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Groundwater uranium stabilization by a metastable hydroxyapatite

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Highlights

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Widespread groundwater U contamination warrants the development of passive in-situ remedies.

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Fish bone derived hydroxyapatite is found to effectively immobilize aqueous U in an aquifer.

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Surface complexation and uranyl phosphate mineralization both contribute to stable U uptake.

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High carbonate alkalinity can reduce efficacy by enhancing aqueous U complexation.

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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Keywords

Uranium

Hydroxyapatite

Groundwater remediation

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](#), [Lovley et al., 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 (UO_2^{2+}) phosphate (U-P) mineral phases within the meta-autunite group ($\text{M}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$), 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](#), [Fuller et al., 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](#), [Wellman et al., 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, 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](#), [Fuller et al., 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](#), [Fuller et al., 2003](#), [Fanizza et al., 2013](#), [Mehta et al., 2014](#), [Mehta et al., 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](#), [Fuller et al., 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.

Table 1. Summary of field-deployed mHAP columns and canisters. Solid mHAP used in this study has a [bulk density](#) of 0.45 kg/dm³.

Well ID	[U] _{g.w.} , µg/L	ID ^a	Volume, L	Deployment time, days	Cumulative flow, L	Residence time, hours	Total U loading, g ^b
MW-S24	2740	A-1a	0.25	25	707	0.21	1.91
		A-1b	0.25	49	1125	0.26	3.04
		A-1c	8.3	96	8086	2.4	21.8
MW-8A	336	A-2a	0.25	30	595	0.30	0.2
		A-2b	8.3	77	6634	2.3	2.21
HBPZ-2R	2103	P-1	0.5	97	–	–	–
MW-S16	128	P-2	0.5	97	–	–	–

a

“A” denotes accelerated flow columns and “P” denotes passive canisters deployed down-borehole. Influent and effluent chemistry for a sub-set of the “A” columns is provided in Supporting Information [Tables S-2 and S-3](#).

b

Total U loading on the columns was calculated by integrating measured U uptake concentrations over cumulative flow through the columns.

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 aqueous U concentrations. Multiple sub-sections of each column and canister were analyzed using XRD and bulk digestion. Selected sub-samples were homogenized, dried under air, and shipped to Southern Methodist University (SMU) in radiation-safe packing material for solid phase analysis.

2.1. Solid phase analytical methods

A sub-set of solid samples were characterized using a variety of [analytical methods](#) including X-ray diffraction (XRD) to determine bulk [mineralogy](#); [scanning electron microscopy](#) with energy-dispersive [X-Ray spectroscopy](#) (SEM-EDS) to determine solid texture and spatial associations of Ca, P and U; a sequential extraction procedure (SEP) to evaluate the stability of immobilized U; and bulk digestion to quantify total solid-associated U. Not all reacted mHAP media samples underwent every solid phase analysis, so the analytical results given below list the ID (given in [Table 1](#)) of each specific canister or column analyzed.

Powder XRD data were obtained using a Rigaku Ultima III from 2 to 70° using a theta/2-theta (2θ) method with a scan interval of 0.01° at 1° per minute. Results were analyzed

via peak matching using JADE software (MDI; Material Data Incorporated), and secondary U-P phases were identified using reflection data obtained from the International Centre for Diffraction Data (ICDD) database. Only phases making up greater than ~1 weight (wt) % of the total sample are detectable by XRD. Solid phase imaging and semi-quantitative elemental mapping were performed on several samples using a Leo-Zeiss 1450VPSE variable pressure [electron microscope](#) equipped with an EDAX Genesis 4000 XMS SYSTEM 60 energy-dispersive [spectrometer](#).

A three-step sequential extraction procedure (SEP) was adapted from [Tessier et al. \(1979\)](#). Extractions were performed on 0.5 g of solids from a sub-set of the field-deployed columns and canisters using solutions prepared with doubly deionized (DDI) water. Each extraction stage and target phase is listed below in order of least to most chemically aggressive.

1

Weakly Sorbed/Exchangeable. The sample was extracted at room temperature for 1 h with 20 mL of sodium [acetate](#) solution (1 M NaOAc solution at pH 8.2), continuously rotated.

