Chemical Geology 357 (2013) 158–163

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Influence of sediment redox conditions on uranium mobilisation during saline intrusion

Jane Eagling [a,b,*], Paul J. Worsfold [a], William H. Blake [b], Miranda J. Keith-Roach [a,b,c]

[a] Biogeochemistry and Environmental Analytical Chemistry Group, Biogeochemistry Research Centre, Plymouth University, Plymouth PL4 8AA, UK
[b] Consolidated Radio-isotope Facility, Plymouth University, Plymouth PL4 8AA, UK
[c] Kemakta Konsult, Box12655, 112 93 Stockholm, Sweden

ARTICLE INFO

Article history:
Received 24 April 2013
Received in revised form 16 August 2013
Accepted 18 August 2013
Available online 28 August 2013

Editor: David R. Hilton

Keywords:
Uranium
Porewater salinization
Desorption
Transport
Oxic and reduced sediments
Oxidation

ABSTRACT

In the UK, several coastal nuclear sites have been identified as vulnerable to future sea level rise. Legacy contamination at these sites has accumulated in sub-surface sediments at risk of future seawater inundation and intrusion. Porewater salinization, changes in pH and the influx of oxygen into sediments may impact the stability of sediment associated uranium (U). In this study, saturated column experiments were performed to compare the mobilisation of U from oxic and reduced sediments into seawater under environmentally relevant flow conditions. Uranium release profiles were independent of the initial geochemistry of the sediments. Uranium release from the sediments was kinetically controlled, showing relatively slow desorption kinetics, with release initially limited by the impact of the sediments on the pH of the seawater. Significant U release only occurred when the pH was sufficiently high for the formation of U-carbonate complexes (pH_{oxic} 6.3; $pH_{reduced}$ 7.5). Uranium was more strongly bound to the reduced sediments and after 400 pore volumes of seawater flow, release was more extensive from the initially oxic (46%) compared with initially nitrate reducing (27%) and iron reducing (18%) sediments. The products of iron cycling appeared to act as a buffer limiting U mobilisation, but the ongoing dissolution of the Fe-phases suggests that they did not form a permanent protective layer.

1. Introduction

Radioactive waste is generated throughout the nuclear cycle and accidental discharges, and 70 years of nuclear activities have resulted in a significant legacy of contaminated soil and sediment at nuclear facilities worldwide (Reistad et al., 2008; McKenzie and Armstrong-Pope, 2010; Zachara et al., 2013). Due to their need for cooling water several nuclear facilities (e.g. in the UK, the USA and Japan) are located in low lying coastal areas and this close proximity to the shoreline raises questions regarding their future safety with respect to projected climate change and rising sea levels.

Much of the contamination at nuclear sites has accumulated in the sub-surface sediments (McKinley et al., 2006; McKenzie and Armstrong-Pope, 2010) and these will be at risk of seawater inundation and intrusion. Uranium is a long lived radionuclide (^{238}U $t_{1/2} = 4.5 \times 10^9$ years) and is both a persistent and widespread contaminant found at uranium mining and mill tailings sites, nuclear facilities and waste disposal sites worldwide (Riley and Zachara, 1992; McKinley et al., 2006). All of the U isotopes are alpha emitters, chemotoxic and radiotoxic and any remobilisation of U from sediments may lead to human dietary exposure through the consumption of contaminated food (Belles et al., 2013).

Localised areas of reduced sediments are found in sub-surface environments at legacy nuclear sites. The redox conditions in sub-surface sediments are variable; therefore uranium is found in both the reduced U(IV) and oxidised U(VI) forms (Zhou and Gu, 2005; Sharp et al., 2011). Uranium(VI) sorbs to a variety of minerals and related phases including clays (Whicker et al., 2007; Rodriguez et al., 2008), iron (oxy)hydroxides (Martinez et al., 1995; Gómez et al., 2006; Duquene et al., 2008; Sherman et al., 2008) and aluminium and silica oxides (Sylwester et al., 2000). Uranium(VI) can also co-precipitate with iron oxyhydroxides and calcium carbonates (Reeder et al., 2000; Duff et al., 2002) and so its behaviour, at least in some situations, can be influenced by the cycling of other elements in the system. Uranium(IV) species form under reducing conditions, and have a higher affinity for surface binding sites and a lower solubility than U(VI) species (Langmuir, 1978). The product of U(VI) reduction is often uraninite (UO_2) (Ginder-Vogel et al., 2006; Campbell et al., 2011). Additionally, U(VI) that is sorbed to sediment surfaces can be reduced to sorbed U(IV) phases (Gu et al., 2005; Begg et al., 2011).

