



# Fate of $^{90}\text{Sr}$ and $\text{U(VI)}$ in Dounreay sediments following saline inundation and erosion



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## HIGHLIGHTS

- Investigated U and  $^{90}\text{Sr}$  release from Dounreay sediment into seawater.
- Batch and column experiments used, together with sequential extractions.
- $^{90}\text{Sr}$  was exchangeable and mobilised rapidly under erosion and inundation scenarios.
- U release was limited by the sediment's influence on the porewater pH (5.0–6.9).
- At pH > 6.9, U elution profile revealed slow release from a range of binding sites.

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## ABSTRACT

There is concern that sea level rise associated with projected climate change will lead to the inundation, flooding and erosion of soils and sediments contaminated with radionuclides at coastal nuclear sites, such as Dounreay (UK), with seawater. Here batch and column experiments were designed to simulate these scenarios and sequential extractions were used to identify the key radionuclide solid phase associations. Strontium was exchangeable and was mobilised rapidly by ion exchange with seawater  $\text{Mg}^{2+}$  in both batch and column experiments. In contrast, U was more strongly bound to the sediments and mobilisation was initially limited by the influence of the sediment on the pH of the water. Release was only observed when the pH increased above 6.9, suggesting that the formation of soluble  $\text{U(VI)}$ –carbonate species was important. Under dynamic flow conditions, long term release was significant (47%), but controlled by slow desorption kinetics from a range of binding sites.

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## 1. Introduction

Future sea levels are projected to increase as a result of climate change and this raises concerns regarding the gradual inundation, flooding and erosion of low lying coastal areas (Choudhury et al., 2001). The Dounreay nuclear site (Scotland, UK) is currently undergoing decommissioning, but was the centre for the UK's fast reactor research programme and was used for reprocessing and fuel fabrication operations. It is sited  $\approx 50$  m from the shoreline at an elevation of 9–15 m above sea level and has been identified as a UK legacy nuclear sites vulnerable to sea level rise and coastal erosion within the next 160–400 years (Hutchinson et al., 2001; Nirex, 2005).

In general, laboratory and field experiments indicate that a higher salinity has the potential to promote metal mobility by, for example complexation of metal cations by seawater anions ( $\text{CO}_3^{2-}$  and  $\text{Cl}^-$ ) and increased competition for sorption sites ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) (Acosta et al., 2011). Therefore, contaminated sediments at nuclear sites have the potential to act as a future source of radionuclide contamination to the marine environment.

Strontium-90 and U are important components of radioactive waste;  $^{90}\text{Sr}$  ( $t_{1/2}$  29 years) is a high energy,  $\beta^-$ -emitting fission product and U, as the fuel itself, is a major and persistent ( $t_{1/2} = 4.5 \times 10^9$  years) radioactive contaminant found at nuclear facilities, mines and waste disposal sites. Both have been reported in contaminated soils, sediments and groundwater at legacy sites, including Dounreay and Sellafield (Savage et al., 2009; McKenzie and Armstrong-Pope, 2010), and will persist in the environment for long enough to be impacted by predicted sea level rise.

Strontium occurs in most ground and surface waters as the hydrated divalent ion,  $\text{Sr}^{2+}$  and sorbs to a variety of clays (Chen and

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Hayes, 1999; Bellenger and Staunton, 2008), iron oxides (Chiang et al., 2010), quartz (Chen et al., 2006) and silica (Lu and Mason, 2001). In these studies, strontium was electrostatically bound to the matrix as outer-sphere complexes with ion exchange the dominant sorption mechanism. Outer-sphere complexes are weakly associated with surface binding sites and so are generally reversibly bound and mobilised as the porewater pH decreases or ionic strength increases (Stumm and Morgan, 1996; Chen and Hayes, 1999). Surface associated strontium can readily exchange with  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Na}^+$  in solution (Ahmad, 1995; McKinley et al., 2007). Strontium has a relatively weak affinity for solid particles in seawater (Benes and Poliak, 1990) and can be readily released from marine sediments (Benkdad et al., 2008) and river sediments when suspended in seawater (Standring et al., 2002). In addition to ion exchange there is also some evidence of the specific adsorption of strontium on hydrous Fe, Al and Mn oxide coatings on streambed sediments, sand grains and mineral phases (Jackson and Inch, 1989; Trivedi and Axe, 1999), the formation of inner sphere complexes on hematite (Karasyova et al., 1999) and incorporation of strontium into the interlayers of the montmorillonite structure (Lu and Mason, 2001).