2

Strongly Sorbed/Weak Acid Extractable. The residue from stage 1 was extracted at room temperature with 20 mL of 1 M NaOAc solution adjusted to pH 5.0 with [acetic acid](#) (HOAc), continuously rotated for 8 h.

3

Recalcitrant. The residue from stage 2 was digested using reverse *aqua regia* of 3 parts concentrated HNO₃ to 1 part concentrated HCl. The acid was boiled off at 90 °C and more acid added until digestion was complete. The remaining salts were then dissolved in 5% HNO₃ for analysis.

Following the first two stages, samples were centrifuged at 3900 rpm for 10 min. After extracting the supernatant with a micropipette, all samples were filtered through 0.45 µm PTFE filters. The first 2 mL through the filter was discarded, and the remainder was collected for analysis. The solid residues of stages 1 and 2 were rinsed with 8 mL of DDI water and centrifuged between stages. Aqueous supernatants were acidified to pH 1 using 5% HNO₃ immediately following filtration. Extractions were run in duplicate when sufficient material was available. Total digestions of 0.1 g of material were performed on several samples in reverse *aqua regia* (3 parts concentrated HNO₃ to 1 part concentrated HCl) to obtain bulk elemental compositions and to compare U loading with SEP results. The acid was boiled off at 90 °C and more acid added until digestion was complete. The remaining salts were then dissolved in 5% HNO₃ for analysis.

Elemental concentrations of Ca, P, and U from sequential extractions and total digestions were measured using a Thermo X Series 2 inductively coupled plasma-mass spectrometer (ICP-MS) in collision cell mode with [kinetic energy](#) dispersion. Calibration standards generally ranged from 0.05 µg/L to 200 µg/L and were prepared in 5% HNO₃ from certified single-element standards. A 5% HNO₃ blank was also analyzed every 10 samples for [quality control](#). [Trace metal](#) grade HNO₃ (Fisher Scientific, Pittsburgh, PA) was used to prepare the 5% HNO₃ solution for dilutions, calibration standard preparation, and blanks. Elemental detection limits were determined by 3 standard deviations of the blank concentration for a given element, which amounts to 0.2 µg/L for U, 48 µg/L for Ca and 19 µg/L for P. Total uncertainties on the extracted concentrations of Ca, P and U are approximately 10%. The concentration of U in mHAP blanks were estimated to allow subsequent calculation of sequestered U. These blank values were calculated as the weighted average of the total U extracted from the raw material by SEP and by total digestion.

2.2. Geochemical calculations

Calculations were performed to assess the cause of changes in groundwater composition upon interaction with mHAP and to evaluate the total aqueous U concentration in equilibrium with U-P phases. Groundwater compositions and mineral solubilities were modeled using Geochemist's Workbench® and PhreeqC, respectively, using stability constants from [Gorman-Lewis et al. \(2009\)](#) based on updated values for aqueous [complexation](#) reactions ([Martell, 2001](#), [Guillaumont et al., 2003](#)). The solubilities of solid uranyl [orthophosphate](#), autunite, and chernikovite were also obtained from [Gorman-Lewis et al. \(2009\)](#) and are summarized in the Supporting Information, [Tables S–1](#). The solubility product of mHAP expressed as Ca₅(PO₄)₃(OH) was also added to the [thermodynamic](#) database using a value determined by [Oliva et al. \(2012\)](#). For the dissolution reaction,

[Oliva et al. \(2012\)](#) reported a logK_{sp} of -50.8 ± 0.82 at 25 °C.

Forward geochemical modeling was performed to determine the expected major element chemistry of groundwater following equilibration with mHAP. Modeling in Geochemist's Workbench® was performed using the React module, which completes an initial speciation step to estimate the composition of the influent groundwater followed by a second step to simulate equilibration of the influent water with mHAP, without allowing secondary phases to form. The geochemical composition of the solution was input as the average value of the MW-S24 influent solution (Supporting

Information, [Tables S–2](#)). A second set of geochemical speciation calculations was performed in PhreeqC to evaluate the impact of uranyl phosphate mineralization on total U solubility. The total aqueous U concentrations in equilibrium with mHAP and the uranyl phosphate phases autunite, chernikovite, and uranyl orthophosphate were calculated to determine the phase(s) most likely to limit U solubility.

