

Sorption of radionuclides to a cementitious backfill material under near-field conditions

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ABSTRACT

The sorption behaviour of I^- , Cs^+ , Ni^{2+} , Eu^{3+} , Th^{4+} and UO_2^{2+} on NRVB (Nirex reference vault backfill) a possible vault backfill, at pH 12.8 was studied. Sorption isotherms generated were compared to results obtained in the presence of cellulose degradation products (CDP). Whereas Cs was not affected by the presence of the organic compounds, a notable reduction in the sorption of Th and Eu to cement was observed. The results also indicated limited removal of Ni from solution (with or without an organic ligand) by sorption, the concentration in solution seemingly being determined solely by solubility processes. In the case of uranium, the presence of CDP increased the sorption to cement by almost one order of magnitude. Further studies into the uptake of CDP by cement are being undertaken to identify the mechanism(s) responsible.

KEYWORDS: vault backfill, europium, geological disposal, radioactive waste, sorption, thorium, uranium, uranyl.

Introduction

ILLUSTRATIVE concepts for the disposal of intermediate-level and some long-lived low-level radioactive waste (ILW and LLW) in the UK are based on deep geological disposal using a multi-barrier system (Nuclear Decommissioning Authority, 2010). The packaging of much ILW for disposal is based on conditioning by mixing or encapsulation with a cement grout in stainless steel containers. These would then be placed in an underground vault or tunnel, depending on the concept chosen. The waste form and the container (together forming the waste package) provide the first two barriers to migration of radionuclides. The vault or tunnel would eventually be backfilled with further cementitious material such as NRVB (Nirex reference vault backfill) (Nirex, 1997) to buffer the pH of the repository to highly alkaline

values. It is anticipated that the high pH, in combination with reducing conditions produced by the corrosion of metals in the wastes and containers, will decrease the solubility and retard the migration of many radionuclides. This ‘chemical containment’ contributes another barrier to radionuclide migration as part of the multi-barrier system.

The aim of this work is to demonstrate the viability of the above approach to chemical containment. In this paper, the sorption capabilities of NRVB are assessed and compared with the behaviour of its individual components, namely: ordinary Portland cement (OPC), limestone flour and hydrated lime. The radionuclides studied (I^- , Cs^+ , Ni^{2+} , Eu^{3+} , Th^{4+} and UO_2^{2+}) cover a wide range of oxidation states and aqueous speciation.

Some waste packages will contain a significant amount of cellulosic material that may undergo alkaline degradation under the repository conditions. The result of this chemical decomposition is a complex mixture of water-soluble organic

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compounds that may affect both the solubility of key radionuclides and also their sorption behaviour. These compounds are known collectively as cellulose degradation products (CDP) with α -isacosaccharinic acid and β -isacosaccharinic acid (ISA) amongst the most abundant products along with variable amounts of low molecular weight organic acids (e.g. acetic acid) and miscellaneous unidentified compounds (Pourchez *et al.*, 2006). The CDP may affect the effectiveness of the waste disposal system by modifying the sorption of radionuclides to cement (van Loon and Glaus, 1998) and/or contributing to the generation of gas (CO_2 and CH_4) by microbial means (Small and Dutton, 2009). In the present work, the sorption of a selection of radionuclides to the backfill material NRVB has been assessed in the presence of the CDP leachates under conditions of significance to the UK repository concept.

Experimental

Preparation of NRVB and composition of equilibrated water

The NRVB is a high porosity cement containing 450 kg m^{-3} OPC, 170 kg m^{-3} hydrated lime, 495 kg m^{-3} limestone flour and 615 kg m^{-3} water (Holland and Tearle, 2003). The three solid components of the NRVB were mixed as powders on a bench top conical mixer in a polypropylene hexagonal barrel (Pascall Lab-mixer II, Pascall Engineering, Crawley, UK) at

6 rpm for at least 4 hours until homogenized. The required amount of water was added to the powder and mixed together by hand. The resulting mixture was poured into a 70 cm^3 polypropylene container, tapped to remove air bubbles and allowed to set for 24 h before removing from the moulds and curing under water in closed containers. After a period of 4 months the NRVB blocks were dried under vacuum to avoid carbonation and then manually crushed and sieved. The fraction between 250 and $500 \mu\text{m}$ was selected to perform the sorption experiments. The BET (Brunauer Emmett Teller) surface area was measured using a Micromeritics Gemini VI physisorption system at the British Geological Survey (Keyworth, UK). The resulting value for NRVB was $17.07 \pm 0.12 \text{ m}^2 \text{ g}^{-1}$ (\pm standard deviation, SD). Powder XRD data were collected using a Bruker D8 Advance diffractometer in reflection geometry, $\text{CuK}\alpha_1$ radiation and a linear position sensitive detector. For phase identification, data were collected over the range $5\text{--}90^\circ 2\theta$ with a step size of 0.007° and a count time of 0.1 s. The XRD spectrum (Fig. 1) shows that the main component of cured NRVB is portlandite, with significant calcite from the limestone. For comparison purposes, the spectra of an older specimen of NRVB and fresh (uncured) NRVB are shown. In fresh NRVB, calcite dominates and there is also some contribution from hatrurite (Ca_3SiO_5). The change in the peak intensity ratios indicates that, in the older specimens, the latter

