Europium interaction with a vault backfill at high pH

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ABSTRACT

Batch experiments have been used to assess the sorption properties of a potential cementitious repository backfill, NRVB (Nirex reference vault backfill), using Eu^{3+} as a model trivalent radionuclide and ethylenediaminetetraacetic acid (EDTA) as a competing ligand. The NRVB is an effective scavenger of Eu from solution, with most sorbed within minutes onto the crushed material and less than 1.5% remaining in solution after one day (R_d values in the range $0.3-2.4 \times 10^4 \, l \, kg^{-1}$). Ultrafiltration showed that nearly all of this remaining Eu (>94%) is attached to NRVB derived colloids or particulates that are mainly retained by a 100 kDa ultrafilter. High concentrations of EDTA (>0.01 M) reduced the extent of sorption at apparent equilibrium. The addition of EDTA to a pre-equilibrated system of Eu^{3+} and NRVB resulted in a temporary suspension of some Eu, but this very quickly returned to the solid phase. There is some irreversibility in these systems, with EDTA able to prevent removal of Eu(III) from solution, but unable to bring it back into solution under the same conditions.

Introduction

GEOLOGICAL disposal is UK Government policy for the long-term management of higher activity radioactive wastes (Department for Environment Fisheries and Rural Affairs *et al.*, 2008). The UK currently has no site identified for a geological disposal facility (GDF) and is considering a number of illustrative disposal concepts (Nuclear Decommissioning Authority, 2010). For intermediate-level and some low-level wastes, these include multi-barrier concepts, where waste packages in underground vaults will be backfilled with a cementitious material as part of the engineered barrier system (EBS). One potential backfill is NRVB (Nirex reference vault backfill; Nuclear Decommissioning Authority, 2010; McCarter *et al.*, 2004). Degradation of the backfill will generate a region of high alkalinity (Braney, 1993; Nuclear Decommissioning Authority, 2010) in and around a GDF, which will promote metal

ion hydrolysis and sorption. The NRVB has been designed to provide these properties. It is based on ordinary Portland cement (OPC) with aggregate material containing crushed limestone and hydrated lime. The composition of NRVB (weight fraction) is OPC 26%; limestone 29%; hydrated lime 10 %; water 35%. The backfill, when cured, has a porosity of 0.5, a density of 1730 kg m^{-3} and a compressive strength of 6 MPa (Francis *et al.*, 1997). The aim of this work is to study the sorption of Eu(III) by the NRVB.

A number of authors have studied the interactions of trivalent lanthanide and actinide ions with cements (e.g. Dario *et al.*, 2006), concretes (e.g. Baston *et al.*, 1995), calcium silicate hydrates (C-S-H) (e.g. Pointeau *et al.*, 2001) and calcite (e.g. Zavarin *et al.*, 2005). Pointeau *et al.* (2004) have suggested that C-S-H is the most important phase in cements (although they studied uranyl ions). For Nd(III), the sorption seems to be dominated by C-S-H, and portlandite and silica interactions are expected to be much less important if they are present (Mandaliev *et al.*, 2010). Pointeau *et al.* (2001) used lumines-

cence spectroscopy to study Eu interactions with C-S-H. Sorption was very strong ($R_d > 1.8 \times 10^5$ l kg^{-1}) for all values of calcium to silicon ratio, C/S, in the C-S-H (0.66−1.25). For higher C/S systems (0.83−1.65), two distinct types of Eu were found, which were assigned as surface complex and incorporated within the structure. The spectra were similar to that of Eu sorbed to tobermorite. Although portlandite was present in the C/S = 1.65 sample, there was no evidence for Eu sorption to it. Later, Tits *et al.* (2003) also used luminescence to identify two types of Cm(III) interactions with C-S-H, one where the Cm retains 1.4 coordinated waters and another with none. Both types are assumed to represent Cm incorporated in a tobermorite-like structure at the Ca sites: the first type is consistent with a labile 7-coordinate Ca site with 2 waters and/or a site with coordination by six structural oxygen atoms and one water; the second type is consistent with a 7-coordinate Ca site, where all coordinating oxygen atoms are structural. With time, transfer of Cm was observed from the type 1 to type 2 sites. Tits *et al.* (2003) reinterpreted the data of Pointeau *et al.* (2001), and showed that the Eu data indicated one site with two waters and another with none, and so Cm and Eu behaviour are very similar. Schlegel *et al.* (2004) studied Eu interactions with C-S-H as a function of C/S. For all samples, removal from solution is rapid, and the net result is incorporation of Eu within a C-S-H structure (at Ca sites). For the lower C/S systems (0.7−1.0), the process seems to be initial surface complexation, followed by 'diffusion' into the structure. However, batch data suggested that at high C/S (1.3), the Eu is at least partly removed from solution by co-precipitation. Despite the different mechanisms, the final coordination environment was the same. Mandaliev *et al.* (2010) studied Nd(III) interactions with C-S-H using EXAFS. Changes in Nd−Ca/Si bond lengths are consistent with initial inner sphere complexation at the surface, followed by progressive incorporation of Nd at Ca sites within the C-S-H structure. There is some incorporation after 1 day, and there is a significant increase over the following 45 days. Sorption of Eu(III) to calcite is also strong (R_d in the range 3×10^4 to 10^5 l kg^{-1},) and rapid at high pH (13.3) (Tits *et al.*, 2005). There is spectroscopic evidence that trivalent radionuclides [Cm(III)] form inner sphere surface complexes on contact with calcite, but that incorporation within the structure takes place with time (Stumpf and Fanghanel, 2002).

