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Effect of Bicarbonate, Calcium, and pH on the Reactivity of As(V) and U(VI) Mixtures

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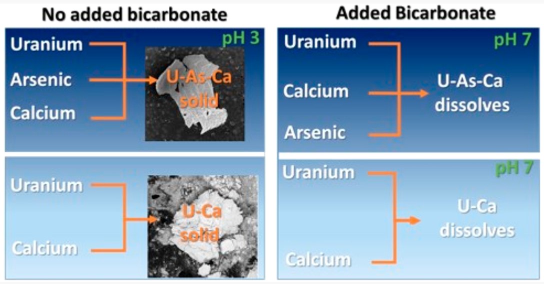
ABSTRACT: Natural or anthropogenic processes can increase the concentration of uranium (U) and arsenic (As) above the maximum contaminant levels in water sources. Bicarbonate and calcium (Ca) can have major impacts on U speciation and can affect the reactivity between U and As. We therefore investigated the reactivity of aqueous U and As mixtures with bicarbonate and Ca for acidic and neutral pH conditions. In experiments performed with 1 mM U and As mixtures, 10 mM Ca, and without added bicarbonate ($pCO_2 = 3.5$), aqueous U decreased to <0.25 mM at pH 3 and 7. Aqueous As decreased the most at pH 3 (∼0.125 mM). Experiments initiated with 0.005 mM As and U showed similar trends. X-ray spectroscopy (i.e., XAS and EDX) and diffraction indicated that U-As-Ca- and U-Ca-bearing solids resemble uranospinite [$Ca(UO_2)_2(AsO_4)_2 \cdot 10H_2O$] and becquerelite [$Ca(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)$]. These findings suggest that U-As-Ca-bearing solids formed in mixed solutions are stable at pH 3. However, the dissolution of U-As-Ca and U-Ca-bearing solids at pH 7 was observed in reactors containing 10 mM bicarbonate and Ca, suggesting a kinetic reaction of aqueous uranyl-calcium-carbonate complexation. Our study provides new insights regarding U and As mobilization for risk assessment and remediation strategies.



■ INTRODUCTION

Natural processes and anthropogenic activities such as mining and management of nuclear wastes can contaminate water sources. Previous studies have found uranium (U(VI)) and arsenic (As(V)) exceeding the USEPA maximum contaminant levels in water sources nearby abandoned mine waste located in Native American communities.[1,2] The concentration of U(VI), As(V), and other metals can range from μg L^{-1} to thousands of mg L^{-1} at mine waste,[1−3] in situ leaching,[4,5] mill tailings,[6,7] roll front deposits,[8] and post restoration sites. Aside from industrial activities, groundwater sources that supply more than 100 million inhabitants contain As concentrations higher than 0.01 mg L^{-1}.[9] Several countries deal with high concentrations of As in their water sources.[10,11] Uranium and As at these concentrations pose potential health hazards for communities located near abandoned mine sites or near water sources with high geogenic concentrations.[12]

The mobility of both U and As in water depends on redox conditions, pH, organic and inorganic ligands such as carbonate or phosphate, iron (Fe), Ca, and a variety of complex biogeochemical processes.[13] Oxidation of U(IV) through natural weathering or anthropogenic processes can generate U(VI)-bearing minerals such as schoepite $(UO_2)_8O_2(OH)_{12} \cdot 12(H_2O)$, becquerelite [$Ca(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)$], liebigite [$Ca_2UO_2(CO_3)_3 \cdot 11H_2O$], or autunite [$Ca(UO_2)_2(PO_4)_2 \cdot 11H_2O$].[14−16] Oxidation of arsenopyrite transforms As to As(III) and As(V) and Fe to Fe(III), producing a variety of secondary minerals such as As coprecipitated with jarosite [$KFe^{III}_3(OH)_6(SO_4)_2$] and other Fe(III) oxides (e.g., ferrihydrite [$Fe_2O_3 \cdot 0.5H_2O$], goethite [α-FeO(OH)], hematite [Fe_2O_3]), which have a high binding affinity for As(V) at pH < 8.5.[17] Uranium(VI) and As(V) are the predominant oxidation states for redox conditions characteristic of surface oxidizing environments. Sorption and oxidative dissolution processes of these secondary minerals can release U and As into water.

Under oxidizing conditions, U in the aqueous phase generally occurs as the uranyl ion (UO_2^{2+}) while As occurs as the pentavalent arsenate (AsO_4^{3-}) oxyanion. Uranyl can complex with other ligands such as carbonate or phosphate. The formation of ternary U-Ca−CO_3 aqueous complexes facilitates the mobility of U at pH values higher than 6[18−21] whereas uranyl and phosphate (PO_4^{3-}) form a stable insoluble complex over a wide pH range.[22] Arsenate remains negatively charged within a wide pH range given that arsenic acid has

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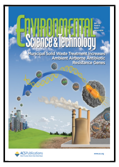

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similar acidity constants as phosphoric acid.[23] Arsenic and phosphorus have similar atomic radii, the same number of valence electrons, and nearly identical electronegativity and orbital configurations.[24,25] The similarities of phosphate (PO_4^{3-}) and arsenate (AsO_4^{3-}) ions can potentially affect the mobility of both U and As in natural waters.

Simultaneous occurrence of U and As in U ores can lead to the contamination of water bodies.[6] Uranium and As have been found in surface waters, mine waste, and background soil.[2,3] Uranium and As can form various uranyl-arsenate complexes depending mainly on the pH and U and As concentrations. For 1:1 conditions, $UO_2(H_2AsO_4)(H2O)_3^+$, $UO_2(HAsO_4)(H_2O)_3^0$, $UO_2(AsO_4)(H_2O)_3^-$ are the dominant species.[26] Uranyl-arsenate complexes deprotonate even at acidic pH increasing their capacity to react with iron (Fe) and aluminum (Al) surfaces and to form other U-As bearing minerals. Thus, the reactivity of U-As complexes may be relevant for the formation of U-Ca, As-Ca, or U-As-Ca minerals in Ca-rich waters.[6,13] Calcium is commonly accompanied by carbonate in minerals (e.g., calcite, aragonite, vaterite).[27] Carbonate can limit the interaction between U, As, and Ca by forming highly stable and mobile U(VI)(hydroxy)-carbonate and calcium-uranyl-carbonate aqueous complexes.[18,28] The reactions between As(V) and Fe(III), and U(VI) and phosphate and the stability of uranyl-arsenate mineral phases have been widely studied.[13,15,29] However, the underlying mechanisms of the aqueous reactions affecting U(VI) and As(V) reactivity[26] and the effect of Ca and carbonate on the mobility of U-As complexes in water are still unresolved.[26]

The objective of this study is to determine the effect of Ca, carbonate, and pH on the chemical reactivity of As(V) and U(VI) in oxic conditions by integrating batch experiments, aqueous chemistry, microscopy, and spectroscopy. Our study advances understanding regarding the role of Ca and carbonate in the precipitation and solubility of U(VI) and As(V) at pH 3 and 7. The information obtained from this study will provide new insights concerning the effect of bicarbonate and Ca on the reactivity and mobility of U(VI) and As(V) in acidic and neutral waters which is relevant for transport and remediation applications. Hereafter, we will refer to U(VI) and As(V) as U and As, respectively.