3. Results and discussion

3.1. In-situ uranium stabilization under passive groundwater flow

In-situ uptake of U on mHAP was measured over a 97-day period in two existing well bores, HBPZ-2R and MW-S16, with high (2103 µg U/L) and low (128 µg U/L) U concentrations respectively ([Table 1](#)). Passive [groundwater flow](#) through canisters deployed down the well [borehole](#) led to the accumulation of U on the mHAP media. Total [uranium](#) loadings on the media were determined by summing the uranium concentrations of various solid fractions measured in [sequential extractions](#) for both canisters and also by total [acid digestion](#) of multiple sub-samples of the canister deployed in well HBPZ-2R ([Table 2](#), [Table 3](#)). The average total U loading on the mHAP deployed in the high U well (HBPZ-2R) was 61 ± 9 mg/kg (2 s.e., n = 6) over 97 days. Subtracting the average U concentration in the blank of 9.6 mg/kg, which is a weighed average of the total U concentrations of mHAP given in [Table 2](#) (0.5 g samples) and [Table 3](#) (0.1 g samples), the total accumulated U was approximately 51 mg/kg. The U groundwater concentration at MW-S16 is considerably lower, and the blank-subtracted U accumulation on mHAP in well MW-S16 was 9 mg/kg ([Table 2](#)). Given the canister deployment down-wellbore, it was not possible to quantify the total groundwater flow through these canisters or the fraction of U immobilized. Instead, we focus on determining the stability of U sequestered in-situ based on sequential extractions.

Table 2. Results of [sequential extractions](#) performed on raw and reacted mHAP. Replicates indicate measurements on separate aliquots of each sub-sample indicated.

Well/Column ID ^a	Sub-sample ^b	Replicate	Stage 1 ^c		Stage 2 ^d		Stage 3 ^e		Total U, mg/kg
			U, mg/kg	% of total U	U, mg/kg	% of total U	U, mg/kg	% of total U	
mHAP	–	1	0.01	0.08	0.00	0.07	6.86	99.85	6.87
		2	0.00	0.00	0.00	0.01	9.19	99.99	9.19
HPBZ-2R/P-1	–	1	0.27	0.55	0.63	1.30	47.76	98.16	48.65
		2	0.04	0.07	0.67	1.24	53.11	98.69	53.81
MW-S16/P-2	–	1	0.00	0.00	0.07	0.36	18.50	99.64	18.57

Well/Column ID ^a	Sub-sample ^b	Replicate	Stage 1 ^c		Stage 2 ^d		Stage 3 ^e		Total U, mg/kg
			U, mg/kg	% of total U	U, mg/kg	% of total U	U, mg/kg	% of total U	
MW-S24/A-1a	0–1.3 cm	1	1.74	0.00	27.53	0.07	57,390	99.78	57,520
		2	1.92	0.00	99.52	0.24	39,250	99.93	39,280
MW-S24/A-1b	0–2.5 cm	1	2.27	0.00	125.68	0.22	41,360	99.76	41,460
MW-S24/A-1c	0–2.5 cm	1	1.03	0.00	22.70	0.06	37,640	99.94	37,660
		2	5.21	0.01	21.91	0.05	41,190	99.93	41,220
MW-8A/A-2b	0–2.5 cm	1	0.64	0.01	6.59	0.14	4822	99.85	4829
		2	0.72	0.01	12.09	0.14	8766	99.85	8778

a

“A” denotes accelerated flow columns and “P” denotes passive canisters deployed down-borehole.

b

Sub-sample indicates column sample region as distance from the groundwater inlet.

c

Weakly sorbed/exchangeable ion fraction extracted using NaOAc (pH 8.2).

d

Strongly sorbed/weak acid soluble fraction extracted using NaOAc with HOAc (pH 5).

e

Recalcitrant fraction extracted using reverse *aqua regia* on remaining material.

Table 3. Results of total solid digestions in reverse *aqua regia* on at least two separate replicate aliquots for validation of total [sequential extraction](#) results.