For Eu in particular, there is evidence that incorporation is possible (Curti *et al.*, 2005).

Although there are a number of studies in the literature on europium interactions with calcite, cements and hydrated calcium silicates, there are none describing the interactions with NRVB. Therefore, the primary aim of this work is to study the interactions of Eu^{3+} (as a surrogate trivalent actinide) with NRVB and to test whether any Eu associated particulate material is produced in solution. The effect of ethylenediaminetetraacetic acid (EDTA) on sorption is also studied, because as a strongly complexing ligand, it allows us to assess the strength of the NRVB as a sorber and also to test sorption reversibility, which is rarely studied in the literature. Some radioactive wastes may have EDTA present due to its use as a decontamination agent at nuclear facilities (e.g. Toste *et al.*, 1995) and organic ligands can affect the transport of radionuclides by competing with sorption and hydrolysis (Keith-Roach, 2008). Ethylenediaminetetraacetic acid has the ability to chelate trivalent and tetravalent actinides and is known to be persistent in the environment (Means *et al.*, 1980). However, the amounts that may be present in UK wastes disposed to a GDF are relatively small compared to the amounts of cellulosic materials that may degrade to form complexants (estimated 2005 UK inventory, 850 kg; Heath and Williams, 2005).

Experiments were performed in 'NRVB water', which is water that has been allowed to equilibrate with NRVB. The solutions are in equilibrium with portlandite and represent the likely background solution in the engineered barrier system during its evolution. The effect of added NaClO$_4$ has been studied to determine the effect of changes in the background electrolyte, which might take place during the life of a GDF.

Experimental

For all experiments, a controlled atmosphere Perspex glove box filled with N$_2$ was used to exclude CO$_2$ and prevent carbonation (pCO$_2$ <5 ppm). Before it entered the box, the N$_2$ gas (supplied as CO$_2$ free) passed through two Dreschel bottles, with sintered frits, full of saturated NaOH solution to remove any remaining traces of CO$_2$, followed by a further water filled Dreschel bottle to remove any NaOH aerosols. Even though the samples were kept in the glovebox, they were kept in sealed, gas tight containers, apart from the short time during sampling.

The three components of NRVB (ordinary Portland cement, limestone flour and hydrated lime) were mixed in the ratio 265:291:100 for 20 min. Water was then added in a ratio of 1.8:1 (solid:water). The mixture was stirred for 3 h, and then left to set and cure in the glove box for 28 days. The cured cement samples were crushed using a tungsten carbide grinder and then sieved. Only the $125-250$ μm fraction was used in the experiments described here. The Ca and Si contents of the OPC (as SiO_2 and CaO) are 19.5 and 64.4%, respectively. Taking into account the limestone and hydrated lime, the C/S ratio is 8.5.

Batch experiments were prepared in polypropylene tubes (Fisher Scientific). The ^{152}Eu radiotracer was added to each system, so that the total Eu concentration (stable plus radiotracer), $[Eu^{3+}_T]$, was 7.91×10^{-10} M; NRVB was added to each system in multiples of 0.05 g. Experiments were performed with and without $NaClO_4$ added to the NRVB water. In some systems, EDTA was added to give final, total concentrations of 0.1, 0.01 or 0.001 M. Where EDTA was added, the final pH was the same as the equivalent experiment in the absence of EDTA to allow comparison. The total solution volume was 10 ml.

The solutions were sampled following centrifugation (3000 rpm; 5 min). Based on the density of the NRVB, the rotational velocity, sampling depth, rotor arm length and spinning time, assuming spherical particle shapes, the centrifugation is approximately equivalent to filtration with a 0.5 mm pore size filter. The Eu concentrations were obtained using a Ge semiconductor γ-ray detector (121.88 keV γ-ray line); EDTA concentrations were measured using UV−visible spectroscopy. The UV−Vis spectra were recorded on a double beam Cary Varian 500 scan UV−vis–nIR spectrophotometer (range $200-800$ nm, typical scan rate 600 nm min^{-1}). The pH measurements were made with a Sentex combination pH electrode and a Seven Easy, Mettler Toledo meter. The electrode was calibrated with pH 7 and 9 buffer capsules (Whatman), and its response tested against a pH 13 buffer solution. Following the approach of Pointeau *et al.* (2004), uncertainties were estimated by repeating a representative system five times.