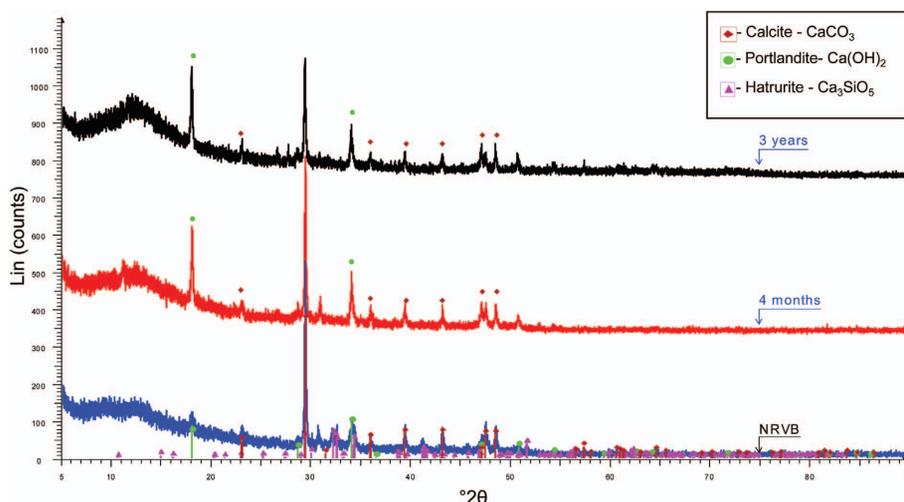


FIG. 1. XRD spectra of fresh NRVB powder (dry components), an NRVB specimen after 4-months and after 3-years curing.

contribution disappears and crystalline portlandite dominates the mineralogical composition. Only minor differences are apparent between the 4-month and 3-year cured specimens.

For the preparation of NRVB-equilibrated water, the cement was mixed with previously boiled and N₂-sparged deionized water at a solid:liquid ratio of 1:50, and kept agitated in an orbital shaker under CO₂-free conditions. After 8 days equilibration, the solution was filtered prior to use in the sorption experiments. The total inorganic carbon was determined using a wet oxidation TOC analyser (GE) and the elemental composition was determined by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent, 7700x series) in semi-quantitative mode. Table 1 shows the main characteristics of the NRVB-water.

Preparation of cellulose degradation products and elemental composition

The preparation of CDP followed a modification of the procedure reported by Chambers *et al.* (2004); 750 cm³ deionized water was placed in a stainless steel can and sparged with N₂ (1 h); 30 g

of Kimwipe tissues were cut into small pieces (approximately 2 cm²) and added to the steel canister, followed by 370 g of powdered NRVB. After mixing, it was purged again for 30 min, and finally, the container was closed tightly, weighed and placed in an oven at 80°C for 30 days. In all cases, evaporation over the preparation period was below 1%. The solution was filtered under CO₂-free conditions before use in the sorption experiment. The main characteristics of CDP liquor are summarized in Table 1. The amount of α-ISA in the mixture, determined by reversed phase HPLC (C18 column and UV-Vis detection) was approximately 1.5 × 10⁻³ mol dm⁻³ (see Heath, 2008 for more details on the chromatographic method).

Batch sorption experiments

All experiments were carried out in quadruplicate, in 25 cm³ polypropylene tubes, in a glove box under a controlled N₂ atmosphere at room temperature; 50 mg of the powdered NRVB or its components were weighed into a tube and mixed with 20 cm³ of either NRVB-water or water containing CDP, followed by the addition

TABLE 1. Composition of NRVB-water and CDP mixture.

Element	Concentration (average±1SD, mol dm ⁻³)	
	NRVB-water	CDP
Ca	(8.7±0.1) × 10 ⁻³	(8.6±0.2) × 10 ⁻³
Na	(4.3±0.7) × 10 ⁻⁴	(4.0±0.9) × 10 ⁻³
K	(3.6±0.1) × 10 ⁻⁴	(7.7±0.2) × 10 ⁻³
S (total)	(2.0±0.4) × 10 ⁻⁴	(2.3±0.6) × 10 ⁻⁴
Si	(9.6±0.1) × 10 ⁻⁵	(9.6±0.2) × 10 ⁻⁵
Sr	(1.13±0.07) × 10 ⁻⁵	(3.0±0.1) × 10 ⁻⁵
Cl	(3.0±0.2) × 10 ⁻⁴	(3.5±0.1) × 10 ⁻⁴
Li	(2.7±0.1) × 10 ⁻⁵	(1.4±0.1) × 10 ⁻³
Mg	(3.8±0.1) × 10 ⁻⁷	(2.6±0.1) × 10 ⁻⁷
Al	(3.4±0.2) × 10 ⁻⁷	(7.9±0.2) × 10 ⁻⁷
Ba	(1.6±0.1) × 10 ⁻⁶	(3.5±0.1) × 10 ⁻⁶
P	(5.0±0.1) × 10 ⁻⁶	(8.4±0.2) × 10 ⁻⁶
Ni	(7.0±0.4) × 10 ⁻⁹	(1.2±0.3) × 10 ⁻⁷
Cs	(3.0±0.1) × 10 ⁻⁸	(4.2±0.1) × 10 ⁻⁷
Eu	(6.2±0.9) × 10 ⁻¹⁰	(5.3±0.3) × 10 ⁻⁷
U	(1.0±0.3) × 10 ⁻¹⁰	(3.4±0.5) × 10 ⁻¹¹
Th	(9.6±0.8) × 10 ⁻¹¹	(6.4±0.7) × 10 ⁻¹¹
TIC (total inorganic carbon, ppm as C±SD)	5.8±0.3 ppm	6.9±0.8 ppm
TOC (total organic carbon, ppm as C±SD)	—	639±35 ppm
pH	12.8–12.9	12.7–12.8

