



Groundwater uranium stabilization by a metastable hydroxyapatite



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ABSTRACT

In-situ remediation of groundwater uranium (U) contamination via the precipitation of uranyl phosphate (U-P) minerals is a promising, passive remedial approach for aquifers impacted by mobile hexavalent U (U(VI)). We demonstrate the efficacy of U stabilization in a contaminated aquifer using a metastable form of hydroxyapatite (mHAP) derived from fish bone. This material was reacted with depleted uranium (DU) contaminated groundwater both under ambient flow in-situ, and under pumped flow ex-situ. The U immobilized under both ambient and accelerated flow conditions was strongly bound in solid phases, with greater than 99% U removal from groundwater. Stable U uptake in excess of 50 g U/kg solid was achieved due to the precipitation of the crystalline U-P mineral chernikovite. Prior field trials yielded U immobilization by sorption alone [Fuller et al., 2003, *Env. Sci. Technol.* **37**, 4642.], likely due to higher pH and alkalinity groundwater conditions, which increase the solubility of U-P phases via aqueous complexation. Our study is the first to demonstrate the feasibility of U immobilization by U-P precipitation from natural groundwater. These findings suggest that in groundwaters contaminated by U(VI) with circumneutral pH and low carbonate alkalinity, fish bone-derived hydroxyapatite is an effective material for in-situ U remediation that can be readily implemented, requiring no redox manipulation.

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1. Introduction

In-situ passive remediation of oxidized uranium (U(VI)) has proven difficult due to its relatively high solubility, especially in the presence of complexing ligands (Grenthe et al., 1992; Murphy and Shock, 1999; Simon et al., 2003; Wan et al., 2005; Curtis et al., 2006; Davis et al., 2006). Uranium contamination in groundwater can be remediated through the reduction of U(VI) to U(IV) using microbial amendments (Lovley et al., 1991, 1993; Uhrie et al., 1996; Abdelouas et al., 1998) or zero valent iron (ZVI; Simon et al., 2003), but bio-reduced U is susceptible to reoxidation and remobilization (Wan et al., 2005). Further, the lifetime of ZVI PRBs is limited due to surface oxidation and subsequent occlusion (Henderson and Demond, 2007). The increasing emphasis being placed on in-situ remedies by the U.S. Environmental Protection Agency (USEPA, 2007) has motivated the development of in-situ remedial alternatives for U that can be considered permanent. The phosphate-

induced immobilization of U and certain other contaminant metals and radionuclides has been suggested as a remedial alternative that does not rely on local alterations to the redox environment of the groundwater (Krestou et al., 2004). Uranium is known to form a host of sparingly soluble uranyl (UO₂²⁺) phosphate (U-P) mineral phases within the meta-autunite group (M(UO₂)₂(PO₄)₂·nH₂O), and studies of natural analog systems have demonstrated that uranium can be sequestered as meta-autunite over long (>10,000 yr) timescales (e.g., Jerden and Sinha, 2003).

Both bench and pilot field-scale studies have been performed to investigate the sequestration of metals including Pb, Cd, Zn, Al, Cu, and U and other actinide elements by promoting the precipitation of low-solubility metal-phosphate phases (Krestou et al., 2004; Bostick, 2003; Fuller et al., 2002, 2003; Wellman et al., 2008a; Simon et al., 2008; Mehta et al., 2014). Tests of in-situ phosphate-induced U immobilization have been implemented using (1) polyphosphate-rich fluids (Vermeul et al., 2007; Wellman et al., 2007, 2008a) and (2) solid forms of hydroxyapatite (HAP; Fuller et al., 2003; Simon et al., 2008) or related minerals. Overlapping injections of polyphosphate-rich and calcium-rich fluids should theoretically promote the precipitation of hydroxyapatite in-situ,

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with U-P immobilized as a coprecipitate (Vermeul et al., 2007). Bench scale treatability tests using this method successfully immobilized U (Wellman et al., 2008a), but these results were not replicated at the field-scale due to permeability loss, which prevented successful injection of both the Ca- and polyphosphate-rich amendments, and due to high groundwater flow velocities, which limited mixing of the amendment plumes (Vermeul et al., 2009).

The efficacy of U retention by several different solid Ca phosphates has been tested, including bone charcoal (Fuller et al., 2003), crystalline HAP (Fuller et al., 2002, 2003; Simon et al., 2003; Krestou et al., 2004; Wellman et al., 2008a; Simon et al., 2008), crystalline fluorapatite (FAP; Ohnuki et al., 2004), and the metastable fish bone-derived hydroxyapatite known as Apatite II™ produced by Phosphate Induced Metal Stabilization (PIMS) NW, Inc. of Richland, WA (Bostick et al., 2000; Bostick, 2003; Conca and Wright, 2006; Raicevic et al., 2006). In several comparative studies, uptake of uranium by bone meal and bone charcoal was over an order of magnitude greater than by phosphate rock (Fuller et al., 2003), and uranium uptake by Apatite II™ was around an order of magnitude greater than by bone charcoal (Bostick et al., 2000). Although many solid Ca phosphates such as OCP phases bear significant structural similarity to HAP (cf. Wang and Nancollas, 2008), fish bone is thought to primarily consist of poorly crystalline HAP (Rey et al., 2009). Due to the higher solubility of Apatite II™ compared with pure crystalline hydroxyapatite (Oliva et al., 2012), we refer to this material as metastable hydroxyapatite (mHAP). The enhanced reactivity of mHAP has been attributed to its amorphous to nano-crystalline structure and extensive carbonate substitution for OH⁻ and/or PO₄³⁻ in the HAP lattice (Bostick, 2003; Conca and Wright, 2006), which is known to increase the solubility and reactivity of apatite (Onuma et al., 1995; Wang and Nancollas, 2008).

