



Uranium speciation in acid waste-weathered sediments: The role of aging and phosphate amendments

Nicolas Perdrial^{a,*}, Angélica Vázquez-Ortega^{b,c}, Guohui Wang^d, Masakazu Kanematsu^e, Karl T. Mueller^d, Wooyong Um^{d,f}, Carl I. Steefel^g, Peggy A. O'Day^h, Jon Chorover^b

^a Department of Geology, University of Vermont, VT 05405, United States

^b Department of Soil, Water and Environmental Science, University of Arizona, Tucson, AZ 85721, United States

^c Department of Civil and Environmental Engineering and Earth Sciences, University of Notre Dame, IN 46556, United States

^d Pacific Northwest National Laboratory, Richland, WA 99354, United States

^e Anchor QEA, LLC, Portland, OR 97219, United States

^f Pohang University of Science and Technology (POSTECH), Pohang, South Korea

^g Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States

^h School of Natural Sciences, University of California, Merced, CA 95343, United States

ARTICLE INFO

Keywords:

Uranium
Hanford
Acid waste
Phosphate
Uranyl silicates

ABSTRACT

Uranium speciation and lability are strongly coupled to mineral transformations in silicate sediments, particularly for sediments subjected to weathering in acidic, high-level radioactive waste, as occurred at the Department of Energy's Hanford (WA) site. In this study, uncontaminated Hanford sediments were reacted for 365 days with acidic (pH 3), uranium-bearing waste solutions, with and without phosphate in batch experiments, prior to detailed characterizations using electron microscopy, x-ray diffraction and x-ray absorption spectroscopy. In PO₄-reactant free systems, uranium speciation was controlled initially by precipitation of compreignacite [K₂(UO₂)₆O₄(OH)₆·8H₂O]- and becquerelite [Ca(UO₂)₆O₄(OH)₆·8H₂O]-like species. Subsequent further removal of uranium coincided with that of Si and accumulation of boltwoodite, [(K, Na)(UO₂)₂O₄(HSiO₄)₂·0.5(H₂O)]-like species of uranium at 180 and 365 days. When present, PO₄ exerted a direct and strong control over U speciation. The detection of meta-ankoleite, [K₂(UO₂)₂O₄(PO₄)₂·6H₂O] at all reaction times when U was present emphasizes the importance of dissolved phosphate as a control on U speciation. Here, meta-ankoleite appears well crystallized and when it occurs as the principal product of sediment weathering, its low solubility is expected to limit dissolved U(VI) concentrations in groundwater. Although boltwoodite solubility is also low, it is formed more slowly (and only when PO₄ is absent), after initial precipitation of more soluble, less crystalline uranyl hydroxides. In the context of Hanford crib waste our results suggest that with PO₄ present, nearly all uranium would have precipitated in the upper soil.

1. Introduction

The infusion of acidic uranium waste to the Hanford vadose zone represents a case study of process coupling between geochemical weathering and contaminant attenuation. Proton attack, which drives silicate mineral weathering at low pH (Oelkers et al., 2009), is controlled by proton adsorption and associated cleavage of Si-O bonds (Hellmann et al., 2012; Mantha et al., 2012). As a result, dissolution rates trend positively with H⁺ concentration, and exhibit strong dependency on adsorbed proton charge density. In the context of acidic U bearing high level radioactive wastes, the co-occurrence in pore water solutions of soluble products of sediment dissolution and contaminant

discharges can lead to the nucleation and crystal growth of neo-precipitates that can potentially sequester U into immobile forms.

The Hanford Site (WA, USA) covers 1518 km² (586 mi²). Past nuclear weapon-production activities at Hanford resulted in approximately 1.7 trillion L (450 billion gal.) of liquid waste being released to the subsurface vadose and saturated zones (<https://energy.gov/em/hanford-site>). Initial waste-sediment reaction occurs principally in the vadose zone, and much of this liquid waste discharge occurred in the Central Plateau, a 194 km² (75 mi²) area that includes approximately 800 waste sites and 900 facilities that were operated to extract and purify plutonium. The byproducts of this activity were effluents contaminated to varying degrees with radionuclides and chemical

* Corresponding author.