Media and Replicate		mg P/kg solid	mg Ca/kg solid	mg U/kg solid
mHAP	1	63,570	193,500	31.3
	2	83,700	213,900	3.1
HPBZ-2R P-1 ^a	1	76,900	212,100	78.3
	2	75,620	209,700	59.4
	3	80,320	254,000	56.5
	4	82,120	227,500	70.7
MW-S24 A-1c (0–2.5 cm)	1	84,680	230,100	53,030
	2	98,840	269,800	38,700

a

Replicates numbered 1–4 indicate measurements on separate sub-samples of the canister. Sequential extraction results indicate that the U sequestered in-situ was strongly bound to the mHAP. The U associated with the ion exchangeable and weak acid soluble/strongly sorbed fractions (SEP stages 1–2) did not exceed 0.27 and 0.67 mg/kg, respectively ([Table 2](#)). The vast majority of U was associated with the recalcitrant fraction (SEP stage 3), with over 98% of U bound in the recalcitrant fraction for HPBZ-2R and 99.6% for MW-S16. Results of XRD on samples exposed to passive groundwater flow in both MW-S16 and HBPZ-2R were indistinguishable from the original mHAP (Supporting Information, [Fig. S-3](#)). However, the maximum observed U loading of 78 mg/kg amounts to less than 0.1% uranyl phosphate by weight, which is well below the XRD detection threshold. We conclude that the solid-associated U is strongly bound as surface complexes, as secondary U-P mineral phases, or as a combination of the two. The potential for uranyl [phosphate mineral](#) formation driven by groundwater reaction with mHAP was assessed instead using ex-situ accelerated flow columns as proxies for extended material deployment under a passive groundwater gradient.

3.2. Ex-situ uranium stabilization under accelerated groundwater flow

Site groundwater was pumped through mHAP-packed columns at [wellheads](#) MW-S24 (2740 µg U/L) and MW-8A (336 µg U/L) for up to 96 days ([Table 1](#)). The efficacy of U stabilization by mHAP deployed ex-situ was calculated as the percent difference in total uranium concentration between the column influent (*i.e.*, raw groundwater) and the column [effluent](#) ([Fig. 1](#); Supporting Information, [Tables S–2](#)). Average U removal was 99.6% at well MW-S24 and 98.8% at well MW-8A. Average total U concentrations in the effluent of MW-S24 and MW-8A were 8.4 ± 10.8 and 5.2 ± 3.6 µg/L (2 s.e.), compared with average influent concentrations of 2740 ± 529 and 336 ± 89 µg/L (2 s.e.) respectively. The maximum effluent total U concentration from MW-S24 was 34 µg/L, and this was the only effluent sample with a U concentration exceeding the USEPA maximum contaminant limit (MCL) for U of 30 µg/L. The minimum concentration of U in the effluent of MW-S24 was 0.85 µg/L, and this concentration was measured on the final day of the experiment (Supporting Information, [Tables S–2](#)). The effluent U concentrations did not change consistently with time, indicating the columns were not approaching U breakthrough. On average, over 99% of groundwater U introduced to the columns was removed by the solids ([Fig. 1](#)), and U breakthrough was not observed in the columns after greater than 1700 L of groundwater flow per kg mHAP

(~930 pore volumes) in MW-8A (A-2b) and 2100 L of flow per kg mHAP (~1100 pore volumes) in MW-S24 (A-1c).

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Fig. 1. Measured total [effluent](#) concentrations of (a) Ca and (b) P, and measured total influent and effluent U from accelerated mHAP columns A2-b and A1-c deployed at the (c) MW-8A and (d) MW-S24 [wellheads](#) respectively. Influent groundwater Ca and P concentrations are indicated by wide dashed lines, and calculated Ca and P concentrations upon equilibration with mHAP are drawn as solid lines. Column effluent major element concentrations indicate that groundwater rapidly equilibrates with the mHAP during flow through the column. Effluent total U concentrations were well below the U MCL for the majority of the [field test](#), with the exception of one slight exceedance recorded early in the test.