In one experiment, the solution obtained following centrifugation was analysed by ultrafiltration using a Millipore device attached to a nitrogen cylinder, according to the technique of Pitois *et al.* (2008). The membranes had pore sizes of 100, 10 and 3 kDa (approximately equivalent to 3.1, 1.4 and 0.9 nm, respectively).

Before use, the cell and the membranes were washed repeatedly with deionized water and pre-treated once with 10^{-4} M $Eu(NO_3)_3$ solution to saturate the membrane sorption sites: a previous study (Pitois *et al.*, 2008) had shown this was necessary to prevent sorption of ^{152}Eu. Note: the solutions were not routinely ultrafiltered.

Speciation calculations were performed using the United States Geological Survey thermodynamic speciation code *PHREEQC Interactive* (version 2.17.5.4799, released September 2010) and using the Specific Interaction Theory Database '*ThermoChimie v.7.b*', developed by Amphos 21, BRGM and HydrAsa for ANDRA. The thermodynamic datum for Eu^{3+} and EDTA interaction was obtained from Martell and Smith (1974) and corrected to zero ionic strength using the Davies equation.

Results

Figure 1 shows the percentage of Eu remaining in solution after centrifugation (in absence of $NaClO_4$) plotted *vs.* the mass of NRVB after 24 h equilibration time. Time series experiments (data not shown) showed that apparent equilibrium was achieved after only a few hours. Only small quantities (<1.5%) of Eu could be detected in solution after 24 h. Control experiments and speciation calculations confirmed that, at the concentrations reported in this work, Eu^{3+} is not subject to precipitation as a simple hydroxide. The pH of the NRVB water in contact with 0.005 and 0.02 g ml^{-1} NRVB was 12.4±0.1 and 12.5±0.1, respectively.

Europium was equilibrated with NRVB (0.005 g ml^{-1}). The supernatant was then ultrafiltered through 100 kDa, 10 kDa and 3 kDa membranes to determine Eu size fractionation (Fig. 2). Ninety-four percent of all Eu in the solution phase was present as clusters or colloidal material (i.e. it appeared in the >3 kDa fractions) and 6% was present as free ion or 'simple complexes' in solution. In fact, most Eu (92%) was in the largest (>100 kDa) fraction. These colloids/large species must be NRVB derived, because in the absence of NRVB, but at the same pH, the Eu is in the <3 kDa fraction. Therefore, the sorption data suggest that the Eu is largely NRVB associated in these systems, either bound directly to the bulk NRVB or to NRVB derived colloids/particulates, and very little of the solution phase loading can be thought of as true solution (e.g. $Eu(OH)_{3(aq)}$, $Eu(OH)_{4^-(aq)}$).

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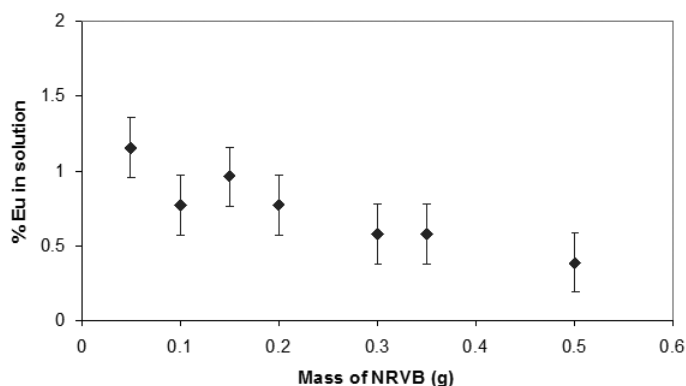
FIG. 1. Plot of Eu^{3+} remaining in solution relative to NRVB mass; equilibrated for 24 h; no added $NaClO_4$; solution volume = 10 ml; $[Eu_T] = 7.91 \times 10^{-10}$ M.

Figure 3 shows the the effect of added $NaClO_4$ (0.1 M) on Eu^{3+} sorption. For the 0.005 g ml^{-1} system, more Eu (approximately 4%) remains in solution compared to a system with no added $NaClO_4$ (compare the data in Figs 1 and 3, final time point), but for the 0.01 and 0.015 g ml^{-1} systems, the increase is modest (<1%), and for the 0.02 g ml^{-1} system, there is no significant difference. As for NRVB water systems, the process is NRVB mass dependent, and a 0.005 g ml^{-1} NRVB system has 6% Eu remaining in solution, compared to approximately 2% for $0.01-0.015$ g ml^{-1} systems and 0.2% for a 0.02 g ml^{-1} system. For solid:solution ratios greater than 0.02 g ml^{-1}, no Eu remained in solution at equilibrium. The pH of the solutions in contact with 0.005 and 0.02 g ml^{-1} NRVB was 13.1±0.1 and 12.9±0.1, respectively.