of 1 cm³ of the radionuclide solutions. Uranium, thorium and nickel were added as nitrates of the natural isotopes, at concentrations ranging from 10⁻¹⁰ to 10⁻⁵ mol dm⁻³; 10⁻¹² to 10⁻⁷ mol dm⁻³; and 10⁻¹⁰ to 10⁻⁵ mol dm⁻³, respectively; ¹³⁷Cs, ¹⁵²Eu and ¹²⁵I were used as radiotracers in non-active solutions of CsNO₃, EuCl₃ and NaI in the concentration range 10⁻⁷ to 10⁻⁴ mol dm⁻³; 10⁻¹⁰ to 10⁻⁵ mol dm⁻³; and 10⁻⁸ to 10⁻⁵ mol dm⁻³, respectively. For the generation of the isotherms, sorption of the radionuclides was tested at 8 concentration levels. The sorption of all analytes was assessed individually after 8 days of constant agitation on an orbital shaker by determining the concentration remaining in the liquid phase after filtration through a 0.22 μm PES membrane syringe filter. Inductively coupled plasma mass spectrometry (Agilent, series 7700x) was used to determine U, Th and Ni. Gamma counting was used to determine Cs, Eu and I based on isotope exchange. Calculations of the expected speciation in solution were made using *JChess* (van der Lee, 1998) and the species from the *HATCHES* database (Harwell/Nirex thermodynamic database for chemical equilibrium studies, version NEA18; Cross and Ewart, 1990).

Results

Sorption isotherms in the absence of CDP

The results for the sorption studies to NRVB and its individual components (namely, OPC, limestone flour and hydrated lime) in the absence of CDP can be represented as the concentration of radionuclide sorbed to the solid (C_s) against the concentration remaining in solution (C_l). In some cases, there is a linear relationship between the concentration in solution and on the solid; the proportionality constant that relates them is called the distribution ratio (R_d) which can be calculated from the concentration initially added and that remaining in solution as follows:

$$R_d (\text{dm}^3 \text{ g}^{-1}) = \frac{[\text{Rn}]_{\text{sorbed}} (\text{mol g}^{-1})}{[\text{Rn}]_{\text{solution}} (\text{mol dm}^{-3})} = \frac{[\text{Rn}]_{\text{initial}} - [\text{Rn}]_{\text{solution}}}{[\text{Rn}]_{\text{solution}}} \times \frac{\text{solution volume (dm}^3\text{)}}{\text{solution mass (g)}} \quad (1)$$

This equation does not imply any specific sorption process. Sorption isotherms may deviate from linearity due to saturation of the available sites or precipitation of the radionuclide of interest. Table 2 summarizes the results obtained

for the isotherms of all elements included in the present study. Note that the R_d values provided in Table 2 and discussed below correspond to the slopes of the isotherm curves in their linear range, and that errors are the standard deviation obtained from the least squares fit.

Iodine, as I^- , shows poor sorption to NRVB, as expected at the pH of the NRVB-water (~12.8) as the surfaces of the NRVB particles will be negatively charged. The NRVB shows similar sorption (in terms of R_d , ~0.033 dm³ g⁻¹) to OPC and the limestone flour. Hydrated lime alone showed the lowest capacity for the retention of I^- , with an R_d value of 0.02 dm³ g⁻¹ and clear saturation of the solid surface at iodine concentrations higher than 5 × 10⁻⁶ mol dm⁻³.

Of the cations included in this study, Cs shows the lowest sorption; OPC and NRVB gave higher uptake of Cs (~0.1 dm³ g⁻¹), than hydrated lime. The latter proved to have little capacity to sorb the alkaline metal, becoming saturated at concentrations above 5 × 10⁻⁵ mol dm⁻³. The experimental results indicate that sorption of Ni occurs only in a very narrow concentration range, exhibiting linear behaviour only up to 5 × 10⁻⁷ mol dm⁻³ (Table 2). To understand this behaviour, it is necessary to take into account the concentration of Ni originally present in the NRVB-water (~10⁻⁸ mol dm⁻³ from Table 1) and the limited solubility of this element, which at high pH is approximately 3 × 10⁻⁶ mol dm⁻³ (solubility determined in saturated Ca(OH)₂; Warwick and Felipe-Sotelo, 2009). Limestone flour showed higher Ni sorption than NRVB by almost one order of magnitude (58 dm³ g⁻¹ vs. 3.6 dm³ g⁻¹), but again over a narrow concentration range; precipitation was observed for solution concentrations higher than 5 × 10⁻⁷ mol dm⁻³. Conversely, the removal of Ni from solution in the presence of OPC and hydrated lime did not show linear behaviour and the results do not fit either the Langmuir or Freundlich isotherm.

The uptake of Eu by both NRVB and limestone flour was significant, with R_d values of approximately 2 × 10³ dm³ g⁻¹. The OPC alone showed lower Eu uptake of ~660 dm³ g⁻¹ and it was even lower in the case of hydrated lime at ~274 dm³ g⁻¹. For both OPC and hydrated lime, precipitation was observed for concentrations higher than 5 × 10⁻⁹ mol dm⁻³ before saturation on the solid surface was reached; OPC has the highest sorption capacity for Th (R_d ~6000 dm³ g⁻¹), followed by NRVB (R_d ~4000 dm³ g⁻¹). The R_d for the sorption of Th to limestone flour and

TABLE 2. Summary of the sorption isotherms in the absence of CDP ($R_d \pm SD$, in $\text{dm}^3 \text{g}^{-1}$).