■ MATERIALS AND METHODS

Reactants. $Na_2HAsO_4 \cdot 7H_2O$ (>98% purity) was purchased from Sigma-Aldrich and $UO_2(CH_3COO)_2 \cdot 2H_2O$ (98%), $NaHCO_3$ (>99.7%), and $CaCl_2$(>96%) were acquired from ACS chemicals.

Aqueous Chemistry. Experiments were carried out to investigate the reactivity of soluble As, U, Ca, and bicarbonate at acidic pH 3 and neutral pH 7. The high and low concentrations of U and As were selected to represent relevant conditions found at mine waste,[1−3] in situ leaching,[4,5] mill tailings,[6,7] roll front deposits,[8] and post restoration sites. Experiments were supplied with stock solutions to reach an initial concentration of either 1 or 0.005 mM of As and U, 10 mM Ca, and 10 mM bicarbonate. Treatments without added bicarbonate were also included. Experiments with added bicarbonate were assumed as closed systems with the exception of a short period of time during the initial preparation and sampling, and experiments without added bicarbonate were assumed to be at equilibrium with atmospheric CO_2. Individual 4 mM stock solutions were prepared to provide a source of As and U ions using $Na_2HAsO_4 \cdot 7H_2O$ and $UO_2(CH_3COO)_2 \cdot 2H_2O$, respectively. Another set of 20 mM stock solutions was prepared to provide a source of Ca and bicarbonate ions using $CaCl_2$ and $NaHCO_3$, respectively. In order to reach the desired pH, all stock solutions of $Na_2HAsO_4 \cdot 7H_2O$, $UO_2(CH_3COO)_2 \cdot 2H_2O$, $NaHCO_3$, $CaCl_2$, and DI water (for dilution purposes) were independently adjusted dropwise to pH 3 using 12.4 N HCl and dropwise to pH 7 using 10 N as required before any mixing occurred. Subsequently, the solutions were mixed as required for each treatment (Table 1). The final pH was recorded to ensure that it remained in the desired value (Table S1). Once the appropriate mixtures were prepared, the vials were mixed at 60 rpm in an analog rotisserie tube rotator (Scologex MX-RL-E, Rocky Hill, CT, US) and an initial 1 mL sample was taken from the supernatant. Next, 1 mL samples were taken from the supernatant at 0.25, 0.5, 1, 2, 4, 24, and 48 h. These samples were filtered through 0.2 μm syringe filter membranes (Pall Acrodisc, Westborough, MA, USA), acidified with high purity HNO_3, and refrigerated at 4 °C for subsequent analysis. Soluble As, U, and Ca concentrations were quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES) and trace metal concentrations by inductively coupled plasma optical mass spectroscopy (ICP-MS). If precipitates formed, a sample of the solids was taken and then analyzed with scanning electron microscopy/emission diffraction spectroscopy (SEM/EDS), X-ray diffraction spectroscopy (XRD), and X-ray absorption spectroscopy (XAS). The pH of all vials was measured at the end of the experiment. (Note that the Na concentration was not evaluated.)

Table 1. Experimental Setup for the Reactivity of Soluble Species[a]

Treatment description	pH	As (mM)	U (mM)	Ca (mM)	Bicarbonate (mM)
Arsenic, calcium, and bicarbonate	3 or 7	1	0	10	10
Arsenic and calcium without added bicarbonate	3 or 7	1	0	10	$pCO_2 = 3.5$
Uranium, calcium, and carbonate	3 or 7	0	1	10	10
Uranium and calcium without added bicarbonate	3 or 7	0	1	10	$pCO_2 = 3.5$
Uranium, arsenic, calcium, and carbonate	3 or 7	1	1	10	10
Uranium, arsenic, and calcium without added bicarbonate	3 or 7	1	1	10	$pCO_2 = 3.5$

[a] An analogous experiment was performed at 0.005 mM As and/or U.

Solid Analyses. Solid samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). The details of these analyses are described in the Supporting Information.

Inductively Coupled Plasma Analyses. The soluble metal concentration was measured using a PerkinElmer Optima 5300DV ICP-OES with a detection limit of 0.5 mg L^{-1}. Trace elemental concentrations were measured with a PerkinElmer NexION 300D (Dynamic Reaction Cell) ICP-MS with a detection limit of 0.5 μg L^{-1}. Both ICPs were calibrated with a five-point calibration curve, and QA/QC measures were taken to ensure quality results.

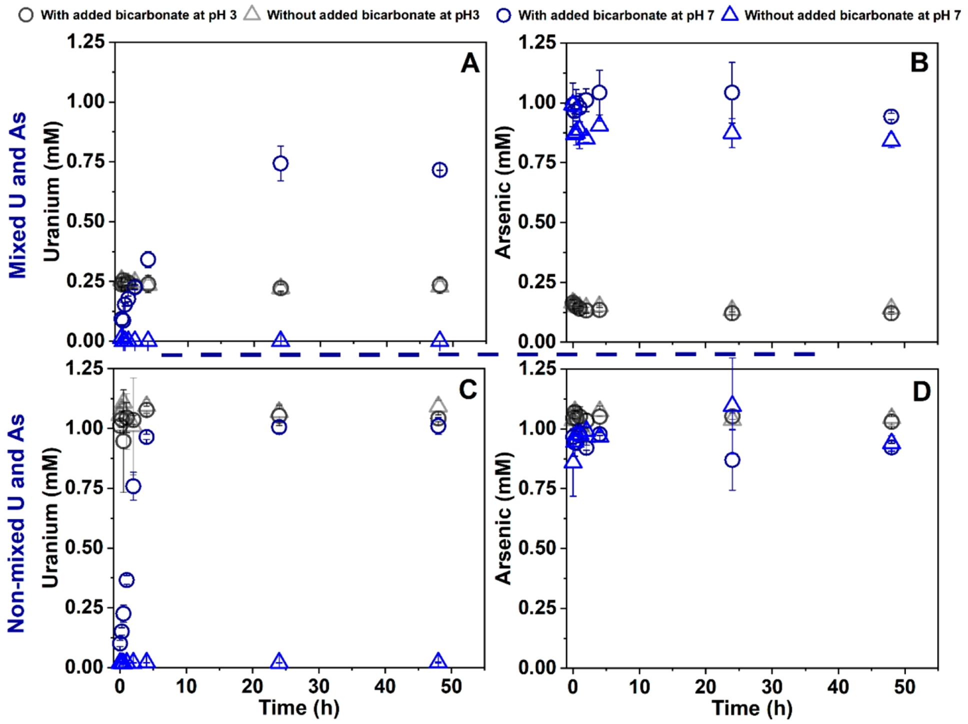


Figure 1. Aqueous concentration of U and As plotted as a function of time. Assays were initiated with a mixture of 1 mM U and/or As at pH 3 and pH 7 (A and B) and with 1 mM of U (C) or As (D) at pH 3 and pH 7. Assays were supplied with 10 mM of calcium (Ca^{2+}), with 10 mM of bicarbonate (HCO_3^-), and without added bicarbonate (pCO_2 = 3.5). Error bars represent the standard deviation of triplicate treatments.