In oxic, circumneutral pH environments U(VI) sorbs to mineral surfaces via surface complexation and can accumulate in soils and sediments. Clays (Whicker et al., 2007; Rodriguez et al., 2008), iron (oxy)hydroxides (Gómez et al., 2006; Sherman et al., 2008) and aluminium and silica oxides (Sylwester et al., 2000) are particularly important phases for retaining U(VI) in soils and sediments. Uranium(VI) sorption to soils (Braithwaite et al., 1997), sediments (Zheng and Wan, 2005) and pure phases such as goethite (Giammar and Hering, 2001) has been found to be reversible. Bicarbonate and carbonate are major components of seawater and U(VI) is known to form stable, soluble carbonate complexes. Therefore, during inundation and erosion, the formation of U(VI) carbonate complexes, such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$  or  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Zhou and Gu, 2005; Choy et al., 2006) may increase the mobility of surface associated U(VI).

Batch experiments have been widely used to examine radionuclide mobilisation and/or mobility. Since interactions with sediments influence radionuclide mobility, solid phase speciation characterisation via sequential extraction can identify important binding phases and give a better insight into radionuclide release processes. Sequential extractions can be criticised for a lack of selectivity (Bacon and Davidson, 2008), but are often the only available method when a radionuclide is present in the environment at concentrations below the detection limits of direct speciation techniques such as XANES and EXAFS. Sequential extractions are particularly useful when they are used to compare the association of different contaminants with sediments or to monitor changes in solid phase associations over time (Standring et al., 2002; Wallace et al., 2012). Flow-through column experiments offer an opportunity to examine the mobilisation behaviour of contaminants under dynamic hydrological conditions, which can be poorly represented by the batch approach (Chang and Wang, 2002; van der Sloot et al., 2006). Column experiments represent the saturated sub-surface environment particularly well, and the elution profiles can provide detailed information on the release processes taking place (Eagling et al., 2012).

In this study, the mobilisation of  $^{90}\text{Sr}$  and U release from Dounreay sediments is assessed using batch and dynamic flow experiments that model inundation, temporary flooding and erosion scenarios. Sediments sourced from Dounreay were contaminated in the laboratory with  $^{90}\text{Sr}$  and U and aged for 6 months to simulate field-contaminated sediments. Prior to mobilisation experiments, changes in the association of radionuclides with the sediments over time were identified using sequential extractions. Batch experiments were used to investigate the processes driving

radionuclide release during inundation and flooding scenarios by comparing release into the end member waters, i.e. groundwater (salinity 0) and seawater (salinity 35). A low salinity water (salinity 4) was chosen to represent the mixing of the inundating seawater with fresh porewater during the early stages of seawater intrusion. Short term (<48 h) experiments were designed to simulate erosion scenarios using a lower sediment:solution ratio in groundwater and seawater. Finally, saturated column experiments were used to investigate radionuclide release into seawater under more environmentally relevant flow through conditions.

## 2. Materials and methods

### 2.1. Sediment and water sampling

Sediments from the nuclear facility at Dounreay (Scotland, UK) were supplied by the Land Remediation Site Dounreay Project Delivery Unit. Sediments were sieved (<2 mm) and homogenised prior to use in the experiments. Seawater (salinity 35) was sampled from the L4 coastal monitoring station in the Western English Channel (<http://www.westernchannelobservatory.org.uk>). Salts were dissolved in Milli-Q water to create a synthetic groundwater representative of that found at the low level waste repository at Drigg (Cumbria, UK; see Supplementary data Table S1 for the constituents) (Wilkins et al., 2007). Low salinity water (salinity  $\approx 4$ ) was prepared by mixing the groundwater and seawater end members (ratio  $1_{(\text{seawater})}:9_{(\text{groundwater})}$ ).

### 2.2. Sediment characterisation

The mineralogy of the sieved sediments was determined by X-ray diffraction (Siemens D5000). Particle size distribution was determined by laser diffraction (Malvern Long-bed Mastersizer-X) and the specific surface area determined using BET  $\text{N}_2$  adsorption (Micromeritics Gemini). Cation exchange capacity was determined by cation exchange with sodium ions following the US Environmental Protection Agency SE-846 Method 90812. Major elemental composition was determined using ICP-MS (Thermo X Series 2, Thermo Scientific) following an aqua regia (3:1  $\text{HCl}:\text{HNO}_3$ ) digestion. Organic carbon content was determined using an elemental analyser (EA 1110 CHN Analyser) after digestion of inorganic carbon (4 M HCl > 48 h). Sediment pH was measured in Milli-Q water using a (1:1) sediment to solution ratio.