Uranium(VI) mobilisation can be promoted by the formation of U(VI) carbonate complexes, such as $UO_2(CO_3)_2^{2-}$ or $UO_2(CO_3)_3^{4-}$, when the pH is >6 (Zhou and Gu, 2005; Choy et al., 2006). Thermodynamic data suggests that carbonate does not complex U(IV) or promote UO_2 dissolution under reducing conditions (Guillaumont et al., 2003).

---

[*] Corresponding author at: Biogeochemistry and Environmental Analytical Chemistry Group, Biogeochemistry Research Centre, Plymouth University, Plymouth PL4 8AA, UK. Tel.: +44 1752584568.
E-mail address: jane.eagling@plymouth.ac.uk (J. Eagling).

0009-2541/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.chemgeo.2013.08.030

However, the production of CO_3^{2-} and HCO_3^- during microbial respiration has been shown to promote the formation of stable uranyl carbonate complexes under reducing conditions (Wan et al., 2008).

Since sediments can interact with seawater and lower its pH until the sediment's reactive phases are exhausted, column experiments have been shown to be more appropriate than batch experiments for investigating the impact of seawater inundation on U mobilisation from oxic Dounreay sediments (Eagling et al., 2013). In these column experiments, pH changes were monitored as a function of flow volume and U mobilisation, which began when the pH reached 6.9 due to the formation of U-carbonate complexes. As the pH increased further, mobilisation of U was slow and the elution profile was consistent with kinetically slow release processes.

As well as inducing porewater salinization and altering the porewater pH, seawater intrusion introduces oxygen into reduced sediments, allowing the re-oxidation of sediment associated U(IV). Uranium re-oxidation has been observed in batch experiments at circumneutral pH where U(IV) was rapidly oxidised to U(VI), followed by mobilisation (Law et al., 2011), and this can be accelerated by bicarbonate complexation (Ulrich et al., 2008). However, sediment re-oxidation may not always lead to the mobilisation of U(VI); e.g. Zhong et al. (2005) found that during re-oxidation U mobilisation from Fe-rich Oak Ridge sediments was limited by sorption of U(VI) to the secondary Fe(III) minerals formed. Additionally, Fe(II) sorbed to the outer surface of sediments may re-oxidise to form an Fe(III) oxide veneer that acts as a diffusional barrier, protecting against U(IV) re-oxidation (Zhong et al., 2005).

Relatively few studies have investigated the mobilisation of U(VI)/(IV) from sediments under more environmentally relevant flow conditions (Abdelouas et al., 1999; Moon et al., 2007; Komlos et al., 2008a,b; Moon et al., 2009). Re-oxidation studies have shown that secondary products formed during Fe reduction did not protect U(IV) from oxidation and mobilisation under flow conditions (Moon et al., 2007; Komlos et al., 2008b). A similar effect resulting from the low solubility of Fe reoxidation products has been observed during Tc remobilisation from Fe rich sediments, with flow conditions promoting more Tc mobilisation compared with batch systems (Eagling et al., 2012). However, iron sulphide precipitates formed under more extensively reducing conditions have been reported to act as a buffer, preventing U oxidation and/or release under flow conditions (Abdelouas et al., 1999; Moon et al., 2009). Mackinawite was particularly effective and provided long term protection when formed in sufficient quantities (Abdelouas et al., 1999). Uranium oxidation and/or release from geochemically reducing sediments into seawater has not, however, been investigated.

The aim of this study was to investigate how the initial geochemical conditions of an Fe-rich sediment affect the mobilisation of U during seawater intrusion. Iron-rich sediments with similar properties to the Sellafield, UK site were contaminated with U and either stored open for six months in the dark, or sealed and stored in the dark for different lengths of time to allow the natural microbial communities to change the geochemical redox conditions to nitrate-reducing and then iron-reducing. The sediments were then used in column experiments simulating seawater intrusion to investigate U cycling and release processes in sub-surface environments under environmentally relevant flow through conditions.