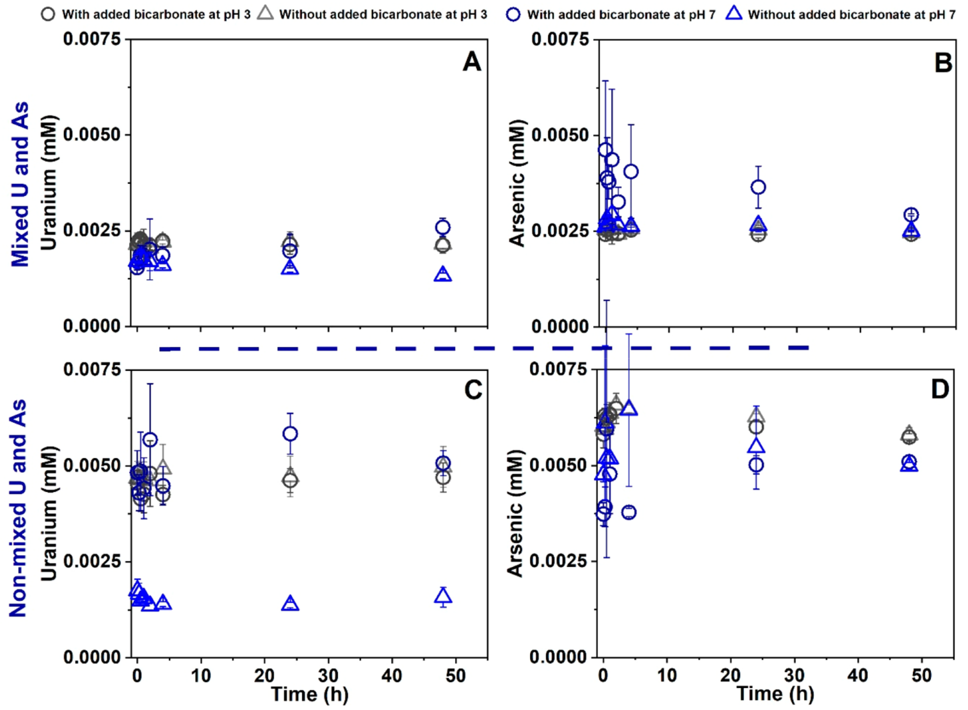


Figure 2. Aqueous concentration of U and As plotted as a function of time. Assays were initiated with a mixture of 0.005 mM U and/or As at pH 3 and pH 7 (A and B) and with 0.005 mM of U (C) or As (D) at pH 3 and pH 7. Assays were supplied with 10 mM calcium (Ca^{2+}), with 10 mM of bicarbonate (HCO_3^-), and without added bicarbonate (pCO_2 = 3.5). Error bars represent the standard deviation of triplicate treatments.

Speciation Calculations. Calculations were carried out using the open-source computer code PFLOTRAN that runs on MacOSX, linux, and Windows.[30] Speciation calculations were based on chemical equilibrium modeling using inputs from experimental conditions used in this study as a tool to gain insight about aqueous complexation and solid saturation state. PFLOTRAN can perform speciation calculations with options to input total and free ion concentrations, mineral and gas equilibrium constraints, and charge balance. The extended Debye- Hückel algorithm is used to compute activity

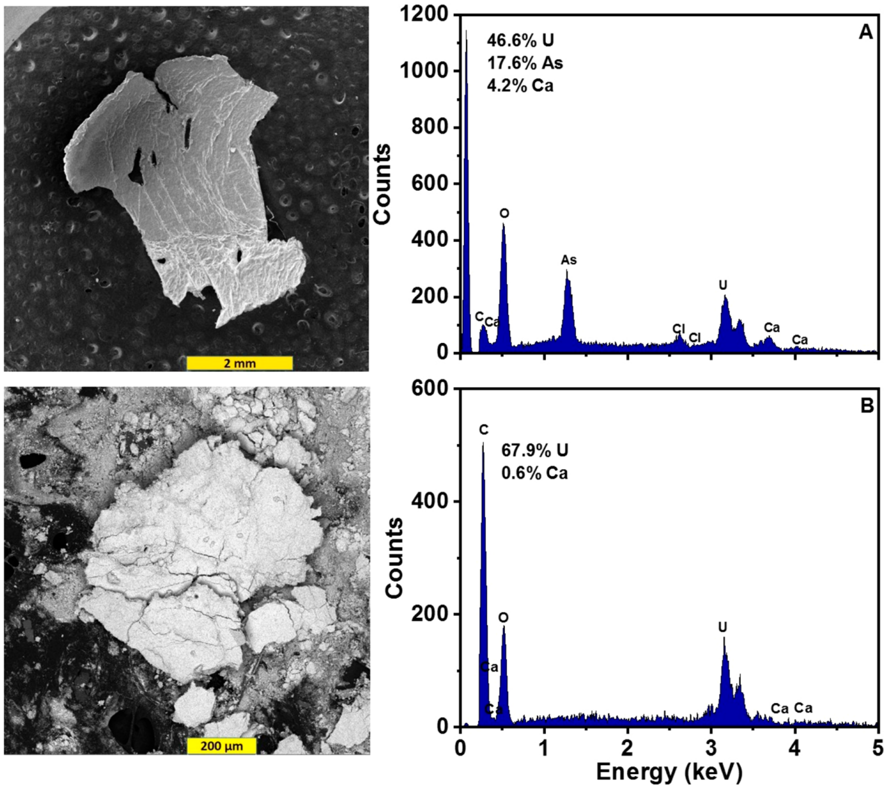


Figure 3. SEM/EDS analyses of precipitates recovered from experiments initiated with 1 mM U and As and 10 mM Ca at pH 3 (A), and 1 mM U and 10 mM Ca at pH 7 (B).

coefficients. The PFLOTRAN thermodynamic database was expanded to include equilibrium constants for becquerelite and liebigite taken from Gorman-Lewis et al.[31] and for troegerite from Nipruk et al.,[32] and includes the most recent update to U complexes.[18,19,33] The geochemical system was described with eight primary species (UO_2^{2+}, AsO_4^{3-}, Ca^{2+}, Na^+, H^+, CO_3^{2-}, Cl^-, and acetate$^-$). In the experiments without added bicarbonate, we assumed a partial pressure of CO_2 in the atmosphere of $10^{-3.5}$ bar (pCO_2 = 3.5).