### 2.3. Sediment contamination and ageing

Sediments (<2 mm fraction) were amended with a simulated groundwater solution containing (a)  $^{90}\text{Sr}$  (Amersham International) to give a final concentration of  $200 \text{ Bq mL}^{-1}$  ( $4.4 \times 10^{-10} \text{ M}$ ) and (b) uranium (25  $\mu\text{M}$  added as  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ). Separate incubations were used to contaminate the sediments with  $^{90}\text{Sr}$  and U respectively. Incubations were prepared using a 1(g):1(mL) ratio, and were shaken in the dark for 7 d. After a 7 d sorption period the sediment was separated from the solution by centrifugation (10 min at 7500g). Blanks showed that there was no adsorption to the vessel walls and the  $^{90}\text{Sr}$  and U associated with sediments was calculated by mass balance. After contamination, sediments were homogenised and transferred to separate plastic storage boxes and incubated in the dark at  $21 \pm 0.5^\circ\text{C}$  for 6 months, with periodic opening to re-supply  $\text{O}_2$  to the sediments prior to use in the batch and column mobilisation experiments. An adapted five step Tessier sequential extraction procedure (Tessier et al., 1979) was adopted to investigate any differences in the sorption of  $^{90}\text{Sr}$  and U to the sediments and changes in the operationally defined chemical associations during the ageing period. In the sequential extractions

sediments were progressively leached in triplicate to determine the exchangeable fraction (1 M  $\text{MgCl}_2$ /pH 7/1 h), carbonate fraction (1 M sodium acetate/pH 5/5 h), reducible fraction (0.1 M ammonium oxalate/pH 2/16 h), oxidisable fraction ( $\text{H}_2\text{O}_2$ /followed by 1 M ammonium acetate/in 6%  $\text{HNO}_3$ /16 h) and the residual fraction (aqua regia/2 h).

#### 2.4. Batch mobilisation

After 6 months ageing the sediments were homogenised, subsampled and transferred to centrifuge vessels (polycarbonate) before use in mobilisation experiments. All experiments were conducted in triplicate using separate experiments for  $^{90}\text{Sr}$  or U contaminated sediments. To simulate inundation scenarios, aged contaminated sediment samples were amended with groundwater, low salinity water (salinity 4) or seawater (salinity 35) to give a 1(g):1(mL) sediment:solution ratio and shaken (70 rpm) in the dark ( $21 \pm 0.5^\circ\text{C}$ ) for pre-determined times up to 90 d. To simulate erosion aged sediments were re-suspended in groundwater or seawater at a lower sediment to solution ratio of 1 g:10 mL ( $^{90}\text{Sr}$  and U) and 1 g:100 mL (U only). Slurries were shaken to ensure that particles were permanently in suspension for up to 48 h. At pre-determined time intervals, batch experiments were destructively sampled, the pH was measured, the sediment was separated from solution by centrifugation and the supernatant was analysed for Ca, Mg, U and  $^{90}\text{Sr}$ .

#### 2.5. Column design and operation

Each contaminated, aged sediment was packed into a polyetheretherketone (PEEK) self-pack column (50 mm  $\times$  10 mm; Applied Biosciences, Foster City, USA) with a 0.2  $\mu\text{m}$  in-line filter frit following Eagling et al. (2012). Columns were packed in small increments and the column was tapped gently to allow the sediment to settle and eliminate air pockets. Columns were saturated with seawater using an upwards flow and a constant flow rate (1.2 mL  $\text{h}^{-1}$ ) was achieved using a HPLC pump. The column outflow was collected at regular intervals using an automated sample fraction collector. Columns were characterised using a conservative bromide tracer. Both Br profiles exhibited similar narrow peaks which suggests that the columns were packed consistently and that there were no preferential flow paths. The linear flow velocity was calculated to be 253  $\text{m y}^{-1}$  ( $^{90}\text{Sr}$ ) and 229  $\text{m y}^{-1}$  (U) respectively which is within the natural range of flow velocities observed in sandy aquifers (Mackay et al., 1985).

