U.S and identified solid uranium-bearing phases that could potentially precipitate from solutions approximating pore water compositions after pH manipulations via ammonia gas injections. Triplicate samples were prepared using six Si (5, 50 100, 150, 200, and 250 mM), six HCO_3^- (0, 3, 25, 50, 75, and 100 mM), and two Ca^{2+} (5 and 10 mM) concentrations. The concentration of aluminum and uranium was kept constant at 5 mM and 0.0084 mM, respectively, in all synthetic formulations tested. Results showed that the percentage of U(VI) removal was controlled by the Si/Al molar ratios and Ca^{2+} concentrations. Regardless of the bicarbonate concentration tested, the percentage of U(VI) removed increased as the Si/Al ratios were increased. However, higher Ca concentrations correlated with higher U(VI) removal, ranging between 96% and 99%, at low Si/Al ratios. The SEM images of dried precipitates displayed dense amorphous regions high in silica content, where EDS elemental analysis unveiled higher U atomic percentages. The formation of uranyl silicate and carbonate minerals was also predicted by the speciation modeling. XRD analysis revealed the presence of uranyl carbonate mineral phases (andersonite, grimselite); however, uranyl silicates predicted (Naboltwoodite) were not identified experimentally, possibly due to the amorphous nature of the silica solid phases observed in our experiments.

1. Introduction

The reprocessing of irradiated fuel to produce plutonium for atomic weapons has left about 202,703 kg of uranium (U) contamination in the subsurface at the U.S. Department of Energy's Hanford Site. This U is a potential source of groundwater contamination and a risk to human health and the environment through water uptake from contaminated wells or discharges to surface water. Uranium is a redox-sensitive element and, depending on the oxidation reduction conditions, mainly occurs in two states: hexavalent uranium [U(VI)] and tetravalent uranium [U(IV)]. These oxidation states determine its mobility in unsaturated and saturated natural systems. In oxic conditions, the chemistry of hexavalent uranium is governed by the dioxo cation (UO_2^{2+}) which is highly soluble and mobile and can readily form complexes with a variety of organic and inorganic ligands depending on the aqueous composition (e.g., proton H^+, anions, cations, and organic ligands). In the absence of the most relevant ligands in aqueous solutions, such as CO_3^{2-}, SiO_4^{4-}, and SO_4^{2-}, the speciation of U is dominated by

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the UO_2^{2+} cation until pH < 5. Between pH 6 and 10, the major dissolved uranyl species are uranyl-hydroxides [e.g., $UO_2(OH)_3^-$, $(UO_2)_2OH^{5+}$, and $(UO_2)_3(OH)_7^-$)]. In carbonate-bearing systems, uranyl carbonate complexes [e.g., $UO_2CO_3(OH)_3^-$, UO_2CO_3(aq), $UO_2(CO_3)_2^{2-}$, and $UO_2(CO_3)_3^{4-}$] are the predominant aqueous species and $UO_2(CO_3)_3^{4-}$ dominates the speciation at pH > 9 (Elless and Lee, 1998). In Ca- and carbonate-rich subsurface environments, typical for western U.S. arid and semi-arid regions including the Hanford Site, U (VI) forms highly soluble and stable calcium-uranyl-carbonate complexes [$Ca_2UO_2(CO_3)_3°$(aq), $CaUO_2(CO_3)_3^{2-}$] (Bernhard et al., 1996, 2001; Kalmykov and Choppin, 2000). This can explain the high mobility of U in the Hanford vadose zone (VZ) sediments given its low partition coefficient (K_d) value ranging from 0.2 to 4 mL/g (Cantrell et al., 2003; Zachara et al., 2007). In VZ sediments with abundant calcite and in the presence of complexing anions such as carbonates (CO_3^{2-}) and hydrous silicates ($H_3SiO_4^-$), uranium tends to form uranyl carbonate and uranyl silicate minerals. Uranophane and boltwoodite are the most common uranyl silicate solid phases found in the VZ environment at Hanford (Szecsody et al., 2012; Um et al., 2009; Zachara et al., 2007). In addition, the VZ sediments contain uranyl carbonate solids, liebigite and rutherfordine, that were found at medium to high concentrations (Szecsody et al., 2012). Radionuclides contaminated the deep (80–100 m) VZ at the Hanford Site 200 Area, requiring in-situ stabilization to convert aqueous mobile uranyl carbonates to lower solubility precipitates that are stable in the natural environment. Wellman et al. Wellman et al. (2012) investigated U(VI) stabilization through injections of a sodium tripolyphosphate amendment into the saturated sediments which led to formation of sodium uranyl phosphate mineral phases. However, the addition of liquid amendments into the VZ can cause undesirable downward migration of U and co-contaminants, instigating contamination of the underlying aquifer. Injection of reactive gases such as NH_3 to create alkaline conditions in the VZ is an innovative technology aiming to decrease uranium mobility in the unsaturated zone contaminated with radionuclides without the addition of liquid amendments. The injection of a highly soluble ammonia gas to the VZ prompts the formation of NH_4OH following a subsequent increase in pH from 8.0 to about 11.02 for 0.1% NH_3 (~0.063 mol/L NH_3 (aq)) and 11.87 (~3.1 mol/L NH_3 (aq)) for 5% NH_3 (Szecsody et al., 2012; Zhong et al., 2015). This manipulation, triggered by the alkaline pH, can significantly alter the sediment pore water composition and greatly enhance the solubility rates of most minerals such as quartz, calcite, feldspar, and iron oxides that are abundantly present in the sediments. Chou and Wollast (1984) suggested that the rate of mineral dissolution may increase by two to three orders of magnitude with an increase in pH from 8 to 12 at 23 °C. The dissolution of minerals at high pH conditions can induce the release of silica, carbonate, aluminum, calcium and the alkali metals sodium and potassium to the pore water (Zhong et al., 2015). The subsequent decrease in pH to natural conditions would lead to precipitation of U-phases such as Na- or NH_3-boltwoodite or re-precipitation of various silica and aluminosilicate solid phases and calcium carbonates that may incorporate uranium in a process called co-precipitation (Szecsody et al., 2010b; Zhong et al., 2015). Previous laboratory evaluations showed a decrease in U mobility after ammonia gas injection in the low water content sediments (Szecsody et al., 2010a; Zhong et al., 2015). Another possible mechanism contributing to the decrease of uranium mobility after ammonia gas applications is the coating of U-bearing phases by a low solubility non-uranium precipitate such as cancrinite and sodalite (Zhao et al., 2004) or phyllosicates, carbonate and sodalite, as was found in water-saturated systems of uranium-contaminated sites (Qafoku and Icenhower, 2008). The objective of this research was to examine the effect of calcium ions on the removal/precipitation of U(VI) from synthetic pore water (SPW) solutions composed of variable molar ratios of silicon to aluminum in the presence of bicarbonate. The removal of U (VI) from the synthetic solutions treated with NH_3 gas was quantified for six molar ratios of silica to aluminum and prepared in a wide range of bicarbonate and two calcium concentrations. Manipulations with pore water constituencies can simulate the conditions occurring in the subsurface typical for arid and semi-arid environments throughout the western United States and explain changes in the removal of elements through co-precipitation with silica and aluminosilicates. Parallel studies have focused on the detailed characterization of the uranium-bearing precipitates created after ammonia gas injection.