Changes in the influent and effluent compositions reported in [Tables S-2 and S-3](#) (Supporting Information) are used to evaluate the major geochemical processes occurring during the reaction of site groundwater with mHAP. The most significant change in the major element concentrations in groundwater upon reaction with mHAP is

a substantial increase in total and dissolved aqueous calcium and phosphorus. Total phosphorus concentrations in site groundwater are relatively low, typically less than 0.1 mg/L, while the average of groundwater calcium concentrations is 20 ± 1.4 mg/L, 2 s.e (Supporting Information, [Tables S–2](#)). The higher effluent concentrations of both P (5.4 ± 0.9 mg/L, 2 s.e.) and Ca (35.8 ± 4.2 mg/L, 2 s.e.) indicate dissolution of the column material during equilibration of groundwater that is initially undersaturated with respect to mHAP. Effluent Na and K concentrations were not consistently different from the influent concentrations. The average pH of groundwater increased from 6.3 to 6.7 in the MW-S24 system and from 6.2 to 6.8 in the MW-8A system, possibly due to buffering by [orthophosphate](#) or by [dissolved inorganic carbon](#). The increase in DOC and pH and decrease in DO and ORP suggest that [microbial activity](#) may be occurring in the columns, causing a shift to more reducing [redox conditions](#).

Column-averaged U loadings were calculated based on the total flow through the column and average influent and effluent U concentrations ([Table 1](#)). The column with the greatest accumulation of U was the MW-S24 accelerated column A-1c, with an estimated total U mass exceeding 21 g accumulated over 96 days of column deployment. Sequestered U was not homogeneously distributed throughout the column; the majority of U accumulated within the first 3 cm of mHAP near the column inlet. Total digestions on aliquots collected near the influent end of column A-1c showed substantial U loading ranging from 38.7 to 53.0 g U/kg solid. Thus we conclude that reacted mHAP solids can sequester greater than 5 wt % U and that the kinetics of uranium uptake are fast enough that no breakthrough was observed even under a high uranium flux for over 90 days.

Sequential extractions were performed on the accelerated flow column solids to assess the long-term stability of the sequestered U. The ion exchangeable (SEP stage 1) U does not exceed 0.01% of the total sequestered U for all columns. The strongly sorbed and weak acid soluble (SEP stage 2) fraction contains less than 0.25% of total U in all samples, which totals up to 126 mg U/kg for samples collected near the column inlets. Over 99.7% of the total sequestered U could not be leached by ion exchange or by weak acid reaction, and is therefore considered recalcitrant and resistant to in-situ [remobilization](#). As with the passive canister material, the vast majority of sequestered U is associated with the recalcitrant fraction (SEP stage 3).

Solid phase analyses of accelerated column material demonstrate that significant amounts of U-P minerals formed close to the influent end of the columns, where aqueous U concentrations were highest. Results of XRD indicate that a mixture of crystalline chernikovite and poorly crystalline [hydroxyapatite](#) are present near the

column inlets, and the fraction of chernikovite decreases with distance from the inlet (Fig. 2; Supporting Information, Fig. S-4). Despite the shift towards a more reducing redox environment within the column, the abundance of chernikovite (a U(VI) phosphate) and the absence of uraninite (a U(IV) oxide) suggests that the vast majority of immobilized U remained in the +6 oxidation state. All three of the MW-S24 accelerated flow columns (A-1a through A-1c) show pronounced chernikovite reflections in inlet samples, indicating a high degree of crystallinity (Fig. 3). The accelerated flow column solids from well MW-8A also show chernikovite formation near the inlet, but with lower intensity reflections than the MW-S24 columns (Fig. 3). This is expected, as the groundwater U concentration and total column U loadings at well MW-S24 are much higher than MW-8A (Table 1). Solids sampled near the outlet of all columns have significantly lower concentrations of U, and uranyl phosphate minerals were not detected (Fig. 2). Although we cannot explicitly differentiate surface complexed and crystallized U using our extraction technique, we infer from the large recalcitrant fraction and the XRD and SEP results that chernikovite mineralization contributes significantly to U uptake.

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Fig. 2. X-Ray diffraction data for aliquots of column MW-S24 A1-c solids sampled along a transect parallel to [groundwater flow](#). All measurements are given as distance from the inlet port of the column. The U-bearing mineral phase chernikovite was detected up to 10.2 cm from the influent port, corresponding to zones of highest U loading ([Table 2](#)). Intensities of the uranyl phosphate phase peaks decreased to below detection towards the [effluent](#) port.