#### 2.6. Radionuclide and metal determinations

Aqueous  $^{90}\text{Sr}$  was determined by liquid scintillation (Beckman LS6500 scintillation counter) after a 28 d delay to ensure equilibrium between  $^{90}\text{Sr}$  and  $^{90}\text{Y}$  had been re-established. Uranium, Fe and Br were determined by ICP-MS (Thermo X series 2) and Ca and Mg were determined by ICP-OES (Varian 725-ES).

### 3. Results and discussion

#### 3.1. Sediment characteristics

Dounreay sediments were composed of quartz and phyllosilicates. Sediments were classified as a sandy loam composed of sand (52%) and silt (43%) and low clay content (5%). This classification is consistent with the low specific surface area (5.92  $\text{m}^2 \text{g}^{-1}$ ), cation exchange capacity ( $12 \pm 1 \text{ cmol kg}^{-1}$ ), and pH of  $4.4 \pm 0.2$ . The major element composition of the sediments ( $\text{mmol kg}^{-1}$ ) determined following an aqua regia digestion was Al ( $300 \pm 9$ ), Ca ( $33 \pm 3$ ), Fe

( $280 \pm 8$ ), Mg ( $140 \pm 4$ ), Mn ( $5.0 \pm 0.3$ ), Si ( $25 \pm 1$ ) and Sr ( $0.10 \pm 0.01$ ) respectively; there was no detectable  $^{90}\text{Sr}$  or U in the sediments. The total organic carbon content of the sediments was 4% by mass.

#### 3.2. Uptake and solid phase associations

Uranium and  $^{90}\text{Sr}$  sorbed rapidly to the sediments; after the 7 d sorption period  $80 \pm 2\%$  of the  $^{90}\text{Sr}$  and  $99 \pm 4\%$  of the U was associated with the sediments. Aqua regia digestion confirmed that there was no change in the percentage sorbed to the sediments during the ageing period (6 months).

Sequential extractions showed that  $^{90}\text{Sr}$  was predominately associated with the exchangeable fraction (76%) and that this remained the dominant phase after the ageing period (Fig. 1). This has been observed previously in sandy iron rich sediments, aged for 1 year, and suggests that  $^{90}\text{Sr}$  was retained in the sediments as weakly bound outer-sphere complexes that would be readily mobilised from sediments (Wallace et al., 2012).

In contrast, the exchangeable sorption sites were not important for uranium sorption (Fig. 1). Uranium was initially associated with the carbonate and reducible fractions and there was a re-distribution in the association of U with the sediments during the 6 month ageing period. This was characterised by a decrease in the percentage of U associated with the carbonate fraction and the more strongly binding fractions becoming increasingly important.

#### 3.3. Inundation scenario

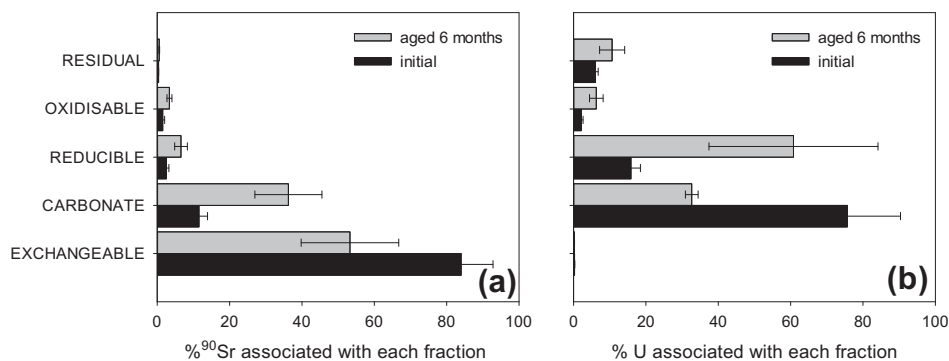
The addition of sediment to the experimental waters resulted in a rapid pH decrease in groundwater (pH 7.35–5.20), low salinity water (pH 7.80–5.80) and seawater (pH 8.20–5.00) (Fig. 2). Strontium mobilised rapidly from the sediment into all three types of water, with a similar total amount ( $\approx 20\%$ ) mobilised into the groundwater and low salinity water (Fig. 2). Therefore the increase in porewater salinity from 0–4 did not promote  $^{90}\text{Sr}$  mobilisation from these sediments. However, inundation with seawater resulted in much greater  $^{90}\text{Sr}$  mobilisation (Fig. 2c). Within 1 h, more  $^{90}\text{Sr}$  was released into seawater than at any point in the other batch experiments ( $37 \pm 2\%$  compared with 17–22%).