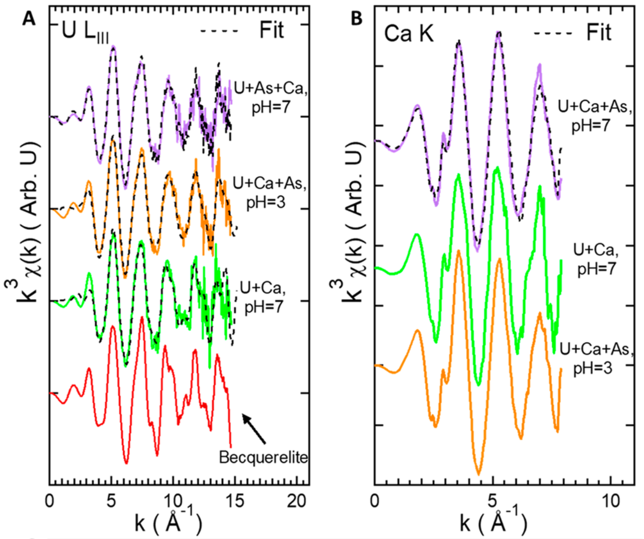
■ RESULTS AND DISCUSSION

Aqueous Chemistry Experiments. Temporal variation on U and As concentrations depended on their mixtures, pH, and addition of bicarbonate (Figures 1 and 2). The concentration of aqueous U and As decreased the most in assays without added bicarbonate (pCO_2 = 3.5). In mixtures of 1 mM U and/or As, and 10 mM Ca performed at pH 3 without added bicarbonate, both aqueous U and As decreased from 1 to <0.25 mM (>75% decrease) (Figure 1). In mixtures of U, As, and Ca performed at pH 7, aqueous U rapidly decreased from 1 mM and remained at <0.0004 mM (>99% decrease, Figure 1A), whereas aqueous As remained ~0.9 mM (Figure 1B). Uranium and As behaved differently when mixed compared to when they were not mixed (Figure 1C and 2D). Aqueous U and As remained close to 1 mM the entire experiment at pH 3 (Figure 1C and 2D). At pH 7, aqueous U rapidly decreased from 1 to ~0.019 mM (~80% decrease, Figure 1C) whereas As concentration remained ~1 mM (Figure 1D). Interestingly, the U concentration increased in mixed and nonmixed reactors containing 10 mM bicarbonate and Ca at pH 7, suggesting a kinetic reaction of U with bicarbonate and Ca (Figure 1A and 1C). In assays containing Ca and bicarbonate, the U concentration returned to its initial concentration of 1 mM after 4 h (Figure 1C). Arsenic concentration remained ~1 mM in assays containing only As, Ca, and bicarbonate (Figure 1D).

Analogous experiments were performed with an initial concentration of 0.005 mM U and/or As, 10 mM Ca, with 10 mM of bicarbonate or without added bicarbonate (pCO_2 = 3.5). Temporal variation in U and As concentrations depended on their mixtures, pH, and addition of bicarbonate (Figure 2). In mixtures of U, As, and Ca performed at pH 3 without added bicarbonate, both aqueous U and As rapidly decreased from 0.005 to ~0.0022 (~55% decrease; Figure 2). In mixtures of U, As, and Ca performed at pH 7, aqueous U decreased from 0.005 to as low as 0.0013 (74% decrease, Figure 1A) and aqueous As decreased from 0.005 to as low as 0.0025 mM (~50% decrease, Figure 2B). Uranium and As behaved differently when they were not mixed (Figure 2C and 2D). At pH 3, the concentration of U and As remained close to the initial concentration (Figure 2C and 2D), whereas at pH 7 the aqueous U decreased from 0.005 to ~0.002 (~60% decrease, Figure 2C). For experiments with an initial concentration of 0.005 mM (Figure 2C), the U concentration did not noticeably increase after reacting with added bicarbonate and supplied with Ca at pH 7 as observed in experiments using initial concentrations of 1 mM (Figure 1 C). In mixtures of U, As, Ca, and bicarbonate, the U concentration increased from 0.0015 to 0.0025 mM (Figure 2A) while the As concentration remained >0.003 mM. In assays with added bicarbonate and supplied with U and Ca, the aqueous U concentration increased over time to its initial value (Figure 2C).

Solid Phase Analyses. Precipitates recovered from the experiments initiated with 1 mM of U and/or As contained mixtures of U, As, and Ca according to the EDS and SEM analyses (Figure 3). The solid that precipitated at pH 3 contained U, As, and Ca (Figure 3A), while the solid that precipitated at pH 7 contained primarily U (Figure 3B). The formation of these precipitates explains the decrease in the aqueous concentration of U and As. Due to a limited amount of solid sample, SEM and EDS analyses were used as an initial analysis of the solid phases. Additional XRD analyses identified a similar pattern to that of meta-zeunerite $[Cu(UO_2)_2(AsO_4)_2\cdot 8H_2O]$ for the solid precipitated at pH 3 (Figure S1 A). However, the XRD pattern of the solid at pH 7 seems to have a mixture of solids with similar chemical structure to becquerelite $[Ca(UO_2)_6O_4(OH)_6\cdot 8(H_2O)]$ and meta-zeunerite (Figure S1 B). Given that our experimental system did not include Cu, it is likely that Ca is part of the structure of the uranyl arsenate mineral to form a solid such as uranospinite $[Ca(UO_2)_2(AsO_4)_2\cdot 10H_2O]$ with similar chemical structure to that of meta-zeunerite.

Results from U L_{III}-Edge EXAFS shell-by-shell fits confirm that a solid with similar chemical structure to uranospinite is the main solid phase formed in mixed U and As experiments at pH 3 (Figure 4, Table S2). For experiments having only U or As at pH 7, U L_{III}-Edge EXAFS shell-by-shell fits indicate that becquerelite is the main solid phase formed (Figure 4, Table S2). These results are confirmed by X-ray diffraction analyses which identify minerals resembling meta-zeunerite (or uranospinite given that our experiments have no Cu) and becquerelite (Figure S1). Note that the structure of uranospinite has not been yet resolved for several decades.[34] Thus, the XRD data for uranospinite are not available in the ICSD database. Instead, meta-zeunerite was used in its place as a surrogate. Linear combination fits for U L_{III}-Edge EXAFS for reacted solids obtained from mixed U and As experiments at pH 7 suggest that a mixture of 82.0% uranospinite and 18.0% becquerelite was formed (Figure 4). The linear combination fits to Ca K-edge spectra yielded a mixture of 71.6% uranospinite and 28.4% becquerelite. The linear combination results for Ca K-Edge EXAFS spectra are within 10% error for the linear combination fits reported for U L_{III}-Edge EXAFS spectra. These results highlight the relevance of precipitation and dissolution of U-, As-, and Ca-bearing solids under the conditions investigated in this study.