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Fig. 3. X-Ray diffraction data for accelerated flow column samples taken nearest the [groundwater flow](#) inlet ports that show the presence of crystalline chernikovite. Chernikovite reflection intensities are significantly less pronounced in the media deployed at the lower-U [wellhead](#), MW-8A ([Table 1](#)).

The distribution of U on mHAP at the micro-scale was investigated using SEM-EDS. Elemental mapping of Ca, U, and P shows co-located U accumulation and Ca depletion in a separate phase with a distinct morphology ([Fig. 4](#); Supporting Information, [Fig. S-](#)

5), which is likely chernikovite. Taken together, these results demonstrate that the vast majority of U reacted with mHAP is strongly sequestered both as a surface complex and in a low solubility uranyl phosphate phase. Geochemical calculations were performed to identify the key processes controlling U-P precipitation as crystalline chernikovite.

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Fig. 4. SEM-BSE image and Ca, U, and P elemental map overlays of reacted mHAP sampled from near the influent of (a) MW-S24 column A1-c and (b) MW-8A column A-2b. Discrete regions of high U and low Ca are visible, consistent with the presence of a separate U-P mineral phase.

3.3. mHAP reactivity and U stabilization

Geochemical modeling of the aqueous effluent composition shows that groundwater rapidly equilibrated with mHAP. Measured concentrations of Ca and P for MW-S24 and MW-8A are shown in [Fig. 1](#), alongside measured influent groundwater concentrations and calculated effluent concentrations modeled based on the solubility of mHAP. The observed increases in effluent total calcium and phosphorus concentrations are consistent with calculated concentrations in mHAP-equilibrated groundwater. The average effluent calcium concentration of 35.8 ± 4.2 mg/L (2 s.e.) is within error of the calculated value (33.9 mg/L); however, the Ca concentrations after ~ 40 days are significantly higher. The higher than expected effluent Ca concentrations observed late in the experiment are likely due to exchange of UO_2^{2+} for Ca^{2+} during the incongruent dissolution of mHAP to form chernikovite:

Aqueous speciation calculations indicate that the column effluent is supersaturated with respect to pure, crystalline hydroxyapatite. Given longer groundwater residence times it is likely that the aqueous phosphorus concentration will decrease as more stable [calcium phosphate](#) phases continue to precipitate.

We performed a series of [thermodynamic](#) calculations to evaluate the driving force for U-P mineral formation. As discussed above, groundwater equilibration with mHAP increases the dissolved phosphorus and calcium concentrations, which in turn increases the fluid saturation with respect to U-P minerals. [Fig. 5](#) shows the calculated aqueous total uranium concentration as a function of pH for several uranyl phosphate mineral phases (chernikovite, uranyl orthophosphate, and autunite), assuming the calcium and phosphate concentrations are controlled by mHAP solubility.

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Fig. 5. Calculated total U concentrations in equilibrium with mHAP and the lowest solubility uranyl [phosphate mineral](#) phases, including autunite, chernikovite, and uranyl [orthophosphate](#), with no added carbonate [alkalinity](#) or background [electrolyte](#). As expected, autunite is the most thermodynamically stable phase of uranyl phosphate in equilibrium with mHAP at circum-neutral pH, reducing total aqueous U to well below the MCL between pH ~5 and 8. As described in Section [2.2](#), these results are based on [thermodynamic](#) data reported in [Gorman-Lewis et al. \(2009\)](#).