In the seawater experiments, both  $\text{Ca}^{2+}$  and  $^{90}\text{Sr}^{2+}$  were mobilised from the sediments while  $\text{Mg}^{2+}$  was removed from the seawater (Fig. 2), indicating that ion exchange with  $\text{Mg}^{2+}$  played a dominant role in  $^{90}\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  release. This exchange mechanism is facilitated by the similarities in ionic radii of these divalent cations (Ahmad, 1995; Bunde et al., 1997; McKinley et al., 2007) and the high  $\text{Mg}^{2+}$  concentration in seawater (53 mM). At the end of the 90 d experiment a significant fraction of the sorbed  $^{90}\text{Sr}$  (59%) was mobilised in the seawater incubations, with 41% remaining associated with the sediment.

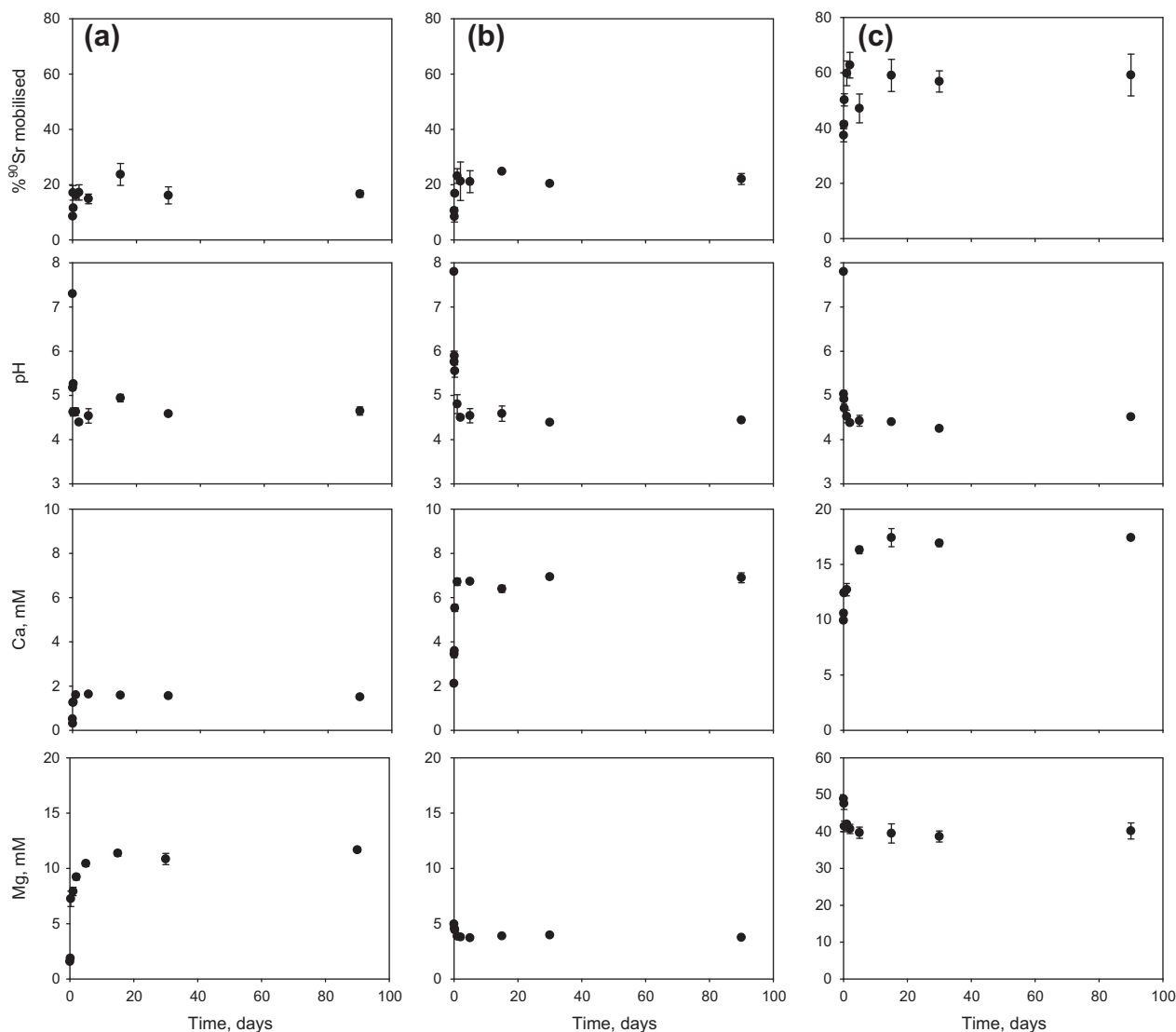
During the inundation scenario there was limited release of U into all of the experimental waters. Mobilisation of sorbed U(VI) is generally enhanced via the formation of soluble uranyl carbonate complexes (Zhou and Gu, 2005; Choy et al., 2006). However, the rapid and significant decrease in the pH of the experimental waters (pH 4.0–5.0) in these experiments due to the high (1:1) sediment:water ratio would remove carbonate, which may explain why U(VI) was retained on the sediments.