	NRVB	OPC	Limestone flour	Hydrated lime
I	Linear over range covered $R_d = 0.033 \pm 0.001$	Linear over range covered $R_d = 0.034 \pm 0.002$	Linear over range covered $R_d = 0.039 \pm 0.001$	Linear up to $5 \times 10^{-6} \text{ mol dm}^{-3}$ $R_d = 0.020 \pm 0.001$
Cs	Linear over range covered $R_d = 0.120 \pm 0.001$	Linear up to $4 \times 10^{-4} \text{ mol dm}^{-3}$ $R_d = 0.097 \pm 0.004$	Linear over range covered $R_d = 0.063 \pm 0.002$	Linear up to $4 \times 10^{-5} \text{ mol dm}^{-3}$ $R_d = 0.048 \pm 0.001$
Ni	Linear up to $1 \times 10^{-7} \text{ mol dm}^{-3}$ $R_d = 3.6 \pm 1.1$	Non-linear behaviour	Linear up to $5 \times 10^{-7} \text{ mol dm}^{-3}$ $R_d = 58 \pm 9$	Non-linear behaviour
Eu	Linear over range covered $R_d = 1954 \pm 79$	Linear up to $1.5 \times 10^{-9} \text{ mol dm}^{-3}$ $R_d = 662 \pm 23$	Linear over range covered $R_d = 2467 \pm 59$	Linear up to $1.5 \times 10^{-9} \text{ mol dm}^{-3}$ $R_d = 274 \pm 4$
Th	Linear up to $5.5 \times 10^{-9} \text{ mol dm}^{-3}$ $R_d = 3674 \pm 533$	Linear up to $1.2 \times 10^{-10} \text{ mol dm}^{-3}$ $R_d = 5845 \pm 1076$	Linear up to $9.0 \times 10^{-10} \text{ mol dm}^{-3}$ $R_d = 442 \pm 47$	Linear up to $3 \times 10^{-9} \text{ mol dm}^{-3}$ $R_d = 780 \pm 16$
U	Linear over range covered $R_d = 33.7 \pm 0.5$	Linear over range covered $R_d = 20.0 \pm 0.2$	Linear up to $8 \times 10^{-8} \text{ mol dm}^{-3}$ $R_d = 4.5 \pm 0.2$	Linear up to $2 \times 10^{-6} \text{ mol dm}^{-3}$ $R_d = 1.25 \pm 0.04$

hydrated lime were almost one order of magnitude lower than for the other two materials; it would appear that limestone flour and hydrated lime simply dilute OPC, the main sorbing component. Note that precipitation was observed in all experiments for concentrations higher than $10^{-10} \text{ mol dm}^{-3}$ for OPC and limestone, and $5 \times 10^{-9} \text{ mol dm}^{-3}$ for NRVB and hydrated lime. Uranium showed moderate sorption to NRVB with an R_d value of $34 \text{ dm}^3 \text{g}^{-1}$, much lower than Eu and Th. The sorption of U to OPC is similar to NRVB and almost one order of magnitude higher than sorption to limestone flour or hydrated lime (Table 2). Sorption was linear for NRVB and OPC over the entire concentration range (10^{-10} to $10^{-5} \text{ mol dm}^{-3}$ U added), corresponding to a final concentration in solution after sorption of 5×10^{-11} to $5 \times 10^{-7} \text{ mol dm}^{-3}$). Precipitation was observed for limestone and hydrated lime for concentrations in solution higher than $2.5 \times 10^{-6} \text{ mol dm}^{-3}$.

Sorption in the presence of CDP

The effect of CDP on the sorption of the radionuclides to NRVB was assessed in addition to the sorption of the organic compounds themselves to the solid matrix. The results obtained are shown (Fig. 2) and compared with the sorption observed in absence of CDP. The total organic content of the CDP mixture was determined by total organic carbon analysis as $639 \pm 35 \text{ ppm TOC}$. The presence of the CDP had no effect on the uptake of Cs by NRVB. The R_d value in the presence of the organic compounds was $0.11 \pm 0.01 \text{ dm}^3 \text{g}^{-1}$ which corresponds to the value obtained in the absence of CDP, $0.120 \pm 0.001 \text{ dm}^3 \text{g}^{-1}$. The sorption of Cs to NRVB in the presence of CDP was linear over the entire experimental range. CDP caused a decrease in the sorption of Eu to cement, with R_d values changing from 1954 ± 79 to $254 \pm 14 \text{ dm}^3 \text{g}^{-1}$, in the absence and presence of CDP, respectively. The sorption showed good linearity up to Eu concentrations of $1.5 \times 10^{-9} \text{ mol dm}^{-3}$; however, there are signs of saturation of the solid surface for concentrations higher than $2 \times 10^{-6} \text{ mol g}^{-1}$. The retention of Th onto NRVB also decreased in the presence of CDP but not as markedly, varying from 3674 ± 533 to $1908 \pm 61 \text{ dm}^3 \text{g}^{-1}$ ($R_d \pm SD$). The sorption was linear up to $5 \times 10^{-10} \text{ mol dm}^{-3}$ and precipitation was observed for concentrations higher than $3 \times 10^{-9} \text{ mol dm}^{-3}$. As noted previously, there is no clear evidence of removal