E-mail address: nicolas.perdrial@uvm.edu (N. Perdrial).

toxicants. The most dangerous waste was stored in 177 underground tanks, and some of this waste has been released to the vadose zone. In addition, liquid waste was also discharged into engineered surface “crib” structures and allowed to percolate directly into the vadose zone. This practice resulted in large-scale contamination of the vadose zone and groundwater underlying the Central Plateau (DOE, 2012). Much of the associated contamination remains in the vadose zone and has the potential to enter groundwater in the future, and some has already reached groundwater (Zachara et al., 2007). These crib structures now overlie inactive wastewater disposal sites in the 200 West Area and are part of the U Plant Closure Area at Hanford. The 216-U-8 crib consists of a 9 m deep excavation containing three wooden cribbed timber structures and the 216-U-12 consisting of a perforated vitrified clay pipe placed in a gravel-filled excavation about 5 m deep. Based on historical information and previous soil characterization, the vadose zone beneath both cribs is known to contain radioactive and non-radioactive contaminants (DOE, 2010). Between 1952 and 1988, uranium-containing acidic wastes resulting from acidic process condensates were discharged into the 218-U-8 and 218-U-12 cribs at the Hanford Site. This resulted in a total discharge of 380,000 m³ of waste to 218-U-8 (operated between 1952 and 1960) and 150,000 m³ into 218-U-12 (1960–1988). Uranium total discharge is estimated at 6500 kg for U-12 and 25,500 kg for U-8 for the entire activity period of the cribs. The pH values of the waste streams are not known precisely but readily calculated to be highly acidic (pH 2–3). Variable concentrations of PO₄ were coincident with waste discharges.

The extent of coupling between weathering and U sequestration that has occurred in the U-8 and U-12 crib locations is currently unknown. While silicate dissolution rates exhibit strong pH dependence, this dependence varies strongly with mineral type and dissolution can be non-stoichiometric due to leached surface layer formation (Casey et al., 1989; Fenter et al., 2003; Hellmann, 1997; Hellmann et al., 2012; Hochella et al., 1988; Mantha et al., 2012; Nesbitt and Muir, 1988; Schweda et al., 1997). In contrast to the surface reaction control of silicate dissolution rate, rates of dissolution for highly soluble minerals (e.g., calcite) result from a balance between surface reaction and transport control, and their respective importance varies with pH (Brantley, 2008; Plummer and Busenberg, 1987). Hence, a priori prediction of pore water compositions and neophase mineral formation – including contaminant co-precipitation – is challenging for complex mixtures such as Hanford sediments.

Whereas numerous studies have documented the pH-dependent dissolution of primary silicates and carbonates in mono-mineralic and complex Hanford sediment systems (Bickmore et al., 2001; Chorover et al., 2008; Rod et al., 2010; Mashal et al., 2004; Qafoku et al., 2004; Wan et al., 2004; Ainsworth et al., 2005; Thompson et al., 2010; Chang et al., 2011; Perdril et al., 2011), no prior studies have assessed the weathering of multicomponent Hanford sediments under conditions representative of acidic uranium waste discharges. Since acidic discharges to the vadose zone are known to have occurred in the U-8 and U-12 locations, developing an understanding of the influence of dissolution and ensuing secondary phase precipitation reactions controlling contaminant fate is essential. We predict that mineral transformation reactions that ensue following acid waste infusion to the subsurface will affect uranium speciation in a manner analogous to what was observed for other radionuclides in hyper-alkaline-waste-weathered systems (e.g., Chorover et al., 2008; Perdril et al., 2011).

The behavior of U in the Hanford subsurface is influenced by its ability to form aqueous complexes, change oxidation state, and precipitate in a variety of solid phases (Maher et al., 2013; McKinley et al., 2007). Under oxic conditions, the uranyl ion (U^{VI}O₂²⁺) predominates in both aqueous complexes and as an ionic species in solid phases. Spectroscopic studies of uranium-impacted field samples from Hanford cores have identified uranyl precipitated in silicate, carbonate, and phosphate phases in “microcracks” in some core samples, and as a sorbed uranyl surface complex (Brown et al., 2010; Stubbs et al., 2009;

Um et al., 2010). Aging of contaminant fluids in contact with vadose zone minerals may play an important role in the dissolution of aluminosilicates and re-precipitation of uranyl-containing minerals as surface coatings or in microcracks. Prior characterization of uranium geochemistry and speciation at the Hanford site has emphasized sediments collected in the 300 Area, close to the Columbia River. This constitutes a notable difference with the conditions of the waste cribs simulated here that, located in the 200 area, were not subjected to the effects of river stage oscillations and associated redox state fluctuations.

