



The influence of calcium, sodium and bicarbonate on the uptake of uranium onto nanoscale zero-valent iron particles



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HIGHLIGHTS

- We test the influence of Na, Ca and HCO_3^- on U removal onto nZVI.
- Ca, Na and HCO_3^- did not significantly inhibit initial U removal onto nZVI.
- Ca-bearing systems exhibited partial U desorption concurrent with nZVI oxidation.
- Ca-absent systems exhibited no U desorption concurrent with nZVI oxidation.
- Ca has a significant inhibitive influence on the long-term retention of U on nZVI.

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ABSTRACT

This work investigates the influence of calcium (Ca), sodium (Na) and bicarbonate (HCO_3^-) on the uptake of uranium (U) onto nanoscale zero-valent iron particles (nZVI). Solutions tested contained U at 1 mg/L, NaHCO_3 ranging from 0 to 100 mg/L and CaCl_2 or NaCl ranging from 625 to 719 mg/L to normalise the ionic strength. Mine water containing a similar concentration of U (1.03 mg/L) and HCO_3^- at 845 mg/L was also tested as a natural analogue. All solutions were stored in sealed glass jars in the open laboratory with headspace comprising ambient air. Results demonstrate Ca, Na and HCO_3^- as having no significant inhibitive influence on the efficacy of nZVI for initial U removal from solution, with $\geq 95.7\%$ uptake recorded for all systems studied after 0.5 h reaction. Similar U retention ($>97.1\%$) was recorded throughout the entire 672 h experiment for all solutions with Ca absent. In contrast, partial U desorption in the latter stages of the experiment was recorded for all solutions with Ca present, with 87.3%, 85.2% and 84.7% removal recorded after 672 h for solutions containing 0, 10 and 100 mg/L HCO_3^- , respectively, and 10.9% removal recorded for the mine water. Maximum U removal onto nZVI was recorded as directly proportional to HCO_3^- concentration for solutions with Ca absent, however, no trend was identified for the Ca-bearing solutions. Overall results demonstrate Ca as having a significant inhibitive influence on the long-term retention (e.g. >48 h) of U on nZVI, which is independent of HCO_3^- concentration when also present at <100 mg/L.

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1. Introduction

A key environmental legacy of mankind's military and civil nuclear activities has been the release of uranium (U) into the environment. U presents a considerable long-term environmental concern and can significantly limit the potential for site redevelopment. In addition, the contamination of groundwater by soluble forms of U can compromise drinking water sources and spread contamination over significant distances. Aqueous U transport in

groundwater is governed by its redox, sorption and complexation behaviour. It can exist in many oxidation states [e.g. U^0 , U^{3+} , U^{4+} , U^{5+} and U^{6+}], however, in natural groundwater systems (e.g. $6 < \text{pH} < 9$) U^{6+} typically predominates as the uranyl ion (UO_2^{2+}), which is prone to complexation with many ubiquitous groundwater constituents, including: phosphate, silicate, sulphate, fluoride and (bi)carbonate [1]. Consequently, more than 42 dissolved U-bearing species, 89 U-bearing minerals and 368 inorganic crystal structures that contain U^{6+} have been documented [2]. The affinity of U with bicarbonate (HCO_3^-) is of great importance due to the extremely high stability of uranyl carbonate complexes in comparison to the other complexes which form in groundwater systems [1].

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In the presence of HCO_3^- and dissolved calcium (Ca), two ternary aqueous uranyl complexes: $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ ($\log \beta_{213} = 30.70$) and $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ ($\log \beta_{113} = 27.18$) become increasingly prominent, and are typically the dominant species in natural groundwater conditions [3]. For example, analysis of groundwater samples taken from a U mill tailing remedial action site in Tuba City, Arizona, USA, determined that they comprised >99% of the U^{6+} in solution [4]. In addition, Fox et al. [5] recorded a decrease from 77% U^{6+} adsorption on quartz using a HCO_3^- bearing solution with no dissolved Ca present compared with 10% adsorption using a similar solution with Ca present at 8.9 mM. As a consequence there is a great need for further investigation into the aqueous chemistry and stability of uranyl-calcium-carbonate complexes, in order to inform the development of new water treatment technologies. In recent years much focus has been applied on the potential utility of nanoscale zero-valent iron (nZVI) for the removal of aqueous U from waste waters [6–17]. It has been demonstrated for circumneutral pH solutions lacking complexing agents (i.e. a uranyl solution with a conservative background electrolyte) near-total chemical reduction of $\text{U}_{(\text{aq})}^{6+}$ to $\text{U}_{(\text{s})}^{4+}$ upon the surface of nZVI can occur [14], whereas the chemical reduction of U^{6+} is suppressed in solutions containing carbonate [6,17,9]. Specific mechanistic and kinetic investigations into the uptake of uranyl-calcium-carbonate complexes onto nZVI, however, are limited at present [18]. Yan et al. [16] investigated the uptake of U onto nZVI in anoxic conditions batch systems containing NaHCO_3 with and without Ca also present. The work demonstrated that the kinetics of aqueous U^{6+} removal is influenced by the concentration of both Ca and HCO_3^- , namely that the kinetics of aqueous U^{6+} removal in mixed systems (1 mM HCO_3^- and Ca) is comparable to those in systems containing 1 mM HCO_3^- or Ca. Overall, the results demonstrate nZVI as highly effective for the removal of U^{6+} from anoxic waters for Ca and HCO_3^- concentrations up to 1 and 10 mM, respectively. To the best of our knowledge, however, the long-term (e.g. >96 h) retention of U on nZVI in the presence of HCO_3^- and Ca is yet to be investigated. The objective of this work is to investigate this process in batch systems with ambient air used as headspace. The work has been established in order to correlate potential U desorption processes with changes in nZVI corrosion product formation, in order to simulate the eventual recovery of a nZVI subsurface treatment zone to redox conditions prior to nZVI injection. Results are intended to evaluate the long-term integrity of *in situ* U treatment using nZVI, namely the potential for U desorption following the ultimate exposure of the treatment zone to the atmosphere.