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	U-As-Ca mixture at pH 3 (%)	U-Ca mixture at pH 7 (%)
UL$_{III}$ U+As+Ca, pH 7	82.0%	18.0 %
Ca K U+As+Ca, pH 7	71.6%	28.4%

Figure 4. EXAFS spectra, shell-by-shell fits, and linear combination fits corresponding to solid samples reacted with U, As, and Ca at pH 3 and 7: U L_{III}-edge EXAFS spectra (A); Ca K-edge EXAFS spectra (B); and results from linear combination fits (C). Solids samples were taken from the experiments supplied with 1 mM of U and As, 1 mM U, 10 mM of Ca and without added bicarbonate (pCO_2 = 3.5).

Solubility Considerations. *Precipitation of Uranyl-Arsenate-Calcium Bearing Solids.* Aqueous U and As decreased in mixtures with Ca and without added bicarbonate (pCO_2 = 3.5) at pH 3 and 7 and aqueous As partially decreased at pH 7 due to precipitation of a U-As-Ca-bearing solid similar to uranospinite. Uranospinite is a hydrated arsenate of Ca and U that usually occurs with other secondary uranium minerals such as zeunerite $[Cu(UO_2)_2(AsO_4)_2\cdot H_2O]$, walpurgite $[(BiO)_4(UO_2)(AsO_4)_2\cdot 2H_2O]$, and troegerite $[(H_3O)(UO_2)(AsO_4)\cdot 3H_2O]$. Uranospinite occurs in small amounts in calcite rocks as a thin pale yellow to white coating associated with calcite.[35] Uranospinite has also been found in U ores[36,37] and in river beds[35] that also contain As. Other minerals such as meta-zeunerite also occur in U ores rich in As and other metals.[38] The formation of U-As precipitates can lead to the sequestration of the aqueous forms of both metals and other cations.[24,38] Early work investigating the synthesis of uranospinite obtained a flocculent lemon-yellow precipitate utilizing calcium chloride, uranyl nitrate, and monohydrogen sodium arsenate in molar ratio of 1:2:2 at room temperature.[39] Such conditions are similar to those employed in our experiment. Therefore, our results suggest that the conditions applied in our experiments likely facilitated the formation of U-As-Ca-bearing precipitates.

Understanding the reactivity between U and As is relevant due to the large number of environments where both U and As simultaneously occur across the world.[6,7,12,38] Previous research investigating the reactivity of U and As has suggested that a fraction of the U-As complexes deprotonate throughout an acid pH range.[26] Complexed U-As species such as $UO_2H_2AsO_4(H_2O)_3^+$ and $UO_2(H_2AsO_4)_2(H_2O)^0$ dominate in an acidic pH range, while $UO_2(HAsO_4)(H_2AsO_4)(H_2O)^-$ species dominate from pH 7.2 to 10.7.[26] These U-As species enable the sorption of U onto Al and Fe oxy(hydroxides)[26] suggesting that an analogue behavior can occur with Ca oxy(hydroxides) as well. The affinity between U, As, and Ca is not surprising as arsenates are usually considered an analogue of phosphate minerals with similar sizes and charges in their ionic units.[24] Phosphates are well-known for forming precipitates of limited solubility with U and Ca such as autunite $(Ca[(UO_2)(PO_4)]_2\cdot 11H_2O)$.[40,41]

Precipitation of Uranyl-Calcium Solids. Experiments showed that the concentration of U decreased in the experiments without added bicarbonate (pCO_2 = 3.5) and supplied either with only U and Ca or with a mixture of U, As, and Ca due to the precipitation of the uranyl-calcium solid resembling becquerelite. Becquerelite $(Ca(UO_2)_6O_4(OH)_6\cdot 8H_2O)$, a hydrated uranyl oxyhydroxide mineral phase, is one of the most commonly occurring secondary uranyl carbonate minerals.[42] Hydrated uranyl oxyhydroxide phases mainly form in uranium rich aqueous solutions and develop early on during the oxidation and corrosion of uraninite-bearing ores.[43,44] Becquerelite and other minerals such liebigite

($Ca_2UO_2(CO_3)_3 \cdot 11H_2O$), K-compreignacite ($K_2(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)$), and Na-compreignacite ($Na_2(UO_2)_6O_4(OH)_6 \cdot 8(H_2O)$) are commonly present in uranium ores with oxidizing conditions and abundance of Ca, K, or Na.[31,45]

According to the speciation calculations, becquerelite is oversaturated (saturation index = 0.56) at pH 7 (Table S3). A recent study suggested that U can form precipitates with Ca and hydroxyl for pH values >5, consistent with our results in absence of bicarbonate or other complexing agents.[46] Research has also suggested that formation of synthetic becquerelite can take place in a circumneutral pH range.[47] Previous work included synthesis of becquerelite by the addition of stoichiometric quantities of uranyl and calcium nitrate at room temperature, basic pH, and oxidizing conditions or by oxidizing schoepite.[44] Our findings suggest that the conditions applied in our experiments facilitated the formation of U-Ca precipitates.

Effect of Bicarbonate on Precipitate Solubility. Bicarbonate facilitated the dissolution of U-As-Ca and U-Ca precipitates (Figures 1A,B,D and 2B,C). Our results suggest that solids that initially precipitated, decreasing the U and As concentration, completely or partially redissolved over time in contact with bicarbonate. Other studies have also observed this phenomenon with U but did not focus the redissolution of U precipitates due to the reaction with bicarbonate.[47,48] Initially, the dissolved U and As concentrations were low leading to low solubility of U-bearing minerals and hence highly supersaturated conditions. As the U reacted over time in both mixed (Figure 1A) and nonmixed systems (Figure 1C), the concentration of uranyl-carbonate complexes increased, and the minerals dissolved until almost complete dissolution took place.