No sorption of EDTA to NRVB was detected at any of the solid:solution ratios studied here. Figure 4 shows the change in solution phase Eu concentration with time as a function of EDTA concentration (with added $NaClO_4$, 0.1 M) at a solid:solution ratio of 0.03 g ml^{-1} NRVB, which was chosen because Eu could not be detected in solution at this solid:solution ratio in the absence of EDTA, and so the effect of EDTA could easily be detected. In this experiment, the Eu and EDTA were allowed to equilibrate first before the introduction of the solid NRVB. The amount of Eu remaining in solution increases with EDTA concentration, with up to 30% for 0.1 M EDTA, whereas 0.01 M allows approximately 20% in the solution phase (Fig. 4). A concentration of 0.001 M EDTA is too small to suspend much Eu indefinitely, however, it does increase the time
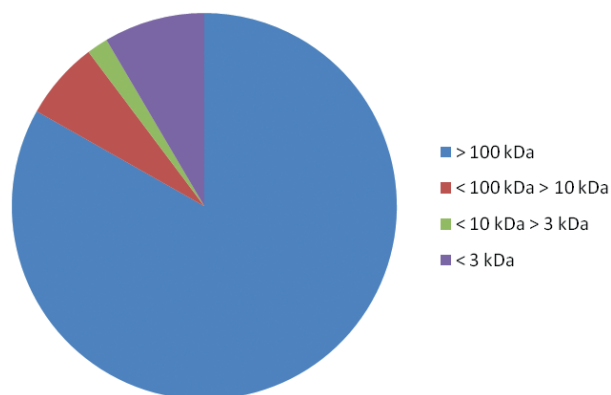

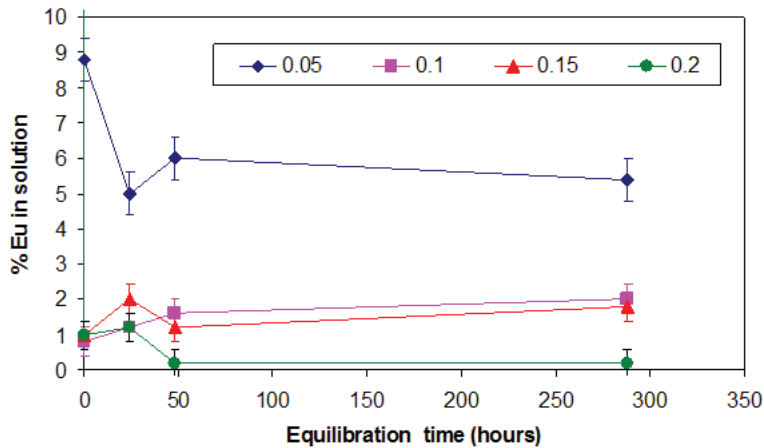FIG. 2. Pie chart showing Eu size fractionation in NRVB water determined by ultrafiltration (no added $NaClO_4$).

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FIG. 3. Plot of Eu^{3+} sorption (plotted as a percentage of Eu remaining in solution) to NRVB *vs*. equilibration time, as a function of NRVB mass (g); Solution volume = 10 ml; $[NaClO_4]$ = 0.1 M; $[Eu_T]$ = 7.91×10^{-10} M.

before the concentration falls towards zero, compared to a system with no EDTA. Note, the apparent increase in concentration at 120 min is probably an artefact. To determine the reversibility of Eu^{3+} sorption to NRVB, Eu^{3+} was pre-equilibrated with NRVB for various times before the addition of 0.1 M EDTA. The results are shown in Fig. 5. In all systems, there is an initial suspension of Eu^{3+} accompanying the addition of EDTA, but the concentration remaining in solution quickly decreases. The reason for the short-term increase in Eu solution concentration is uncertain, but is probably due to the temporary

suspension of NRVB particles following the sudden change in solution chemistry. Whatever the mechanism, such a short-term effect (<1 day) is unlikely to be significant on a geological timescale.

Discussion

Table 1 shows the results of speciation calculations for systems with and without added Na (0.1 M). These NRVB systems are chemically complex. X-ray diffraction confirms the presence of portlandite and calcite in the cured solid.
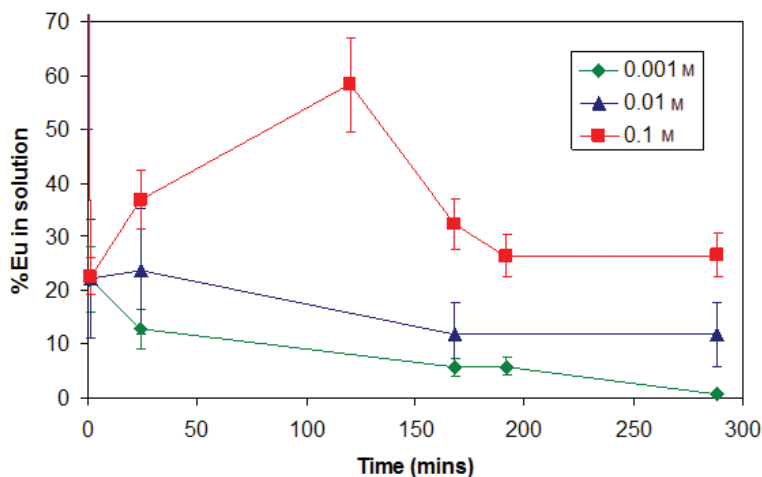

FIG. 4. Plot of Eu^{3+} sorption as a function of EDTA concentration; solution volume = 10 ml; 0.3 g NRVB; $[Eu_T]$ = 7.91×10^{-10} M, $[NaClO_4]$ = 0.1 M.