2. Materials and methods

2.1. Solution synthesis

All chemicals used in this study [CaCl_2 , $\text{C}_2\text{H}_6\text{O}$, $\text{C}_3\text{H}_6\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, HNO_3 , NaCl , NaBH_4 , NaHCO_3 , NaOH and $(\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$] were of ACS reagent grade and all solutions were prepared using Milli-Q purified water (resistivity >18.2 M Ω cm). Three 400 mL solutions were synthesised comprising U at 1 mg/L and HCO_3^- at 0, 10 and 100 mg/L using $(\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$ and NaHCO_3 respectively. NaCl was then added at 696, 688 and 625 mg/L to the batch systems containing 0, 10 and 100 mg/L NaHCO_3 respectively in order to equalise their ionic strength. A further three 400 mL solutions were synthesised comprising U at 1 mg/L, NaHCO_3 at 0, 10 and 100 mg/L. Equal moles of Ca to Na which was added to the aforementioned 0, 10 and 100 mg/L NaHCO_3 solutions, was also added to the batch systems, which comprised 1321, 1308 and 1189 mg/L of CaCl_2 , respectively. The pH of all systems were adjusted to 8.0 using 0.5 M NaOH . The solutions were stored in sealed glass jars (500 mL

Schott Duran) in the open laboratory with headspace comprising ambient air.

2.2. U-bearing mine water

The U-bearing mine water used was taken from the Ciudanovita Uranium Mine, Banat, Romania. The site is valley confined and bounded by limestone ridges which contribute significant concentrations of HCO_3^- to ground and surface waters. The mine water is pumped from approximately 200 m below sea level. It initially contains trace concentrations of dissolved oxygen (DO), however, quickly equilibrates with the atmosphere to reach concentrations more typical for that of vadose and/or surface waters (7–12 mg/L), changing its redox potential and associated U^{6+} transport properties in the process. The mine water was selected for use herein to provide a natural comparator to the aforementioned synthetic U and HCO_3^- bearing solutions. The mine water was stored in a sealed glass jar (500 mL Schott Duran) in the open laboratory with headspace comprising ambient air.

2.3. Zero-valent iron nanoparticle synthesis

Pure nZVI were synthesised following the method first described by Glavee et al. [19], and then adapted by Wang and Zhang [20], which uses sodium borohydride to reduce ferrous iron to a metallic state. 7.65 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in 50 mL of Milli-Q water (>18.2 M Ω cm) and then a 4 M NaOH solution was used to adjust the pH to 6.8. NaOH addition was performed slowly, drop-wise, to avoid the formation of hydroxo-carbonyl complexes. The salts were reduced to nZVI by the addition of 3.0 g of NaBH_4 . The nanoparticle product was isolated from the aqueous phase via centrifugation (Hamilton Bell v6500 Vanguard centrifuge, 6500 RPM for 120 s), rinsed with Milli-Q water (ratio of 50 mL/g of nZVI) and then centrifuged (Hamilton Bell v6500 Vanguard centrifuge, 6500 RPM for 120 s). This step was then repeated but using ethanol and then acetone as the solvent. The nanoparticles were dried in a vacuum desiccator (approx. 10^{-2} mbar) for 48 h and then stored in an argon filled (BOC, 99.998%) MBraun glovebox until required.

2.4. Experimental procedure

Seven 500 mL Schott Duran jars were each filled with 400 mL of each U-bearing solution. A nZVI mass of 0.2 g (0.5 g/L) was then added. In each case, the nZVI was suspended in 5 mL of ethanol and dispersed by sonication for 30 s. Each batch system was sampled at 0, 0.5, 1, 2, 24, 48, 72, 168, 336 and 672 h. Prior to sampling, the jars were gently agitated to ensure homogeneity and pH, Eh and DO measurements were taken using a Hach multi-meter (model HQ40d) using a combination gel electrode for pH measurements, a gel-electrolyte reference ORP electrode for Eh measurements, and a luminescent/optical dissolved oxygen (LDO) probe for DO measurements. Aliquots of 5 mL were then taken from each batch system and centrifuged using a Hamilton Bell Vanguard V6500 desktop centrifuge at 6500 RPM for 30 s to separate the liquid and solid phases. The supernatant was then decanted, filtered through a 0.22 μm cellulose acetate filter and then prepared for measurement by inductively coupled optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) by the additional of HNO_3 at a concentration of 1% by volume. The solid was prepared for measurement by X-ray diffraction (XRD) by rinsing with Milli-Q water (ratio of 50 mL/g of nZVI) and then centrifuged at 6500 RPM for 120 s using a Hamilton Bell v6500 Vanguard centrifuge in order to separate the solid and aqueous phases. The aqueous phase was then decanted. This step was then repeated but using ethanol and then acetone as the solvent.

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