2. Material and methods

Batch experiments were performed to evaluate the effect of Ca^{2+} ions on the removal of uranium from SPW solutions amended with variable Si/Al molar ratio concentrations following NH_3 gas injections. Detailed physical mineralogical and geochemical analysis of Hanford Site VZ soil and porewater compositions that provided concentrations of major cations, anions, alkalinity and pH was reported in a previous study (Serne et al., 2008). For the purpose of this study, the complicated pore water composition was simplified to contain five major components in the SPW: silica, aluminum, uranium, calcium, and bicarbonate with the counter ions, Na^+, K^+, NO_3^-, and Cl^-. The range of Si concentrations was chosen based on previous studies by limiting Si concentrations to a maximum of 250 mM (7.0 g L^{-1}) (Katsenovich et al., 2016; Szecsody et al., 2010b, 2012; Zhong et al., 2015). The aluminum concentration was kept constant at 5 mM, which is slightly higher than was observed in the batch experiments conducted by Zhong et al. (2015), and both Si and Al concentrations were orders of magnitude greater than uranium. CO_3^- and HCO_3^- are the major anions in pore water compositions due to the abundance of calcite in Hanford sediments (Qafoku and Icenhower, 2008; Serne et al., 2008). To cover the concentration range of elements released to the solution mixture due to the alkaline dissolution of soil minerals, SPW compositions were formulated with six Si (5, 50 100, 150, 200, and 250 mM), six HCO_3^- (0, 3, 25, 50, 75, and 100 mM), and two Ca^{2+} (5 and 10 mM) concentrations. The concentration of U was kept constant at 0.084 mM (2 mg/L) in all synthetic formulations tested. The experimental results provided a complete range of data for U(VI) removal in the presence of 5 mM of Al across all Si and HCO_3^- concentrations tested in addition to Ca ions commonly present in the pore water composition. Details on the SPW compositions and chemicals used for the formulations are provided in the supporting information (Tables 1S and 2S).

2.1. Sample preparation procedures

Stock solutions of Al (50 mM), Si (420 mM), HCO_3^- (400 mM), and Ca (500 mM) were prepared in deionized water (DIW) by dissolving Al $(NO_3)_3·9H_2O$, $Na_2SiO_3·9H_20$, $KHCO_3$ and $CaCl_2·6H_2O$ salts individually in 50-mL vials. The 100 µg/mL uranyl stock solution was prepared fresh in DIW from the 1000 µg/mL uranyl nitrate stock (SPEX CertiPrep™). Sample preparation procedures at different molar ratios of Si/Al followed the same methods as described in Katsenovich et al. (2016) by mixing the appropriate volume of stock solutions and injecting NH_3 gas (0.1% NH_3 in 99.9% N_2) through 20 µm pores of a metal gas sparger (Mott Corporation) until the pH of the solutions reached a value of ~11 (0.063 mol/L (aq)). Synthetic pore water samples of 5 mL prepared in triplicate were extracted from NH_3-laden aluminum-silicate-carbonate test solutions into 15-mL polyethylene tubes and mixing rapidly with an aliquot from the $CaCl_2$ stock (50 and 100 µL) depending on the targeted Ca concentration (5 mM or 10 mM) in the mixture. The resulting mixture was then spiked with uranium to yield an overall concentration within a solution matrix of 2 mg/L. The final pH of the prepared samples was in the range of 10.9–11.1 (Orion Versa Star pH Benchtop Meter and Orion Double Junction pH Electrode). Control samples were prepared in DIW amended with U(VI) at the same concentration of 2 mg/L to test for U(VI) losses due to sorption to tube walls and caps (Fig. 1S). All experimental and control tubes were vortexed and kept in an incubator/shaker at 100 rpm and 25 °C. After two days, the tubes were