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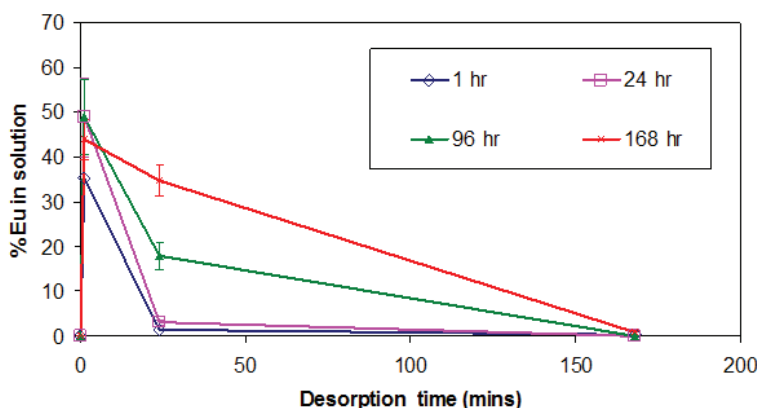
Fig. 5. Desorption of Eu^{3+} with the addition of EDTA (0.1 M) with varying Eu^{3+}/NRVB (0.3 g) equilibration times; $[Eu_T] = 7.91 \times 10^{-10}$ M; $[NaClO_4] = 0.1$ M.

Calcium silicate could not be detected, but it will be present in the NRVB, although at a lower concentration than for previous studies (dilution by hydrated lime and limestone), and as a possibly disordered or amorphous phase, it would be hard to detect by XRD. Therefore, calculations were made assuming equilibrium with: (1) portlandite (only); (2) portlandite and calcite; (3) portlandite, calcite and C-S-H (C/S = 1.6). All data in Table 1 are for system (3). In fact, it was found that the calculated speciation was extremely insensitive to the presence of the calcite or C-S-H. The system is dominated by the portlandite equilibrium, and the concentrations of species with concentrations greater than $1 \times 10^{-4}\%$ are independent of the presence of calcite or C-S-H, which result in very small concentrations of: $EuSiO(OH)_3^{2+}$ (C-S-H) and $Eu(CO_3)^+$, $Eu(CO_3)_2^-$, $Eu(CO_3)_3^{3-}$, $Eu(HCO_3)^{2+}$ (calcite). The NRVB does contain Na and K.

TABLE 1. Europium speciation (expressed as percentages) predicted by *PHREEQC* for solutions in equilibrium with the phases in NRVB (See text for details of the calculations). Data given for systems with no added Na and for solutions with 0.1 M added $NaClO_4$. The final column is for a calculation with final pH forced to 13.1.

PHREEQC predicted values	No added Na pH = 12.48; $I = 0.053$; [Ca] = 0.0205 M	[Added Na] = 0.1 M pH = 12.52; $I = 0.161$; [Ca] = 0.024 M	Final pH = 13.1 pH = 13.1* $I = 0.274$; [Ca] = 0.0029 M
$Eu(OH)_3$	95.36	94.05	94.24
$Ca_2(Eu(OH)_4)^{3+}$	0.90	1.61	0.045
$Eu(OH)_4^-$	1.10	1.31	5.25
$Ca(Eu(OH)_3)^{2+}$	1.22	1.48	0.123
$Eu(OH)_2^+$	1.23	1.22	0.337
$Ca_3(Eu(OH)_6)^{3+}$	0.18	0.33	0.0092
$Eu(OH)^{2+}$	5.97×10^{-5}	7.23×10^{-5}	6.04×10^{-6}
$EuSiO(OH)_3^{2+}$	2.89×10^{-8}	3.49×10^{-8}	2.92×10^{-9}
$Eu(CO_3)^+$	2.52×10^{-8}	2.50×10^{-8}	6.89×10^{-9}
Eu^{3+}	3.44×10^{-9}	6.14×10^{-9}	1.71×10^{-10}
$Eu(CO_3)_2^-$	1.15×10^{-9}	1.38×10^{-9}	5.67×10^{-9}
$Eu(CO_3)_3^{3-}$	2.10×10^{-13}	6.34×10^{-13}	5.49×10^{-11}
$Eu(HCO_3)^{2+}$	2.33×10^{-16}	1.92×10^{-16}	1.31×10^{-17}

* This value set in input data.

Calculations showed that even if all of the alkali metal content of the samples dissolved in the water, there was no significant difference in the Eu speciation.