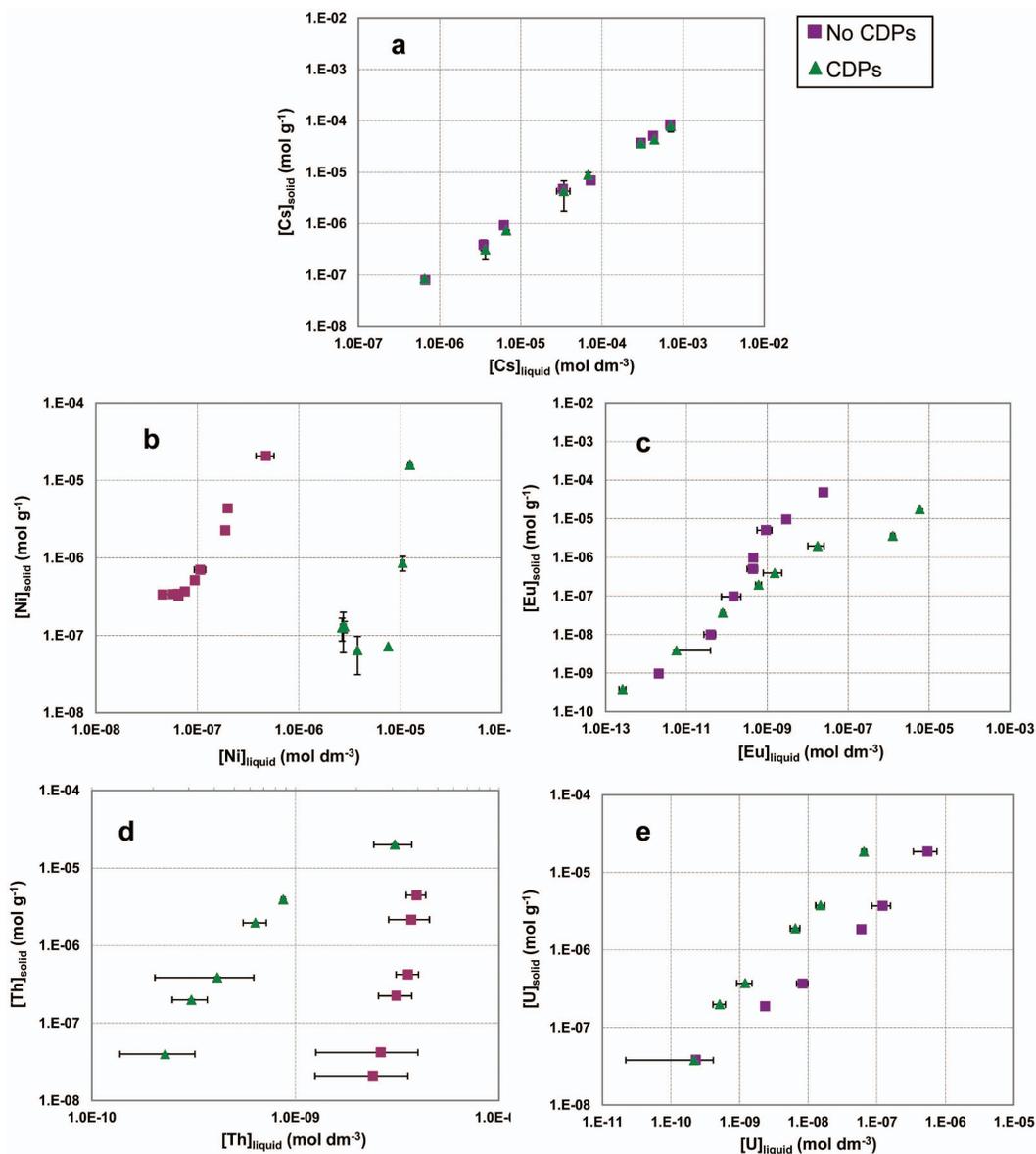


FIG. 2. Sorption of (a) Cs, (b) Ni, (c) Eu, (d) Th and (e) U to NRVB in the absence and presence of CDP.

of Ni by sorption to NRVB in the presence in CDP. In this case (Table 1), the original concentration of Ni in the CDP leachate was one order of magnitude higher than in the NRVB equilibrated water. This is believed to result from the complexation of nickel, present as an impurity in the NRVB, by the products of cellulose degradation during the preparation of the leachate at elevated temperature. Sorption of U(VI) in the

presence of CDP was linear over the whole range studied and showed an R_d value of $282 \pm 4 \text{ dm}^3 \text{ g}^{-1}$ (\pm SD) one order of magnitude higher than in the absence of the organic compounds.

The sorption of CDP to NRVB was also assessed; 20 cm^3 of the CDP mixture were allowed to equilibrate for 1 week under N_2 -atmosphere in the presence of variable amounts of NRVB, from 50 to 700 mg. Each experiment was

undertaken in triplicate. After the equilibration period, the supernatant was filtered with 0.45 μm PES membrane syringe filters and the amount of CDP remaining in solution was determined by TOC analysis. The results were not conclusive and although some retention was observed, ranging from 2 to 7%, a linear trend was not found and the results did not fit either the Langmuir or Freundlich isotherms. Distribution coefficients (R_d) calculated from these experiments ranged between 0.5 and 18 $\text{cm}^3 \text{g}^{-1}$.

Discussion

Sorption in the absence of CDP

When comparing NRVB to its individual components (Table 2), it can be seen that OPC and limestone flour showed very similar results for iodine sorption, similar to NRVB when errors are considered and higher than the value obtained for hydrated lime. The cations Ni and Eu are most strongly retained by limestone flour followed by NRVB, whereas Cs, Th and U are better retained by OPC. For Ni, there is no clear evidence of sorption to OPC or hydrated lime and it appears that the main mechanism of removal from solution is precipitation.

The results for iodine sorption to NRVB fall within the range of R_d values reported by Missana *et al.* (2010) who investigated the sorption of I (3.6×10^{-8} to $1.3 \times 10^{-8} \text{ mol dm}^{-3}$) to NRVB and observed R_d values that ranged from 0.01 to 0.11 $\text{dm}^3 \text{g}^{-1}$, dependent upon the initial concentration of the radionuclide. There is also agreement with the results obtained by Bayliss *et al.* (1996) for the sorption to NRVB in NRVB-equilibrated water under non-saline conditions. However, the same authors observed a marked reduction of the R_d values when the experiments were performed under hypersaline conditions (0.001–0.004 $\text{dm}^3 \text{g}^{-1}$).