There are three previously-identified processes responsible for the immobilization of U by Ca phosphate-bearing solids: (1) dissolution of HAP and subsequent precipitation of U(VI)-phosphates such as chernikovite (also known as H-autunite or uranyl hydrogen phosphate) or autunite (Fuller et al., 2002, 2003; Fanizza et al., 2013; Mehta et al., 2014, 2016), (2) surface complexation (Cheng et al., 2004; Simon et al., 2008; Mehta et al., 2015), and (3) ion exchange (Simon et al., 2008; Mehta et al., 2015). These reactions can occur concomitantly, and will vary in extent depending on the groundwater geochemistry and the concentration of sorbed and aqueous U. Below a threshold aqueous U concentration, the uranyl cation forms ternary inner-sphere complexes at the surface of HAP, and above this threshold, chernikovite and later autunite have also been shown to form (Fuller et al., 2002, 2003). In the past, U-P phases have been observed to form in laboratory batch studies involving apatite but only surface U complexation by apatite was observed in materials recovered from the field (Fuller et al., 2003).

In-situ stabilization of metal contaminants using reactive materials is only viable if the metal-sequestering reactions are fast relative to the contaminant flux and the product is stable. In this study, we assessed the efficacy of mHAP for U removal from groundwater at a site where DU wastes discarded into an unlined basin resulted in the formation of a groundwater U plume in an unconfined alluvial aquifer. This plume has migrated approximately 450 feet down gradient of the source area. Tests were performed both in- and ex-situ, under a wide range of U loadings and groundwater residence times. The performance of mHAP was analyzed based on the extent and mechanisms of U immobilization determined from field-based measurements and solid material characterization. Geochemical calculations were used to investigate the processes controlling U stabilization during reaction with the media. The impact of variable groundwater geochemistry on

the efficacy of mHAP for in-situ U immobilization is assessed in the context of meta-autunite stability.

2. Materials and methods

In-field tests employed two configurations to evaluate the reactivity of mHAP under (1) passive and (2) accelerated groundwater flow conditions (Table 1) in a permeable stratified drift aquifer that consists of relatively homogeneous sandy sediment with isolated silty strata underlain by gneissic bedrock. Passive tests were deployed in wells HBPZ-2R and MW-S16, to investigate U uptake under groundwater flux rates of approximately 1.0 and 0.05 L per day respectively. Accelerated flow tests were also performed at two wells: MW-S24 and MW-8A. In the passive tests, the mHAP material was packed into permeable canisters and lowered into screened monitoring wells, simulating reaction with the U-impacted overburden groundwater under ambient flow conditions. In the accelerated flow tests, groundwater was pumped through ex-situ columns (illustrated in Supporting Information, Fig. S-1) housed in wellhead sheds on-site, exposing the media to a much larger mass flux of uranium. Additional details of the field experimental setup and solid and aqueous sampling are provided in the Supporting Information (section S-1). The mHAP used in both tests was ground to medium to coarse sand-sized particles by the supplier, PIMS™. The resulting particle size distribution is roughly similar to the U-impacted aquifer sediments.

Influent and effluent samples were collected regularly from the accelerated flow columns to monitor groundwater geochemistry and U uptake by mHAP, while groundwater samples were collected only once (well MW-S16) or twice (well HBPZ-2R) for the passive tests. Samples were collected from the accelerated flow test by diverting flow through a sampling port located just upstream and downstream of the mHAP columns for groundwater and column effluent, respectively (Supporting Information, Fig. S-1). Groundwater samples from the passive well tests were collected by first purging the well until at least three consecutive measurements of groundwater geochemical parameters taken at 5 min intervals were within acceptable limits of variation as defined by the USEPA low-flow sampling protocol (USEPA, 2010). Geochemical parameters including temperature (T), pH, specific conductivity (SC), dissolved oxygen (DO), and oxidation-reduction potential (ORP) were measured using a YSI 650XL™ multi-parameter probe. Two types of water samples were obtained for elemental analysis. Dissolved samples were field-filtered using in-line 0.45 μm filters prior to acidification, while total samples were directly acidified (for metals) and then filtered prior to analysis. Each sample underwent at least one of several analyses performed by GEL Laboratories in Charleston, SC: total and dissolved metals and cations (U, Fe, Ca, K, and Na) by inductively coupled plasma-mass spectrometry (ICP-MS; EPA Method 6020A), total phosphorous by colorimetry (EPA Method 365.4 with a 0.01 mg/L detection limit; Gales and Booth, 1974), and total organic carbon (TOC) and total inorganic carbon (TIC) using a carbonaceous analyzer (EPA Method 9060A).

Following extended deployment times (Table 1), the media columns and canisters were frozen and cut open to obtain reacted solid mHAP samples. Sub-samples of the accelerated columns were selected by visually identifying zones of varying properties including color and texture (see Supporting Information, Fig. S-2 for an example). Solids recovered from the passive canisters were divided into 10 equal-sized sub-samples, because there were no visible indicators of alteration that could be used to differentiate zones. A sub-set of samples was selected from the accelerated and passive canisters for solids characterization. In the accelerated columns, only sub-samples nearest the influent ends were used for sequential extractions, because these were exposed to the highest

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