Three separate calculations are reported in Table 1. The first two columns report the results when pH 7 water (first column) and pH 7 0.1 M $NaClO_4$ (second column) are allowed to equilibrate with portlandite, calcite and C-S-H (C/S = 1.6). A slightly higher final pH is predicted for the system with $NaClO_4$, which is due to the effect of the increased ionic strength on the activity coefficients. This is also the reason for the higher Ca concentration in the second column. The activity coefficient effect, combined with the different Ca concentration is responsible for the minor changes in speciation. In the experiments, the systems with added Na do have higher pH than the NRVB water. The NRVB is quite different to the C-S-H and cement samples that have been studied previously, but the pH values recorded here are in the same region as for previous studies. For example, Dario et al. (2006) report cement solution pH in the range $12.3-12.7$ ($I = 0.3$; 0.001 g ml^{-1}), whereas Baston et al. (1995) measured pH 12.4 for concrete and 12.2 for mortar at 0.02 g ml^{-1}, and Pointeau et al. (2008) measured pH 13.2 for fresh cement at 0.940 g ml^{-1}. As the real pH for the data in Fig. 3 is higher than predicted in the second column of Table 1, a third calculation was performed where the final pH was 'forced' to 13.1 to show the effect on the speciation. The most significant result is that the concentration of 'free Eu^{3+}' is negligible in these systems (all columns), and the speciation is dominated by hydroxide complexes (with or without Ca).

The data in Fig. 1 for sorption to NRVB without added Na correspond to R_d values in the range of $0.5-1.7 \times 10^4$ l kg^{-1}, whereas in the presence of added Na (0.1 M, Fig. 3), the R_d range is $0.3-2.5 \times 10^4$ l kg^{-1}. Dario et al. (2006) studied the interaction of Eu(III) with Portland cement: sorption was strong ($R_d = 4 \times 10^6$ l kg^{-1}, $I = 0.3$, pH = $12.3-12.7$, 1 g l^{-1}). Baston et al. (1995) measured Am(III) uptake on concrete ($R_d = 1.3 \times 10^5$ l kg^{-1}, pH = 12.4, 20 g l^{-1}) and mortar ($R_d = 4.5 \times 10^4$ l kg, pH = 12.2, 20 g l^{-1}). Tits et al. (2003) studied C-S-H Eu sorption across the range [Eu] = $10^{-10}-7 \times 10^{-7}$ M. Sorption was strong and rapid, with an R_d of 6×10^5 l kg^{-1} (0.5 g l^{-1}). Zavarin et al. (2005) measured calcite Eu R_d values of $1.3-8.8 \times 10^3$ l kg^{-1} after 1 day, which increased to $0.36-5.1 \times 10^4$ l kg^{-1} with time, but

these data were recorded in equilibrium with the air and in the pH range $7-10$, and so it is hard to compare the values with those reported here. Tits et al. (2005) reported R_d values for Eu^{3+} sorption on calcite of approximately 10^5 l kg^{-1} and 3×10^4 l kg^{-1}, at solid:solution ratios of 0.2 and 2 g l^{-1}, respectively at pH = 13.3 and [Ca] = 1.6 mM. Therefore, the values found here are most similar to those for mortar (Baston et al., 1995), also our solid:solution ratios ($5-20$ g l^{-1}) are in the same range as Baston et al.(1995). However, our R_d values are significantly lower than for the C-S-H systems and calcite (under similar conditions). Several authors have reported that in cement systems, sorption is dominated by C-S-H, and that portlandite is not expected to compete (see above). The C-S-H and calcite content of the solid phase in NRVB is low compared to previous studies (e.g. Tits et al., 2003, 2005), and so the lower R_d values may be a result of the fact that the stronger sorbers are diluted in the NRVB.

There is strong evidence from the literature that Eu(III) sorption to C-S-H and calcite is 'inner sphere' in nature, with direct bonding between the Eu and oxygen atoms of the solid phases (e.g. Tits et al., 2003, Schumpf and Fanghanel, 2002). Sorption to NRVB will be more complex than for these simpler systems, because there are at least three phases present in the solid, and each could have multiple binding sites. Pointeau et al. (2004) found that charge reversal on the surface of C-S-H is possible due to the sorption of Ca^{2+} ions onto the C-S-H surface. The high Ca concentration in the NRVB should result in significant Ca^{2+} sorption, and possibly potential reversal. Beyond any effect on potential, we would expect competition between Eu and Ca for C-S-H binding sites. Also, the NRVB surface binding sites will have to compete with the complexes in Table 1 for Eu. The very low concentration of free Eu^{3+} in the table indicates the strength of competition. In particular, the calculations suggest that hydroxide will compete very effectively for Eu. Therefore, the intrinsic equilibrium constants for sorption are likely to be much higher than the empirical R_d values calculated from the data in Figs 1 and 3.