Uranyl ions form stable aqueous complexes with carbonate and Ca, yielding carbonate, Ca-carbonate, and hydroxycarbonate species that influence uranyl sorption and uranyl mineral solubility (Grenthe et al., 1992; Guillaumont et al., 2003; Rod et al., 2012; Kanematsu et al., 2014; Gartman et al., 2015; Reinoso-Maset et al., 2017). The potential presence of phosphate as a constituent of the waste indicates that uranyl phosphate, efficient at sequestering uranium (Wellman et al., 2008), is a potential solid phase product. Homogeneous precipitation studies have shown that the presence of PO₄ controls U speciation in batch systems with the precipitation of autunite minerals whose specific types are controlled by the composition of cationic co-solutes (Kanematsu et al., 2014; Mehta et al., 2014).

Uranium speciation at Hanford has been mostly studied in the context of systems subjected to caustic, rather than acidic, waste conditions. Its sequestration into neofomed solids from caustic waste-sediment weathering is evidenced from detailed field studies. For example, uranium precipitated as boltwoodite (Na(UO₂)(SiO₃OH)•1.5H₂O) in the micro-fractures of U contaminated sediments under tank BX-102 (impacted by a 2.5–5.0 M Na₂CO₃, pH 10 solution) (Catalano et al., 2004, 2006; McKinley et al., 2007). In the same area at Hanford, Um et al. (2010, 2009) reported that calcium-silicates – uranophane, Ca(UO₂)₂(SiO₃OH)₂(H₂O)₅ – and uranyl phosphates were the main phases immobilizing U. In the 300 area, close to the Columbia River, where processing waste of a wide range of pH (1.8–11.4) has been released, studies have identified uranium phosphate (metatorbernite, Cu(UO₂)₂(PO₄)₂•8H₂O, Arai et al., 2007; Singer et al., 2009) and a rare silicate phase (cuprosklodowskite, Cu[(UO₂)(SiO₂OH)]₂•6H₂O, Singer et al., 2009) as hosts for most of the uranium. In oxic environments (as in much of the Hanford subsurface), previous studies have suggested that solid phase U(VI) is present as the uranyl mineral schoepite (UO₃•2H₂O, Duff et al., 2002). Under caustic conditions (pH 11), Duff et al. (2002) have shown that U incorporation in the hematite structure leads to its immobilization. Murakami et al. (2005) showed field evidence for nanocrystallization of uranyl-phosphate on nano-goethite and nano-hematite.

In the presence of sufficient dissolved Si, uranyl silicates are formed from supersaturated oxic solutions, as was shown when uraninite was reacted for 2 years in oxygenated ground water (Wronkiewicz et al., 1992). According to Burns (2007), uranyl silicates are the most abundant U mineral type, and these also form when spent nuclear fuel reacts with Si-enriched oxic waters, the most common group being the uranophane group.

The objective of this work was to determine the coupling between mineral transformation and U speciation and lability in acid-waste-weathered sediments subjected to a range of influent phosphate and uranium concentrations. Long-term, time series batch reactor experiments were employed to mimic the aging of fluids and solids *in situ* and to assess relations between mineral transformation and contaminant partitioning reactions postulated to have affected Hanford vadose zone sediments when the U receiving cribs were active.

2. Materials and methods

2.1. Batch reaction procedure

To simulate the aging of pristine Hanford sediment during long-term contact with acidic-radioactive-waste, we reacted 20 g of pristine

Download English Version:

<https://daneshyari.com/en/article/8863195>

Download Persian Version:

<https://daneshyari.com/article/8863195>

[Daneshyari.com](https://daneshyari.com)