#### 3.4. Erosion scenarios

Strontium release in the erosion scenario was again more rapid and extensive into seawater than groundwater (Fig. 3), e.g. after 30 min significantly more  $^{90}\text{Sr}$  was mobilised into seawater ( $84 \pm 12\%$ ) compared with groundwater ( $18 \pm 1\%$ ). The initial release of  $^{90}\text{Sr}$  into seawater was also more rapid and greater than



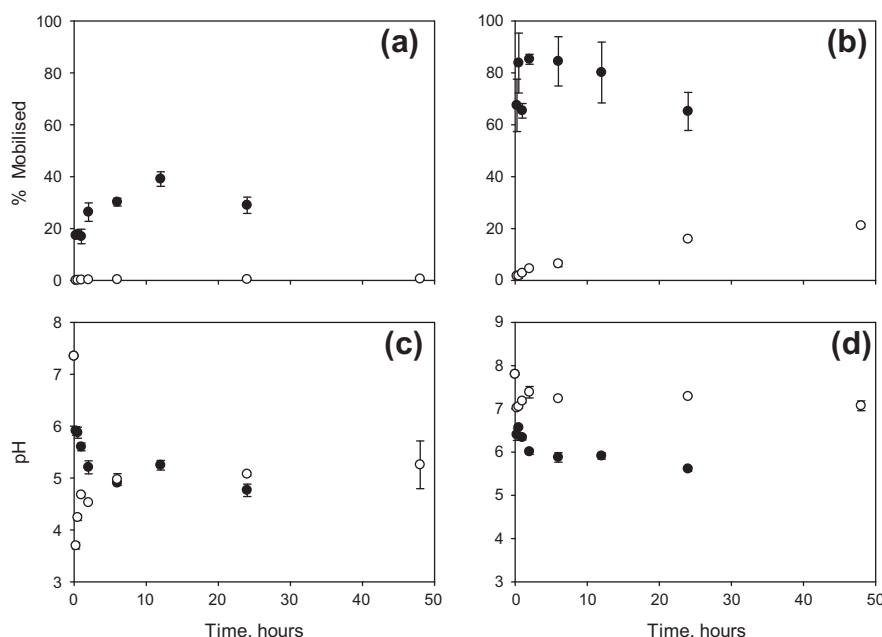
**Fig. 1.** Changes in the association of (a)  $^{90}\text{Sr}$  and (b) U with Dounreay sediments during a 6 month ageing period. Each bar represents the mean of three separate extractions  $\pm 1$  standard deviation.



**Fig. 2.** Changes in the solution phase concentrations of  $^{90}\text{Sr}$ , Ca and Mg and corresponding changes in pH during the inundation 1(g):1(mL) scenario using aged (6 months) Dounreay sediments in (a) groundwater, (b) low salinity water (salinity 4) and (c) seawater (salinity 35). Data show the mean values of three separate extractions, error bars represent  $\pm 1$  standard deviation. Note the different scales for Ca and Mg in the seawater experiments.

seen in the inundation scenario. However, after 2 h the concentration of  $^{90}\text{Sr}$  decreased, showing that a fraction of the  $^{90}\text{Sr}$  was re-adsorbed. Therefore, at the end of the 24 h experiment, a similar fraction of the  $^{90}\text{Sr}$  was dissolved in the seawater in the erosion

( $65 \pm 1\%$ ) and inundation ( $59 \pm 8\%$ ) scenarios. In contrast, release of  $^{90}\text{Sr}$  into groundwater during the erosion scenario was greater than during the inundation scenario throughout the entire experiment. The rapidity of  $^{90}\text{Sr}^{2+}$  desorption into seawater is consistent