The spectroscopic studies in the literature all agree that for C-S-H and calcite, there is direct bonding between the sorbed Eu and the structural oxygen atoms. Most studies have interpreted the data in terms of surface complexation, followed by some degree of incorporation (e.g. Mandaliev et al., 2010; Schumpf and Fanghanel, 2002).

However, Schlegel *et al.* (2004) found that for C-S-H systems with high C/S (like NRVB), the mechanism is co-precipitation of the Eu with C-S-H derived ions, and they found that the loss of Eu from solution was independent of C-S-H mass. In these systems, it seems likely that the calcium and silicon concentrations are determined by equilibrium with portlandite and C-S-H, respectively. In this case, we would expect any C-S-H co-precipitation to be independent of mass of sample. Indeed, Schlegel *et al.* (2004) found that the removal from solution was the same when the solid sample was removed completely. The speciation data (Table 1) lend some support to the suggestion of Schlegel *et al.* (2004), as mixed Eu/Ca clusters are predicted to form. No ternary Eu/Ca/silicate species are predicted in solution or as solids, but the database does not contain the data to allow that prediction.

Figures 1 and 3 both suggest an increase in sorption with mass of NRVB. To test whether the effect of sample mass could be explained by a surface complexation mechanism, the data in Figs 1 and 3 (final time points) were analysed (Fig. 6). Provided that the amount of Eu is small compared to the available number of binding sites and that the relative solution speciation is unaffected by sample mass (i.e. that the background solution chemistry is constant), for surface complexation, the solid:solution distribution ratio will be proportional to the mass of the solid sample, assuming that the concentration of binding sites is proportional to NRVB mass. For both datasets, the distribution ratios for the lowest mass samples were calculated. Then, the ratios at the other masses were estimated, assuming that they were proportional to the mass of NRVB. The lines in Fig. 6 show the results of those calculations. The match is by no means perfect. For the systems with added Na, there is a strong correlation between amount sorbed and mass, which is predicted reasonably well up to a mass of 0.15 g NRVB. For the largest mass, the effect of mass on sorption is greater than predicted (the reason in unclear). For the no added Na system, the change in sorption across the mass range is less than that predicted (note: line misses error bars). Therefore, considering the data in Figs 1 and 3, it seems that some surface complexation is probably taking place in both experiments, because of the dependence of sorption on mass, but that relationship is not exactly as expected from a system where only surface complexation is taking place, and the possibility that some co-precipitation is taking place certainly cannot be ruled out.

Added Na^+ has a relatively minor effect on Eu sorption. It seems highly unlikely that Na^+ ions are directly competing with the Eu^{3+} ions. Further, it seems unlikely that this is a colloidal effect, because an increase in ionic strength would be expected to destabilize any colloids (whatever the polarity of the surface potential), which would lead to a reduction in solution loading. The small observed differences are probably related to the change in the predicted speciation upon addition of $NaClO_4$. At pH = 13.1, there is increased
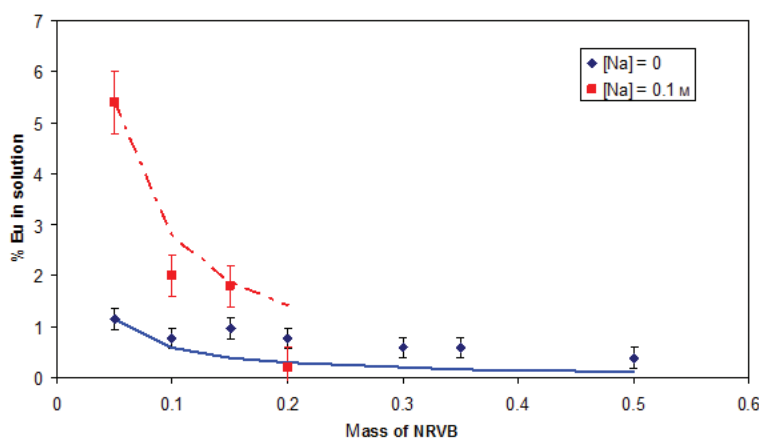

FIG. 6. Percentage of Eu remaining in solution: experimental data, (symbols) for systems with no added Na (squares) and with added [Na] = 0.1 M (diamonds); predictions (lines) of variation in Eu solution loading based on experimental values for the highest and lowest mass systems assuming a pure surface complexation mechanism (full line for systems with no added Na; dashed lines for systems with added [Na] = 0.1 M).

competition from hydroxide complexation (see reduction in Eu^{3+} concentration between first and third columns in Table 1), which could reduce sorption by surface complexation or co-precipitation. For the co-precipitation mechanism of Schlegel *et al*. (2004), the change in the activity coefficients of the ions in solution associated with an increase in total ionic strength could affect co-precipitation. For a system in equilibrium with portlandite, the total Ca concentration is predicted to be lower at pH 13 than at 12.5, which would be expected to reduce Eu removal by co-precipitation of a Eu-containing C-S-H phase.