Speciation calculations using experimental conditions for this study at pH 7 with 1 mM mixtures of U and As and 10 mM of Ca and bicarbonate suggest that the main U aqueous complexes were $Ca_2UO_2(CO_3)$ (74.4%) and $CaUO_2(CO_3)_3^{2-}$ (14.4%). The main As complexes were $HAsO_4^{2-}$ (88.9%) and $H_2AsO_4^-$ (11.1%) for the experiments supplied with U and As (Table S4). Simulations of the experiments supplied with U and As 1 mM mixtures, 10 mM of Ca, and without added bicarbonate (pCO_2 = 3.5) at pH 7 suggest that the main U complex was UO_2HAsO_4(97.7%) while the dominant As complexes were $HAsO_4^{2-}$ (52.9%) and $H2AsO_4^-$ (47.1%) (Table S5). In the experiments supplied with 1 mM of U and 10 mM of Ca and bicarbonate, simulations indicated that the main species were $Ca_2UO_2(CO_3)_3$(79.9%), $CaUO_2(CO_3)_3^{2-}$ (12.8%), and $UO_2(CO_3)_3^{4-}$ (8%) (Table S4), while the main complexes without added bicarbonate (pCO_2 = 3.5) were $(UO_2)_2CO_3(OH)_3^-$ (62.3%) and $(UO_2)_3(OH)_5^+$ (26.7%) indicating the role of bicarbonate complexing with U and Ca (Table S4).

Previous studies have indicated that carbonates facilitate the formation of aqueous uranyl-carbonato complexes[18−20,31,49−51] in agreement with our findings. Aqueous uranyl carbonato complexes alter U sorption at circumneutral pH and high partial CO_2 pressures,[47] and limit retention particularly when Ca is present.[49] The distribution of uranyl-calcium-carbonato complexes depends on the specific aqueous geochemical conditions such as concentrations of alkaline earth metals, pH, pCO_2, U concentration, inorganic and organic ligands, and ionic strength.[18] In our experiments, the reaction of solids with bicarbonate solubilized either partially or completely U over time (Figure 1A,C) as evidenced by the increase in the U concentration with time. The synthetic nature of the precipitates may have facilitated their dissolution since research suggests that synthetic becquerelite is more soluble than natural becquerelite.[44]

The effect of bicarbonate on metal solubility is well-known. Carbonates are typically used to extract metals from soils and sediments including U and As.[52−55] For instance, 1 M sodium bicarbonate extracted ≈97% of U from a contaminated soil.[52] A concentration of 0.5 M sodium bicarbonate leached up to 90% of U in flow-through column experiments.[53] Sodium carbonate and sodium bicarbonate leached from ≈6.5 up to ≈27 more As compared to barium and manganese carbonate salts.[54] These previous results suggest that the 10 mM of sodium bicarbonate added to the system complexed U and As. This assumption was supported by our modeling results.

More information is necessary to better understand the mechanisms affecting the solubility of uranyl arsenate solids in environmentally relevant systems. Other work has observed the increase of aqueous U over time caused by the formation of U-Ca-CO_3 complexes.[56] Additional research is necessary to identify specific equilibrium constants and kinetic constraints of the role U-Ca-CO_3 complexes in the dissolution of U-Ca and U-As bearing solids.

Environmental Implications. Our findings indicate that U, As, and Ca can react to form U-As-Ca precipitates at pH 3 and a combination of U-Ca and U-As-Ca precipitates at pH 7. XAS and XRD analyses suggest that the precipitates resemble uranospinite and becquerelite. These results are in agreement with research indicating that As sequestered U leading to the formation of an immobile U-As mineral phase.[38] Bicarbonate facilitates the dissolution of U-, As-, and Ca-bearing solids. These results agree with previous studies which found that bicarbonate and Ca facilitated the mobilization of uranium and arsenic in the aqueous phase.[18,50,54,57] Future studies are needed to explore the role of kinetics in the formation of uranyl-carbonate complexes that can affect mineral solubility at alkaline pH.

We recognize that these results are derived from data obtained from batch experiments performed under controlled laboratory conditions. Thus, the conditions investigated are simplifications of the natural environment found in mine waste, in situ leaching, mill tailings, roll front deposits, and post restoration sites. More research is necessary to investigate more complex mixtures of metals, pH range, and variability of oxic and anoxic conditions. Nonetheless, our research provides new insights about potential reactions occurring between U and As and the role of bicarbonate and Ca in their mobilization.

In mine tailing management facilities, mine waste, or natural systems where U and As simultaneously occur,[1,6,58] the reactivity between U and As can lead to the formation of precipitates, such as uranospinite, decreasing the mobilization of U and As. However, in mine facilities, if the leachate remains untreated and reaches alkaline water bodies, U and As will likely be mobilized into the aqueous phase. Our results also suggest that U and As can be removed in remediation of systems that already deal with acidic waste, and cations such as Ca may facilitate the precipitation of U-As-bearing minerals. As a whole, our study provides insights about U and As mobilization and information for possible remediation approaches.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b06063. Additional information regarding final pH of the batch aqueous chemistry experiments, solid analyses methods and results, and speciation calculations is available in Supporting Information.

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Notes

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■ REFERENCES

(1) Blake, J. M.; Avasarala, S.; Artyushkova, K.; Ali, A.-M. S.; Brearley, A. J.; Shuey, C.; Robinson, W. P.; Nez, C.; Bill, S.; Lewis, J.; Hirani, C.; Pacheco, J. S. L.; Cerrato, J. M. Elevated Concentrations of U and Co-occurring Metals in Abandoned Mine Wastes in a Northeastern Arizona Native American Community. *Environ. Sci. Technol.* **2015**, *49* (14), 8506−8514.

(2) Blake, J. M.; De Vore, C. L.; Avasarala, S.; Ali, A. M.; Roldan, C.; Bowers, F.; Spilde, M. N.; Artyushkova, K.; Kirk, M. F.; Peterson, E.; Rodriguez-Freire, L.; Cerrato, J. M. Uranium mobility and accumulation along the Rio Paguate, Jackpile Mine in Laguna Pueblo, NM. *Environ. Sci-Proc. Imp.* **2017**, *19* (4), 605−621.

(3) Blake, J. M.; Avasarala, S.; Ali, A.-M. S.; Spilde, M.; Lezama-Pacheco, J. S.; Latta, D.; Artyushkova, K.; Ilgen, A. G.; Shuey, C.; Nez, C.; Cerrato, J. M. Reactivity of As and U co-occurring in Mine Wastes in northeastern Arizona. *Chem. Geol.* **2019**, *522*, 26−37.

(4) Saunders, J. A.; Pivetz, B. E.; Voorhies, N.; Wilkin, R. T. Potential aquifer vulnerability in regions down-gradient from uranium in situ recovery (ISR) sites. *J. Environ. Manage.* **2016**, *183*, 67−83.

(5) Ruiz, O.; Thomson, B. M.; Cerrato, J. M. Investigation of in situ leach (ISL) mining of uranium in New Mexico and post-mining reclamation. *New Mex. Geol.* **2016**, *38* (4), 77−85.

(6) Donahue, R.; Hendry, M. J. Geochemistry of arsenic in uranium mine mill tailings, Saskatchewan, Canada. *Appl. Geochem.* **2003**, *18* (11), 1733−1750.