Missana *et al.* (2010) reported an R_d value of approximately 0.05 $\text{dm}^3 \text{g}^{-1}$ for the sorption of Cs to NRVB, lower than the value reported here (0.120 \pm 0.001 $\text{dm}^3 \text{g}^{-1}$). Baker *et al.* (2002) reported even lower sorption of Cs to NRVB under saline conditions (after addition of 0.5 mol dm^{-3} NaCl to the NRVB water), $R_d = 0\text{--}0.02 \text{ dm}^3 \text{g}^{-1}$. Ochs *et al.* (2006) studied the sorption of Cs on a number of hydrated cement pastes (HCP) and mortars at different stages of degradation and in contact with a variety of solution compositions. A wide range of R_d values was reported varying from 0.001 to approximately

0.6 $\text{dm}^{-3} \text{g}^{-1}$. The authors concluded that competition from other monovalent cations, such as Na and K, was responsible. The range of concentrations of Na and K in young HCP would justify the wide variation in sorption, whereas degraded cements (characterized by low alkali content) have a stable and lower pH because the concentration of Ca is determined by the solubility of portlandite or CSH phases (depending on the stage of degradation). The authors also concluded that a decrease in Ca concentration and reduction of the Ca/Si ratio results in a higher concentration of strong sorption sites and less competition from Ca. In the present study, despite the high concentration of Ca present in NRVB (added as hydrated lime) relatively high sorption of Cs was observed compared to the values reported by Ochs and co-workers. When Komarneni and Roy (1981) studied the mechanisms of immobilization of Cs onto cement and mortar, it was observed that retention was increased notably by formation of carbonate when CO_2 was bubbled into the cement suspensions, ranging from 0 to 62–91%. The authors suggested precipitation of Cs as Cs_2CO_3 as the removal mechanism. The presence of substantial carbonate content in NRVB due to the addition of limestone, both in solution (TIC in Table 1) and in the solid (as calcite, Fig. 1), might then account for the higher removal of Cs from the solution by NRVB observed in the present work when compared to other cements. Further mineralogical studies of the solid phase would be required to probe the presence of Cs_2CO_3 and confirm this removal mechanism.

The concentration of Ni in the NRVB equilibrated water was $\sim 10^{-8} \text{ mol dm}^{-3}$ (Table 1) and in the NRVB experiments, linear sorption was observed only up to a concentration of $1 \times 10^{-7} \text{ mol dm}^{-3}$ Ni in solution; precipitation was observed at higher concentrations as shown in Fig. 2b. The main species under these conditions would be $\text{Ni}(\text{OH})_2$ and the calculated solubility $3.8 \times 10^{-7} \text{ mol dm}^{-3}$. The main mechanism of removal of Ni under repository condition is likely to be precipitation, which corresponds to the findings of Wieland *et al.* (2006). The latter authors suggested that this is related to the concentration of Ni originally present within the cement which is subsequently released into the pore water. Thus, dissolution of Ni from the cement to the equilibrated water will be the factor controlling the concentration of Ni in solution and the uptake of ^{63}Ni under geological disposal

conditions would then be determined by isotope exchange.

Speciation calculations indicate that the main Th species in solution would be $\text{Th}(\text{OH})_4$. Thorium shows the strongest retention to NRVB of the cations studied (Table 2) and the R_d value falls within the range 10^2 to $10^3 \text{ dm}^{-3} \text{ g}^{-1}$ as reported in other studies on cementitious materials (e.g. Evans, 2008). In the case of Eu, the dominant species in solution are $\text{Eu}(\text{OH})_4^-$, followed by $\text{Eu}(\text{OH})_3$. Europium is also well retained by NRVB, with an R_d value similar to that reported by Tits *et al.* (2003) in the presence of CSH phases, $(6\pm 3) \times 10^2 \text{ dm}^{-3} \text{ g}^{-1}$.

Results for U sorption to NRVB in Table 2 are comparable to the study by Baston *et al.* (2010) on simulated aged NRVB (leaching and hydrothermal ageing) who found an R_d value of $70\pm 50 \text{ dm}^3 \text{ g}^{-1}$. The increase of surface area caused by ageing (from 14 to $61 \text{ m}^2 \text{ g}^{-1}$) did not significantly affect the sorption rate nor did the loss of portlandite or the slight increase in crystallinity. The results obtained in the present study and also by Baston *et al.* (2010) are one order of magnitude higher than the results obtained by Bayliss *et al.* (1996), who reported R_d values for the sorption of U(VI) to NRVB of $6 \text{ dm}^3 \text{ g}^{-1}$ and $5 \text{ dm}^3 \text{ g}^{-1}$ in NRVB equilibrated water under non-saline and hypersaline conditions, respectively. Sutton *et al.* (2003) studied the sorption of U(VI) onto ordinary Portland cement (OPC)/pulverized fuel ash (PFA) grouts giving values one order of magnitude lower ($R_d = 34$ vs. $1.5 \text{ dm}^{-3} \text{ g}^{-1}$) than found in this work for sorption to NRVB or OPC. Speciation studies carried out by the authors indicated that aqueous concentrations are dominated by a uranyl trihydroxy complex ($\text{UO}_2(\text{OH})_3^-$). The predominance of carbonate species (e.g. $\text{UO}_2(\text{CO}_3)_3^{4-}$) would require a higher concentration of carbonate than found in their grout leachate (reported as 0.125×10^{-3} to $0.092 \times 10^{-3} \text{ mol dm}^{-3}$ TIC). In the present study, a much higher concentration of carbonate was found, approximately $5 \times 10^{-4} \text{ mol dm}^{-3}$ (assuming all TIC as CO_3^{2-} , Table 1). Speciation calculations with the composition of the NRVB-water in Table 1, nevertheless gave $\text{UO}_2(\text{OH})_3^-$ as the dominant species; carbonate species were not predicted, as would be expected at pH 12.8. When comparing the composition of the OPC-PFA leachate used by Sutton and co-workers with the composition of the NRVB equilibrated water (Table 1) it can be seen that much higher concentrations of Na and K

were found in the OPC/PFA leachate, one order of magnitude higher than in the NRVB equilibrated water used here. It is, thus, possible that competition effects for specific sorption sites are responsible for the differences observed rather than the presence of carbonate in the NRVB.