The ultrafiltration experiment has suggested that some Eu is associated with material in the colloid size range. Ramsey *et al*. (1988*a,b*) studied the production of colloids from OPC, and found relatively large particles in solution (of the order of 1 μm), but some of these were aggregates of smaller species. There was evidence that the colloidal material had grown in solution (rather than formation by fragmentation of the bulk). In experiments with Eu(III), the Eu appeared in the solution phase, probably associated with colloidal calcium silicate (Ramsay *et al*., 1988*b*), which would be consistent with the co-precipitation mechanism of Schlegel *et al*. (2004). Conversely, Wieland and Spieler (2001) studied colloid generation in a mortar (cement/quartz) column. They detected only low concentrations of colloids in the size range 50−1000 nm (their analytical window), by extrapolation they estimated colloid concentrations <100 ppb (10^{12}−10^{14} colloids per litre) across the size range 1−1000 nm. A later study (Wieland *et al*., 2004) found that the concentration of C-S-H derived colloids was reduced by 3 orders of magnitude by raising ion concentrations to those expected in the early stages of cement degradation ([Ca] = 1.7 mM), although their technique was insensitive to colloids in the range <50 nm. Given the large difference in effective size between the cut-off of the centrifugation procedure in this work and the pore size of the 100 kDa ultrafiltration, it is possible that some of the 92% of the Eu in the >100 kDa size range is actually attached to relatively large particulate material (up to 1 μm). However, there is evidence of small amounts of Eu associated with colloidal material in the nanometre size range. These may be Eu associated with NRVB particles/colloids, or they could be co-precipitated material that has formed from the Ca and Si in solution.

It is clear that relatively high concentrations of EDTA can reduce the sorption of Eu in these systems. At equilibrium, 0.001 M EDTA cannot retain Eu in solution, but 0.01 M EDTA is able to compete. Dario *et al*. (2006) studied the effect of EDTA on the interaction of Eu(III) with Portland cement (pH = 12.3−12.7, 1 g l^{-1}). They found that concentrations of EDTA greater than approximately 0.001 M were required to produce a significant effect, but then there was a very strong reduction in sorption with increasing EDTA concentration. This behaviour may be explained qualitatively, as the EDTA complexes Eu^{3+} ions and hinders sorption by competition. Calculations with *PHRREQC* showed that $Eu(EDTA)^-$ accounts for less than 1% of Eu in solution at [EDTA] = 0.001 M, but that increases to 99% at [EDTA] = 0.01M. Therefore, to a first approximation, the behaviour in Fig. 4 and that in Dario *et al*. (2006) is consistent with the predicted speciation.

The results in Fig. 5 suggest that there is significant irreversibility in these systems, because the same concentrations of EDTA are able to prevent Eu sorption if they are added to the Eu before addition to NRVB (Fig. 4), but they cannot bring Eu back into solution once the Eu has interacted with the NRVB. Studies of sorption reversibility are rarely reported. However, it is a significant process as if radionuclide sorption is irreversible to some extent, radionuclide mobility will be reduced even more than predicted by the batch sorption R_d. The EDTA desorption data suggest that there is significant irreversibility in these systems. Irreversibility could be explained by the transfer of Eu(III) from surface complexes to incorporation in the C-S-H or calcite structure that has been observed for trivalent lanthanides and actinides (see introduction and Mandaliev *et al*., 2010; Pointeau *et al*., 2001; Schumpf and Fanghanel, 2002). Alternatively, co-precipitation of Eu within a C-S-H like structure would also result in irreversibility. The fact that irreversibility develops so quickly could suggest that co-precipitation may be responsible, because the transfer between surface complex to incorporated would be expected to take longer (e.g. Mandaliev *et al*., 2010; Stumpf and Fanghanel, 2002).

Conclusions

The NRVB is an effective sorber of Eu^{3+} from solution; addition of $NaClO_4$ produces a small reduction in sorption. Ultrafiltration has shown that the majority of Eu remaining in solution is present as particulate/colloidal species with

effective sizes >100 kDa/3 nm. The solid:solution ratio in a repository would be much greater than 0.02 g ml^{-1} and could be as high as 2.7 g ml^{-1} (Aggarwal *et al*., 2001). The results suggest that the solution concentration, for Eu will be negligible at realistic solid:solution ratios. The EDTA allows a much greater proportion of Eu^{3+} to remain in solution, although only at relatively high concentrations of EDTA (>0.001 M). At the solid:solution ratios expected in a GDF, realistic concentrations of EDTA would not be expected to compete with NRVB sorption (for Eu). Further, there is evidence for the development of some irreversibility with time. Thus, our experiments show that NRVB is a very effective sorber of Eu^{3+}. The mechanism of sorption is unclear, and both surface complexation and co-precipitation may be taking place in these systems. The complex behaviour is probably due to the fact that at least three phases are present in the NRVB, which each have their own interaction mechanism. It is possible that Eu is removed by co-precipitation with ions from one phase, and that surface complexation dominates for another.

Acknowledgements

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