**Fig. 3.** Mobilisation of (●)  $^{90}\text{Sr}$  and (○) U from aged (6 months) Dounreay sediments in (a) groundwater and (b) seawater during erosion scenarios and corresponding changes in pH in (c) groundwater and (d) seawater respectively. A 1(g):10(mL) sediment to solution ratio was used in the  $^{90}\text{Sr}$  incubations and a 1(g):100(mL) sediment to solution ratio in the U incubations. Data show the mean values of three separate extractions, error bars represent  $\pm 1$  standard deviation. The results for the U (1:10) experiments (data not shown) were below the limit of detection.

with an ion exchange process, as identified in the inundation scenario experiment and supported by the sequential extraction data (Fig. 1a).

In these experiments, the pH was again affected by the sediment, particularly for the groundwater incubations. Uranium therefore remained recalcitrant to release into groundwater and seawater at a 1 g:10 mL sediment to solution ratio, but was mobilised at a 1 g:100 mL sediment:solution ratio. Even at this ratio, there was a limited release of U into groundwater (pH 5.3; Fig. 3a); at the end of the 48 h experiment  $\approx 99\%$  of the sediment associated U remained recalcitrant to mobilisation, as seen in the inundation scenario. However, when re-suspended in seawater, the seawater alkalinity played a significant role in buffering the seawater systems more effectively against changes in pH (pH 7.0–7.4). At the end of the 48 h experiment, a significant fraction of the total U had been mobilised, with  $21 \pm 0.7\%$  of the sorbed U released from the sediments.

### 3.5. Release into seawater under dynamic conditions

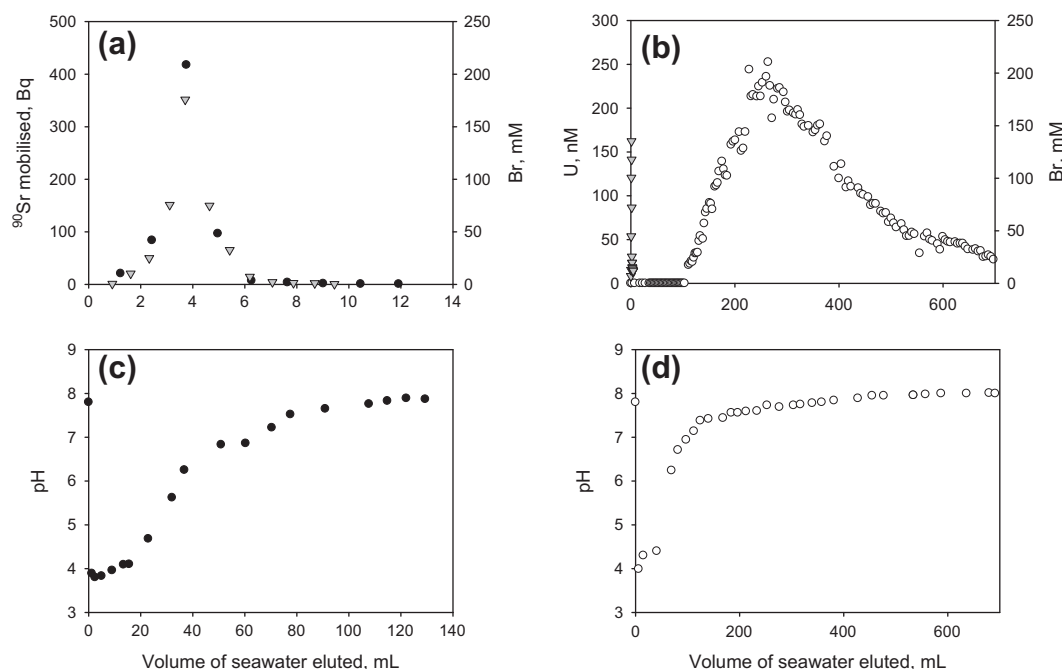
The mobilisation of  $^{90}\text{Sr}$  and U under dynamic flow through conditions is shown in Fig. 4. As seawater flowed through the columns, the sediments initially altered the pH of the seawater from an inflow of pH 7.8 to an outflow of  $\approx$ pH 4.0. This is consistent with the pH changes seen in the inundation batch seawater experiments at a high sediment to solution ratio. The pH of the eluate increased steadily, as more seawater flowed through the column, and then remained relatively constant (pH 7.8–8.0) over the remainder of the experiment.