Effect of CDP on sorption to NRVB

Caesium sorption was not affected by the addition of CDP, which corresponds to Holgersson *et al.* (1998) who observed no effect of isosaccharinic acid on the sorption of Cs onto cement. Holgersson *et al.* (1998) also reported a significant reduction in the sorption of Th, by almost 2 orders of magnitude, in the presence of 100 kg m^{-3} cellulose leachate, much more marked than the reduction observed here, which was 3674 ± 533 to $1908\pm 61 \text{ dm}^3 \text{ g}^{-1}$. Wieland *et al.* (2002) attributed the reduction of Th uptake by cement to the formation of $\text{Th}(\text{IV})\text{:ISA:Ca}$ (1:2:1) complexes in solution; however it was also noted that the large uncertainty in the determination of the R_d values (ranging from 350 to $6000 \text{ dm}^3 \text{ g}^{-1}$) made interpretation of the results difficult. Dario *et al.* (2006) assessed the effect of ISA (among other organic ligands) on the sorption of Eu onto cement at pH 12.5, observing a reduction in sorption above a concentration of approximately $10^{-4} \text{ mol dm}^{-3}$ ISA. They reported R_d values changed from 10^4 to $10^{0.5} \text{ dm}^{-3} \text{ g}^{-1}$ with the addition of $10^{-2} \text{ mol dm}^{-3}$ ISA (note that the CDP mixture used in the present work contained approximately $10^{-3} \text{ mol dm}^{-3}$ ISA, as determined by HPLC).

Whereas the presence of CDP has a negative effect on the sorption of Th and Eu onto NRVB, the retention of U by the cement actually increased in the presence of CDP. This effect has been reported previously for cements and other materials; Baston *et al.* (1994) found that the sorption of U(VI) to tuff at pH 12.8 in the presence of gluconate, isosaccharinate ($2 \times 10^{-3} \text{ mol dm}^{-3}$) and authentic CDP (prepared in a similar way to this work) increased from $0.42\pm 0.04 \text{ dm}^{-3} \text{ g}^{-1}$ to $4\text{--}13 \text{ dm}^{-3} \text{ g}^{-1}$. Biddle *et al.* (2000) also reported an increase in R_d value for the sorption to NRVB, from 8 to $200 \text{ dm}^3 \text{ g}^{-1}$ in the presence of a 1% CDP loading. Conversely, Greenfield *et al.* (1997) reported a decrease in the sorption of U(VI) to NRVB in the presence of 10% cellulose CDP ($0.5 \text{ dm}^3 \text{ g}^{-1}$ in comparison to $6 \text{ dm}^3 \text{ g}^{-1}$ in the absence of CDP); at the present time, there is no clear explanation for these conflicting observa-

tions. The variability in the experimental methodology for the generation of the CDP could be the cause of the differences observed in diverse studies. Practical aspects such as the nature of the cellulosic material, liquid to solid ratio, cellulosic load and temperature could lead to differences in the composition of the CDP liquor, in terms of the nature and concentration of the organic compounds and also the inorganic matrix.

One mechanism that could explain an increase in sorption of U(VI) to NRVB is uptake of the CDP to the cements and formation of ternary complexes. Van Loon *et al.* (1997) studied the sorption of isosaccharinic acid to a hardened Portland cement paste at pH 13.4. They reported that the sorption of ISA could be described by a Langmuir isotherm with two bonding sites and total sorption capacity of approximately 0.3 mol kg^{-1} . Although the authors did not provide a definitive description of the retention mechanism of ISA onto cement, they suggested that it must be due to specific interactions (ligand exchange) as repulsion between the negatively charged cement surface and the negatively charged ISA ions suggests that electrostatic interaction alone can be disregarded. A previous study by Biddle *et al.* (2000) found that the sorption of ISA to NRVB ranged from $R_d = 7$ to $30 \text{ cm}^3 \text{ g}^{-1}$, depending on the concentration of the organic compound. In the present work, sorption of the CDP mixture (639 ± 35 ppm TOC) to NRVB ranged from 2 to 7%, somewhat lower than the values reported by Biddle *et al.* (2000). Moreover, the sorption does not follow a clear trend and cannot be fitted to Freundlich or Langmuir isotherms.

Conclusions

Low sorption of Cs^+ and I^- onto NRVB was observed, with R_d values of 0.12 and $0.03 \text{ dm}^3 \text{ g}^{-1}$, respectively. The uptake of Ni to NRVB seems to be determined by solubility with no clear evidence of Ni removal by sorption alone. Significant concentrations of U(VI), Th(VI) and Eu(III) were retained on NRVB in the absence of CDP. The distribution coefficients (R_d) increased as follows: U(VI) ($\sim 34 \text{ dm}^3 \text{ g}^{-1}$) < Eu ($\sim 2000 \text{ dm}^3 \text{ g}^{-1}$) < Th ($\sim 3700 \text{ dm}^3 \text{ g}^{-1}$). Limestone flour was the component of NRVB that showed the highest partition coefficient for Ni and Eu, whereas Cs, Th and U were better retained by OPC than either limestone flour or hydrated lime.

The presence of CDP had no effect on sorption of Cs. Sorption of Th and Eu to NRVB decreased, reducing the R_d values by a factor of 2 and 10, respectively. Interestingly, the presence of the CDP seemed to increase the sorption of U(VI) to the NRVB by one order of magnitude. An investigation of the sorption of CDP onto NRVB indicates that, although there is some retention of the organic compound on the solid, the absence of a definitive trend militates against a clear explanation for the marked increase in U removal. Further studies are required to understand the effects of CDP on uranium sorption, exploring the possibilities of ternary systems where CDP may act as a link between the U and the cement and whether U competes with CDP for specific sorption sites.