(7) Robertson, J.; Hendry, M. J.; Kotzer, T.; Hughes, K. A. Geochemistry of uranium mill tailings in the Athabasca Basin, Saskatchewan, Canada: A review. *Crit. Rev. Environ. Sci. Technol.* **2019**, *49*, 1−57.

(8) Bullock, L. A.; Parnell, J. Selenium and molybdenum enrichment in uranium roll-front deposits of Wyoming and Colorado, USA. *J. Geochem. Explor.* **2017**, *180*, 101−112.

(9) Mukherjee, A.; Gupta, S.; Coomar, P.; Fryar, A. E.; Guillot, S.; Verma, S.; Bhattacharya, P.; Bundschuh, J.; Charlet, L. Plate tectonics influence on geogenic arsenic cycling: From primary sources to global groundwater enrichment. *Sci. Total Environ.* **2019**, *683*, 793−807.

(10) He, J.; Charlet, L. A review of arsenic presence in China drinking water. *J. Hydrol.* **2013**, *492*, 79−88.

(11) Bundschuh, J.; Litter, M. I.; Parvez, F.; Roman-Ross, G.; Nicolli, H. B.; Jean, J. S.; Liu, C. W.; Lopez, D.; Armienta, M. A.; Guilherme, L. R. G.; Cuevas, A. G.; Cornejo, L.; Cumbal, L.; Toujaguez, R. One century of arsenic exposure in Latin America: A review of history and occurrence from 14 countries. *Sci. Total Environ.* **2012**, *429*, 2−35.

(12) Hoover, J.; Gonzales, M.; Shuey, C.; Barney, Y.; Lewis, J. Elevated arsenic and uranium concentrations in unregulated water sources on the Navajo Nation, USA. *Expos. Health* **2017**, *9* (2), 113−124.

(13) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behaviour and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17* (5), 517−568.

(14) Burns, P. C. U^{6+} minerals and inorganic compounds: insights into an expanded structural hierarchy of crystal structures. *Can. Mineral.* **2005**, *43* (6), 1839−1894.

(15) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. The crystal chemistry of hexavalent uranium; polyhedron geometries, bond-valence parameters, and polymerization of polyhedra. *Can. Mineral.* **1997**, *35* (6), 1551−1570.

(16) Krivovichev, S. V.; Plášil, J.; Burns, P.; Sigmon, G. In *Mineralogy and crystallography of uranium, Uranium: From Cradle to Grave.* Mineralogical Association of Canada Short Courses, 2013; pp 15−119.

(17) Creamer, N. J.; Baxter-Plant, V. S.; Henderson, J.; Potter, M.; Macaskie, L. E. Palladium and gold removal and recovery from precious metal solutions and electronic scrap leachates by Desulfovibrio desulfuricans. *Biotechnol. Lett.* **2006**, *28* (18), 1475−1484.

(18) Dong, W.; Brooks, S. C. Determination of the Formation Constants of Ternary Complexes of Uranyl and Carbonate with Alkaline Earth Metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) Using Anion Exchange Method. *Environ. Sci. Technol.* **2006**, *40* (15), 4689−4695.

(19) Dong, W.; Brooks, S. C. Formation of aqueous $MgUO_2(CO_3)_3^{2-}$ complex and uranium anion exchange mechanism onto an exchange resin. *Environ. Sci. Technol.* **2008**, *42* (6), 1979−1983.

(20) Stewart, B. D.; Mayes, M. A.; Fendorf, S. Impact of Uranyl-Calcium-Carbonato Complexes on Uranium(VI) Adsorption to Synthetic and Natural Sediments. *Environ. Sci. Technol.* **2010**, *44* (3), 928−934.

(21) Othmane, G.; Allard, T.; Morin, G.; Sélo, M.; Brest, J.; Llorens, I.; Chen, N.; Bargar, J. R.; Fayek, M.; Calas, G. Uranium Association with Iron-Bearing Phases in Mill Tailings from Gunnar, Canada. *Environ. Sci. Technol.* **2013**, *47* (22), 12695−12702.

(22) Selvakumar, R.; Ramadoss, G.; Mridula, P. M.; Rajendran, K.; Thavamani, P.; Ravi, N.; Megharaj, M. Challenges and complexities in remediation of uranium contaminated soils: A review. *J. Environ. Radioact.* **2018**, *192*, 592−603.

(23) Benjamin, M. M. *Water chemistry*. Waveland Press, Inc: Long Grove Illinois, USA, 2014.

(24) Dzik, E. A.; Lobeck, H. L.; Zhang, L.; Burns, P. C. High-temperature calorimetric measurements of thermodynamic properties of uranyl arsenates of the meta-autunite group. *Chem. Geol.* **2018**, *493*, 353−358.

(25) Knodle, R.; Agarwal, P.; Brown, M. From phosphorous to arsenic: changing the classic paradigm for the structure of biomolecules. *Biomolecules* **2012**, *2* (2), 282−287.

(26) He, M.; Liu, X.; Cheng, J.; Lu, X.; Zhang, C.; Wang, R. Uranyl Arsenate Complexes in Aqueous Solution: Insights from First-Principles Molecular Dynamics Simulations. *Inorg. Chem.* **2018**, *57* (10), 5801−5809.

(27) Daniels, W. L., The Nature and Properties of Soils, 15th ed.. *Soil Sci. Soc. Am. J.* 2016, *80*, (5), 1428.

(28) Bhattacharyya, A.; Campbell, K. M.; Kelly, S. D.; Roebbert, Y.; Weyer, S.; Bernier-Latmani, R.; Borch, T. Biogenic non-crystalline U((IV)) revealed as major component in uranium ore deposits. *Nat. Commun.* **2017**, *8*, 15538.

(29) Finch, R.; Murakami, T. Systematics and paragenesis of uranium minerals. *Rev. Mineral.* **1999**, *38*, 91−180.

(30) Lichtner, P. C.; Hammond, G. E.; Lu, C.; Karra, S.; Bisht, G.; Andre, B.; Mills, R. T.; Kumar, J.; Frederick, J. M. *PFLOTRAN User Manual*. **2019**.

(31) Gorman-Lewis, D.; Burns, P. C.; Fein, J. B. Review of uranyl mineral solubility measurements. *J. Chem. Thermodyn.* **2008**, *40* (3), 335−352.

(32) Nipruk, O. V.; Chernorukov, N. G.; Pykhova, Y. P.; Godovanova, N. S.; Eremina, A. A. State of uranyl phosphates and arsenates in aqueous solutions. *Radiochemistry* **2011**, *53* (5), 483.

(33) Guillaumont, R.; Mompean, F. J. *Update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium*. Elsevier: Amsterdam, 2003; Vol. 5.

(34) Frondel, C. Systematic mineralogy of uranium and thorium; 1064; *U.S. Geol. Surv.*: **1958**.