The release of  $^{90}\text{Sr}^{2+}$  closely followed the elution pattern of the conservative Br tracer (Fig. 4) showing that  $^{90}\text{Sr}$  was rapidly mobilised and when released had a low interaction with the sediments. The symmetrical shape of the  $^{90}\text{Sr}$  elution peak suggests that  $^{90}\text{Sr}$  association with the sediment is  $K_D$  controlled, i.e.  $^{90}\text{Sr}$  is associated with ion exchange sites with rapid exchange kinetics. Significantly more  $^{90}\text{Sr}$  was mobilised under flow conditions (99%)

compared with the seawater batch experiments (65% after 48 h), despite the sediment:solution ratios of the batch experiments (1:1 and 1:10) being similar to the ratio of the sediment in the column to the amount of solution required to elute all of the  $^{90}\text{Sr}$  ( $\approx 1:2$ ). However, in the 24 h batch erosion experiments, 84% of the  $^{90}\text{Sr}$  was initially mobilised, followed by kinetically controlled re-adsorption of  $\approx 20\%$  of the  $^{90}\text{Sr}$ , which would not happen under flow conditions. The flow rate applied to the column was representative of groundwater flow rates (Mackay et al., 1985) which means that the column data are most appropriate for describing release and transport processes in the sub-surface, and suggest that during dynamic events such as seawater inundation and erosion almost complete release of  $^{90}\text{Sr}$  would be expected.

Since the sediments affected the pH of the seawater (decreased from 8.2 to 4.0), there was an extended period when no U was mobilised from the sediments, and U release was therefore retarded with respect to the Br tracer (Fig. 4 b). Uranium mobilisation was only observed after 110 mL of seawater had flowed through the column and the eluant pH increased above pH 6.9. This is consistent with the batch erosion incubations and suggests that surface associated U(VI) desorption was mediated by the formation of soluble U(VI) species such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$  (Zhou and Gu, 2005; Choy et al., 2006). Following the peak in U release, there was significant tailing in the U release profile. This is indicative of kinetically controlled release from sites with slow desorption kinetics and/or a re-distribution of slow and fast reactive sites, including diffusion from intra-particle regions, prior to mobilisation (Qafoku et al., 2005; Handley-Sidhu et al., 2009). Sequential extractions conducted prior to mobilisation experiments showed that U was associated with a range of binding sites (Fig. 1b). A fraction of the U was exchangeable and therefore rapidly released. In addition, there was some degree of incorporation into the bulk solid material (Fig. 1), resulting in a slower rate of desorption, which would give rise to the broad distribution of release rates observed here. The largest fraction of U was mobilised during the tailing period after the maximum peak (at 260 mL) which suggests





**Fig. 4.** Mobilisation of (a)  $^{90}\text{Sr}$  (●) and (b) U (○) from aged Dounreay sediments during saturated flow through column experiments with seawater. Elution of Br (▼) injected as a tracer are also shown in (a) and (b) respectively. The corresponding changes in pH in the (c)  $^{90}\text{Sr}$  column outflow and (d) U column outflow also shown. Note the different scales for the volume of seawater eluted.

that relatively slow desorption kinetics will dominate the mobilisation of U in the natural environment. At the end of the column experiment 49% of the uranium sorbed to the sediments had been mobilised.

### 3.6. Conclusions and implications for coastal legacy sites

This study has identified two types of mobilisation behaviour during temporary flooding, inundation and erosion of Dounreay sediments with seawater, which relate to the sediment associations of the radionuclides. Strontium-90 was mainly associated with exchangeable and carbonate surface binding sites even after a 6 month incubation period and showed rapid mobilisation into seawater driven by ion exchange with  $\text{Mg}^{2+}$ . The batch experiments showed that kinetically controlled re-adsorption of  $^{90}\text{Sr}$  can take place, but did not affect release under seawater flow conditions.

In contrast, U became increasingly associated with less exchangeable binding sites over the 6 month ageing period. Its release was controlled by the pH of the water phases, which was affected by the sediments. Therefore, when seawater enters U contaminated sediments, mobilisation will initially be limited by the ability of the sediments to control the seawater pH. However, when sufficient seawater has been in contact with the sediment, mobilisation will occur. The column experiments showed that, once the pH was higher than 6.9, U(VI) mobilisation was kinetically controlled and characterised by slow release from a range of binding sites. Surface U(VI) desorption appears to be mediated by the formation of soluble U(VI) species such as  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{CO}_3)_3^{4-}$  in seawater.

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### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.02.059>.

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