All U-P phases compared have a minimum in total aqueous U around circumneutral pH. Total aqueous U concentrations are lowest for the calcium U-P mineral autunite, followed by uranyl orthophosphate and chernikovite. Equilibration of groundwater with autunite is expected to reduce aqueous uranium concentrations to below the MCL over a wide pH range in the presence of mHAP. Although the solution saturation state is calculated to be greatest with respect to autunite, only chernikovite was formed during the field trial, indicating that autunite formation is kinetically inhibited. Kinetic limitation to the formation of autunite under flow and in the presence of Ca^{2+} has been reported previously ([Fanizza et al., 2013](#)), but the eventual precipitation of autunite is expected given sufficient reaction time (cf. [Mehta et al., 2014](#)). The observed column effluent concentrations are considerably less than the solubility of chernikovite, indicating that surface [complexation](#) must be occurring in addition to uranyl phosphate precipitation. This dual mechanism can occur in the presence of high aqueous P ([Mehta et al., 2016](#)), which in this case is maintained by the high solubility of mHAP compared to pure

crystalline hydroxyapatite. Early chernikovite precipitation is expected to occur in the most U-impacted regions of the [aquifer](#), and [recrystallization](#) of chernikovite to the more thermodynamically stable Ca-autunite phase will likely maintain total aqueous U concentrations beneath the MCL, as long as residual mHAP is present.

Prior studies of in-situ U immobilization by bone [apatite](#) using Fry Canyon groundwater as a reactant did not induce chernikovite or autunite formation at U breakthrough ([Fuller et al., 2003](#)). This important discrepancy is likely due to the substantially higher pH and carbonate [alkalinity](#) of groundwater (pH 7.0, 4.8 mM carbonate) in Fry Canyon compared to the aquifer studied here (pH 6.3, ~0.7 mM carbonate). Above pH ~5.8, total aqueous U in equilibrium with chernikovite becomes sensitive to aqueous carbonate concentration, such that Fry Canyon groundwater equilibrated with mHAP is undersaturated with respect to chernikovite at the highest reported U concentration at the site ([Fig. 6](#)). Carbonate complexation labilizes U by aqueous complexation at circumneutral and higher pH, reducing the efficacy of U-P mineralization. High groundwater pH and alkalinity has also been shown to limit the efficacy of in-situ apatite-based amendments in the heavily U contaminated Hanford 300 Area ([Wellman et al., 2008b](#)). Substantial increases in groundwater carbonate alkalinity at the site could therefore lead to U remobilization, but such changes are not anticipated, as the [inorganic carbon](#) content of the fluid does not increase significantly upon reaction with mHAP (Supporting Information, [Tables S-2](#)).

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Fig. 6. Total aqueous U concentration in equilibrium with mHAP and chernikovite in the presence of variable carbonate [alkalinity](#) groundwater: 0.8 mM NaCl and carbonate alkalinity equal to Fry Canyon groundwater (4.8 mM carbonate, red curve), groundwater sampled in this study (0.7 mM carbonate, blue curve), and zero carbonate (green curve). Increasing the carbonate alkalinity increases total aqueous U significantly above pH ~5.8, such that the groundwater is significantly undersaturated with respect to chernikovite at the highest reported U concentration for Fry Canyon (pH 7.0; [Fuller et al., 2003](#)), and aqueous U is well above the MCL. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusions

The results of this study suggest that groundwater U(VI) stabilization by mHAP can be a viable remediation strategy in oxidizing [aquifers](#), leading to aqueous U immobilization through coupled surface [complexation](#) and precipitation of U-P mineral phases. [Uranium](#) sequestered under both passive and accelerated [groundwater flow](#) gradients is strongly bound to the mHAP material, and accelerated flow led to the accumulation of high solids concentrations of U up to in excess of 5 wt %. Although the current study demonstrates that surface complexed U is strongly bound by mHAP, [crystallization](#) of chernikovite significantly increases the total U uptake capacity of the material compared to surface complexation alone. Eventual reprecipitation of chernikovite to the more thermodynamically stable Ca-autunite phase is expected to reduce aqueous U concentrations to well below the MCL as long as solid mHAP is available to maintain locally high aqueous concentrations of Ca and P. Groundwater with high carbonate [alkalinity](#) promotes the formation of aqueous uranyl carbonate complexes that increase the solubility of the U-P phases, thereby inhibiting U-P formation. Thus, implementation of this remedy should be considered where the [groundwater chemistry](#) has been demonstrated to be sufficiently low in pH and carbonate alkalinity to drive chernikovite precipitation.

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Appendix A. Supplementary data

The following are the supplementary data related to this article:

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Supporting information.

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SI Table S-2.

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SI Table S-3.

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