(35) Carlson, S. M.; Robinson, G. W.; Elder, M. J.; Jaszczak, J. A.; Bornhorst, T. J. Greenockite and Associated Uranium-Vanadium, Minerals from the Huron River Uranium Prospect Baraga County, Michigan. *Rocks Miner.* **2007**, *82* (4), 298−309.

(36) Roshani, M.; Mirjalili, K. Studies on the leaching of an arsenic-uranium ore. *Hydrometallurgy* **2009**, *98* (3−4), 304−307.

(37) Castor, S. B.; Henry, C. D. Geology, geochemistry, and origin of volcanic rock-hosted uranium deposits in northwestern Nevada and southeastern Oregon, USA. *Ore Geol. Rev.* **2000**, *16* (1), 1−40.

(38) Corkhill, C. L.; Crean, D. E.; Bailey, D. J.; Makepeace, C.; Stennett, M. C.; Tappero, R.; Grolimund, D.; Hyatt, N. C. Multi-scale investigation of uranium attenuation by arsenic at an abandoned uranium mine, South Terras. *npj Mater. Degradation* **2017**, *1* (1), 19.

(39) Mrose, M. E. Studies of Uranium Minerals (XIII). Synthetic Uranospinites. *Am. Mineral.* **1953**, *38* (11−1), 1159−1168.

(40) Locock, A. J.; Burns, P. C. The crystal structure of synthetic autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_{11}$. *Am. Mineral.* **2003**, *88* (1), 240−244.

(41) Stojanović, M.; Stevanović, D.; Milojković, J.; Mihajlović, M. L.; Lopičić, Z.; Šoštarić, T. Influence of Soil Type and Physical-Chemical Properties on Uranium Sorption and Bioavailability. *Water, Air, Soil Pollut.* **2012**, *223* (1), 135−144.

(42) Frost, R. L.; Erickson, K. L.; Weier, M. L.; Carmody, O.; Cejka, J. Raman spectroscopic study of the uranyl tricarbonate mineral liebigite. *J. Mol. Struct.* **2005**, *737* (2−3), 173−181.

(43) Casas, I.; Bruno, J.; Cera, E.; Finch, R. J.; Ewing, R. C. Characterization and dissolution behavior of a becquerelite from Shinkolobwe, Zaire. *Geochim. Cosmochim. Acta* **1997**, *61* (18), 3879−3884.

(44) Colmenero, F.; Fernandez, A. M.; Timon, V.; Cobos, J. Becquerelite mineral phase: crystal structure and thermodynamic and mechanical stability by using periodic DFT. *RSC Adv.* **2018**, *8* (43), 24599−24616.

(45) Sandino, M. C. A.; Grambow, B. Solubility equilibria in the U(VI)-Ca-K-Cl-H_2O system - transformation of schoepite into becquerelite and compreignacite. *Radiochim. Acta* **1994**, *66*−7, 37−43.

(46) Laurette, J.; Larue, C.; Mariet, C.; Brisset, F.; Khodja, H.; Bourguignon, J.; Carrière, M. Influence of uranium speciation on its accumulation and translocation in three plant species: Oilseed rape, sunflower and wheat. *Environ. Exp. Bot.* **2012**, *77*, 96−107.

(47) Tokunaga, T. K.; Kim, Y.; Wan, J. M.; Yang, L. Aqueous Uranium(VI) Concentrations Controlled by Calcium Uranyl Vanadate Precipitates. *Environ. Sci. Technol.* **2012**, *46* (14), 7471−7477.

(48) Gorman-Lewis, D.; Fein, J. B.; Burns, P. C.; Szymanowski, J. E. S.; Converse, J. Solubility measurements of the uranyl oxide hydrate phases metaschoepite, compreignacite, Na-compreignacite, becquerelite, and clarkeite. *J. Chem. Thermodyn.* **2008**, *40* (6), 980−990.

(49) Zheng, Z. P.; Tokunaga, T. K.; Wan, J. M. Influence of calcium carbonate on U(VI) sorption to soils. *Environ. Sci. Technol.* **2003**, *37* (24), 5603−5608.

(50) Dong, W.; Ball, W. P.; Liu, C.; Wang, Z.; Stone, A. T.; Bai, J.; Zachara, J. M. Influence of Calcite and Dissolved Calcium on Uranium(VI) Sorption to a Hanford Subsurface Sediment. *Environ. Sci. Technol.* **2005**, *39* (20), 7949−7955.

(51) Clark, D. L.; Hobart, D. E.; Neu, M. P. Actinide Carbonte Complexes and Their Importance in Actinide Environmental Chemistry. *Chem. Rev.* **1995**, *95* (1), 25−48.

(52) Zhou, P.; Gu, B. Extraction of Oxidized and Reduced Forms of Uranium from Contaminated Soils: Effects of Carbonate Concentration and pH. *Environ. Sci. Technol.* **2005**, *39* (12), 4435−4440.

(53) Mason, C. F. V.; Turney, W. R. J. R.; Thomson, B. M.; Lu, N.; Longmire, P. A.; Chisholm-Brause, C. J. Carbonate Leaching of Uranium from Contaminated Soils. *Environ. Sci. Technol.* **1997**, *31* (10), 2707−2711.

(54) Anawar, H. M.; Akai, J.; Sakugawa, H. Mobilization of arsenic from subsurface sediments by effect of bicarbonate ions in groundwater. *Chemosphere* **2004**, *54* (6), 753−762.

(55) DeVore, C. L.; Rodriguez-Freire, L.; Mehdi-Ali, A.; Ducheneaux, C.; Artyushkova, K.; Zhou, Z.; Latta, D. E.; Lueth, V. W.; Gonzales, M.; Lewis, J.; Cerrato, J. M. Effect of bicarbonate and phosphate on arsenic release from mining-impacted sediments in the Cheyenne River watershed, South Dakota, USA. *Environ. Sci-Proc. Imp.* **2019**, *21* (21), 456−468.

(56) Lu, G.; Forbes, T. Z.; Haes, A. J. Evaluating Best Practices in Raman Spectral Analysis for Uranium Speciation and Relative

Abundance in Aqueous Solutions. *Anal. Chem.* **2016**, *88* (1), 773−780.

(57) Kelly, S. D.; Kemner, K. M.; Brooks, S. C.; Fredrickson, J. K.; Carroll, S. L.; Kennedy, D. W.; Zachara, J. M.; Plymale, A. E.; Fendorf, S. Ca-UO_2-CO_3 complexation - Implications for Bioremediation of U(VI). *Phys. Scr.* **2005**, *T115*, 915−917.

(58) Moldovan, B. J.; Jiang, D. T.; Hendry, M. J. Mineralogical characterization of arsenic in uranium mine tailings precipitated from iron-rich hydrometallurgical solutions. *Environ. Sci. Technol.* **2003**, *37* (5), 873−879.

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