2. Methods

2.1. Sediment and water

Sandy, iron rich sediments with a similar mineralogical composition (quartz, silicates and feldspars) and geochemical characteristics to the Quaternary alluvial flood plain deposits that underlie the Sellafield site (Cumbria, UK), as previously characterised by Law et al. (2010), were sampled from Crediton UK (Lat: 50°.8091′N; Long: 03°.6815′W), homogenised and sieved (<2 mm) in a field-moist state. Seawater was collected from the L4 coastal monitoring station in the Western English Channel to avoid estuarine influence (see www.westernchannelobservatory.org.uk) and filtered (0.4 μm Nuclepore™ track edge membrane, Whatman). Characterisation of the sediments is detailed elsewhere (Eagling et al., 2012). A synthetic groundwater solution (pH = 7.2) representative of the Sellafield region (Wilkins et al., 2007) was prepared by dissolving salts in Milli-Q water (the constituents are available in SI Table 1).

2.2. Contamination of oxic sediments with U

Sieved sediment (<2 mm) was amended with simulated groundwater containing U ≈ 25 μM ($UO_2(NO_3)_2.6H_2O$) at a 1 (g):1 (mL) sediment to solution ratio. After a 7 day sorption period, the supernatant was separated from the sediment by centrifugation (10 min at 7500 *g*). Moist sediments were transferred to a container and stored in the dark at 21 °C for a 6 month ageing period. Periodically the container was opened to allow entry of air and ensure that the sediments did not become reducing.

2.3. Contamination of anoxic sediments with U

The U-amended synthetic groundwater was added to sieved sediment to give a 1 (g):1 (mL) sediment:solution ratio and incubated anaerobically in 250 mL serum bottles in the dark at 21 °C. The natural microbial consortium reduced the sediments over time without the addition of amendments. At pre-selected time intervals the serum bottles were transferred to an anaerobic chamber (COY Laboratory Products Inc., MI; 95% N_2, 5% H_2, $O_2 < 50$ ppm) and the slurries transferred into centrifuge vessels. The Eh and pH of the slurries were measured using hand held electrodes. Sediments were separated from the porewater by centrifugation and then the U concentration in the supernatant was determined by ICP-MS (Thermo X Series 2, Thermo Scientific). Redox indicators (NO_3^- and SO_4^{2-}) were determined by ion chromatography (Dionex DX-500). Acid (0.5 M HCl) extractable Fe(II) was determined spectrophotometrically ($\lambda_{max} = 562$ nm) using ferrozine (Stookey, 1970; Lovely and Phillips, 1986). The incubations were targeted to obtain nitrate-reducing and iron-reducing conditions.

2.4. Column experiments

Column experiments were used to simulate the intrusion of seawater into the sediment in order to investigate the release of U from contaminated sediments. Each contaminated sediment (i.e. oxic, nitrate reducing and iron reducing) was packed into a separate polyetheretherketone (PEEK) self-pack column (50 mm × 10 mm; Applied Biosciences) according to Eagling et al. (2012). In order to avoid re-oxidation, reduced sediments were packed into the columns within the anaerobic chamber. The columns were then removed from the anaerobic chamber and oxic seawater was pumped through at a constant flow rate of 1.2 mL h^{-1} using an HPLC pump. The eluate was collected in fractions using a fraction collector at 1.2–3.6 mL intervals. Pre-weighed vessels were placed after every 10 sample vials to check the flow rate (uncertainties associated with the flow rate were <5%).

Experiments involving oxic sediment were shorter (400 pore volumes) than those with initially nitrate-reducing and iron-reducing sediments (1000 pore volumes). Flow was stopped for 2 weeks after approximately 765 pore volumes to investigate whether the U in the eluate was in equilibrium with sorbed uranium in the nitrate- and iron-reducing sediment columns (Qafoku et al., 2005; Yin et al., 2011). At the end of each experiment, the column porosity was characterised using a conservative Br tracer injected as a pulse onto the column. There was only minor variation in Br breakthrough (SI Fig. 1), which indicates that there was only minor variability in column packing and hence in the column porosity. The linear column flow velocities were 268 m y^{-1} (oxic aged), 235 m y^{-1} (nitrate-reducing) and 262 m y^{-1} (iron-reducing). These flow velocities are within the range