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References

- Baker, S., Oliver, P. and McCrohon, R. (2002) *Near-field batch sorption studies – 1992 to 1998*. Atomic Energy Authority Technology Report, AEA/ERRA-0345.
- Baston, G.M.N., Berry, J.A., Bond, K.A., Boulton, K.A., Brownsword, M. and Linklater, C.M. (1994) Effect of cellulosic degradation products on uranium sorption in the geosphere. *Journal of Alloys and Compounds*, **213/214**, 475–480.
- Baston, G.M.N., Cowper, M. and Marshall, T.A. (2010) *Sorption of U(VI) onto leached and hydrothermally-aged NRVB*. Serco Assurance Report SA/ENV-0959.
- Bayliss, S., McCrohon, R., Oliver, P., Pilkington, N.J. and Thomason, H.P. (1996) *Near-field sorption studies: January 1989 to June 1991*. Nirex Report NSS/R277.
- Biddle, P., Greenfield, B.F., Pilkington, N.J. and Spindler, M.W. (2000) *Further studies on the effects of the products from the anaerobic degradation*. Atomic Energy Authority Technology Report AEAT/ERRA-0154.
- Chambers, A.V., Cowper, M.M., Myatt, B.J. and

- Williams, S.J. (2004) *Further studies of plutonium uptake by non-aqueous phase liquids*. Serco Assurance Report SA/ENV-0656.
- Cross, J. and Ewart, F. (1990) *HATCHES – A Thermodynamic Database and Management System*. Nirex Report NSS/R212.
- Dario, M., Molera, M. and Allard, B. (2006) Sorption of europium on TiO₂ and cement at high pH in presence of organic ligands. *Journal of Radioanalytical and Nuclear Chemistry*, **270**, 495–505.
- Evans, N.D.M. (2008) Binding mechanisms of radionuclides to cements. *Cement and Concrete Research*, **28**, 543–553.
- Greenfield, B.F., Hurdus, M.H., Spindler, M.W. and Thomason, H.P. (1997) *The effects of the products of degradation of cellulose on the solubility and sorption of radionuclides in the near field*. Nirex Report NSS/R376.
- Heath, C.R. (2008) *Interactions of radionuclides with cellulose degradation products*. Unpublished PhD thesis, Loughborough University, Loughborough, UK.
- Holgersson, S., Albinsson, Y., Allard, B., Borén, H., Pavasars, I. and Engkvist, I. (1998) Effects of glucoisaccharinate on Cs, Ni, Pm and Th sorption onto, and diffusion into cement. *Radiochimica Acta*, **82**, 393–398.
- Holland, T.R. and Tearle, W.M. (2003) *A review of NRVB Mineralogy*. A Serco report for UK Nirex Limited, SERCO/ERRA-0455.
- Komarneni, S. and Roy, D.M. (1981) Mechanisms of immobilisation of nuclear waste elements by cement minerals, cement and mortar. *Cement and Concrete Research*, **11**, 789–794.
- Missana, T., Alonso, U., García-Gutiérrez, M. and López, T. (2010) *Experimental study of sorption of Cs, I and Pu onto wasteform grouts and NRVB*. CIEMAT report LBORO CMNDA4.
- Nirex (1997) *Development of the Nirex Reference Vault Backfill; Report on Current Status in 1994*. Nirex Science Report S/97/014.
- Nuclear Decommissioning Authority (2010) *Geological Disposal: Steps Towards Implementation*. Nuclear Decommissioning Authority Report NDA/RWMD/013.
- Ochs, M., Pointeau, I. and Giffaut, E. (2006) Caesium sorption by hydrated cement as a function of degradation state: Experiments and modelling. *Waste Management*, **26**, 725–732.
- Pourchez, J., Govin, A., Grosseau, P., Guyonnet, R., Guilhot, B. and Ruot, B. (2006) Alkaline stability of cellulose ethers and impact of their degradation products on cement hydration. *Cement and Concrete Research*, **36**, 1252–1257.
- Small, J. and Dutton, M. (2009) *Review of the research on cellulose degradation and input data for the Simplified Model of Gas Generation (SMOGG)*. National Nuclear Laboratory Report NNL(09) 8870.
- Sutton, M., Warwick, P. and Hall, A. (2003) Uranium(VI) interaction with OPC/PFA front. *Journal of Environmental Monitoring*, **5**, 922–928.
- Tits, J., Stumpf, T., Rabung, T., Wieland, E. and Fanghänel, T. (2003) Uptake of Cm(III) and Eu(III) by calcium silicate hydrates: a solution chemistry and time-resolved laser fluorescence spectroscopy study. *Environmental Science and Technology*, **37**, 3568–3573.
- Van der Lee, J. (1998) *Thermodynamic and Mathematical Concepts of CHESS*. Technical Report LHM/RD/98/39, CIG, Ecole de Mines de Paris, Fontainebleu, France.
- Van Loon, L.R. and Glaus, M.A. (1998) *Experimental and theoretical studies on alkaline degradation of cellulose and its impact on the sorption of radionuclides*. PSI Bericht Nr 98-07, Paul Scherrer Institute, Würenlingen, Switzerland.
- Van Loon, L.R., Glaus, M.A., Stallone, S. and Laube, A. (1997) Sorption of isosaccharinic acid, a cellulose degradation product, on cement. *Environmental Science and Technology*, **31**, 1243–1245.
- Warwick, P. and Felipe-Sotelo, M. (2009) *Effect of ‘as disposed’ complexants and polymer encapsulant leachates on the solubility of nickel, thorium and uranium(VI) and uranium(IV)*. Loughborough University Report for the NDA, LBORO CMNDA4.
- Wieland, E., Tits, J., Dobler, J.P. and Spieler P. (2002) The effect of α -isosaccharinic acid on the stability of Th(IV) uptake by hardened cement paste. *Radiochimica Acta*, **90**, 683–688.
- Wieland, E., Tits, J., Ulrich, A. and Bradbury, M.H. (2006) Experimental evidence for solubility limitation of the aqueous Ni(II) concentration and isotopic exchange in cementitious systems. *Radiochimica Acta*, **94**, 29–36.