# Sorption properties of aged cements

G. M. N. Baston[1],*, M. M. Cowper[1] and T. A. Marshall[2]

[1] AMEC, B150 Building, Harwell, Didcot, Oxfordshire OX11 0QB, UK
[2] Research Centre for Radwaste Disposal, School of Earth, Atmospheric and Environmental Science, The University of Manchester, Manchester M13 9PL, UK

## ABSTRACT

Samples of artificially aged Nirex reference vault backfill (NRVB) were prepared by progressive leaching with deionized water, after which some of the samples underwent hydrothermal treatment. Compared to unaltered NRVB, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) provided evidence for the ageing resulting in alteration of the mineralogy, in particular the absence of portlandite was observed. The specific surface area of NRVB initially increased due to leaching, but then decreased after further leaching.

Sorption distribution ratios ($R_D$ values) of uranium(VI), neptunium(IV), tin and zirconium onto aged NRVB samples were measured using the batch sorption technique. For all four elements, there was little difference between $R_D$ values for aged NRVB and those for untreated material. The most probable explanation for these findings is that even though the ageing treatments altered the NRVB mineralogy, calcium silicate hydrate (C-S-H) phases are responsible for most of the radionuclide uptake and their transformation to more crystalline forms has little effect on the bulk sorption capacity of the aged material.

## Introduction

IN a future UK geological disposal facility (GDF), the current concept for intermediate-level wastes (ILWs) is disposal in vaults backfilled with cement (Nuclear Decommissioning Authority, 2010). Nirex reference vault backfill (NRVB) was developed as a potential cement and was designed to maintain a high near-field pH that minimizes the solubility of many radioelements and also to provide a high sorption capacity. Together, these combine to retard the migration of many radionuclides in a GDF (Francis *et al.*, 1994).

The selection and justification of distribution coefficients for the sorption of radionuclides onto the backfill forms an important part of the process providing input data for the post−closure performance assessment of GDF concepts. In the context of the UK cement-based disposal concept, most of the available experimentally determined sorption data have been obtained using as-prepared or 'young' NRVB samples (e.g. Bayliss *et al.*, 1996). However, cementitious materials, such as NRVB are known to alter with time. These alterations are partly the result of the amorphous phases evolving into more stable crystalline forms. In particular, calcium silicate hydrates (C-S-H), a large component of cement pastes, have structures that range from relatively disordered C-S-H gel to semi-crystalline. In recent years, crystallographic and spectroscopic studies of C-S-H phases have been used to help develop structural models of C-S-H (Chen *et al.*, 2004; Garbev *et al*, 2008). The elevated temperatures occurring post closure are expected to contribute to further alteration of the gel with time, a process referred to as hydrothermal ageing. In addition, interactions with groundwater will result in the dissolution of some components,

principally portlandite and C-S-H, which alter the chemical composition of the backfill (Berner, 1992; Hidalgo *et al.*, 1997; Glasser *et al.*, 2008). These changes may affect the sorption capacity of the backfill and this leads to significant uncertainty concerning the evolution of backfill sorption properties with time. Therefore, an understanding of the effects of cement ageing on the evolution of NRVB sorption properties is required.

The aims of this study were to investigate the changes induced by leaching and hydrothermal ageing of NRVB and how these changes may affect the sorption of key radionuclides. The major parts of this study were: the preparation of aged NRVB; characterization of the aged NRVB samples in terms of mineralogy, surface area and chemical composition; and measurement of sorption capacity using the batch sorption technique. The radioelements used in the sorption studies were uranium(VI), neptunium(IV), tin(IV) and zirconium. Significant quantities of uranium are present in ILW and therefore its behaviour is of considerable interest in safety assessments of radioactive waste disposal. For uranium, U(VI) is expected to be the dominant redox state under oxidizing and slightly reducing conditions. Many sorption data have been reported for the uptake of U(VI) including some relating to aged/degraded cementitious materials (Sylwester, 2000; Zhao, 2000; Pointeau, 2004).

In contrast, data for neptunium sorption are relatively scarce, particularly for the Np(IV) redox state and some sorption databases have used estimates based on analogies to other tetravalent actinides (e.g. Wieland and Van Loon, 2002). Recent studies have been aimed at validating these assumptions (Tits, 2012) and at applying spectroscopic techniques to examine the structure of Np(IV) sorbed species (Gaona *et al.*, 2012).

The sorption properties of tin and zirconium are of interest due to the long-lived isotopes $^{126}$Sn (half-life $1.0 \times 10^5$ years), and $^{93}$Zr (half-life $1.5 \times 10^6$ years). To date very few studies are available of the uptake on cementitious materials of tin (Baker *et al.*, 1994; Bonhoure *et al.*, 2003) and zirconium (Brownsword *et al.*, 2002).

## Experimental Methods
### Materials

The formulation of NRVB by weight is: ordinary Portland cement (OPC), 26%; fine limestone

aggregate (primarily calcite) 29%; hydrated lime aggregate (primarily calcium hydroxide) 10%; and water 35% (Francis *et al.*, 1997). The resulting material has a high fractional porosity due to the high ratio of water to cement. This provides sufficient water for total hydration of the hydraulic constituents.

Artificial ageing of NRVB was performed by leaching with deionized water after which some samples underwent hydrothermal treatment. Samples subjected to leaching only were prepared by placing NRVB discs of ~8 g in 1 dm$^3$ volumes of deionized water, with the leachate regularly removed and replaced with a fresh batch of deionized water. Leaching was carried out for either 541 days (a cumulative leachate to solid ratio of 3.9 m$^3$ kg$^{-1}$) or 1272 days (a cumulative leachate to solid ratio 5.3 m$^3$ kg$^{-1}$). Hydrothermally treated NRVB was first leached by placing 100 g of crushed NRVB (500−5000 μm size fraction) in 1 dm$^3$ of deionized water as discs were not available for this part of the study. The leachate regularly replaced with deionized water over 536 days (cumulative leachate to solid ratio 0.30 m$^3$ kg$^{-1}$). A 25 g sample of leached material was then sealed in a Parr acid digestion vessel with ~40 cm$^3$ of the final leachate solution. The digestion vessel was placed in an oven at 80ºC for 1183 days. This temperature was selected as being the maximum that may be reached in the GDF ILW vaults due to cement hydration reactions.

The aged NRVB samples were separated from the leachates and allowed to dry at ambient temperature, then crushed and sieved (particle size <250 μm). All work was carried out in a nitrogen-atmosphere glovebox to minimize carbonation of the NRVB samples.

Samples of untreated NRVB were also prepared as controls. These were produced from cast cylindrical specimens. The cured cylinders were transferred to a nitrogen-atmosphere glovebox and the outer faces removed and discarded to separate out any potentially carbonated material. The centres were then crushed to a particle size of <250 μm.

### Analysis of leachate solutions

The final leachate solutions were separated from the solid material using 0.45 μm filtration. A second filtration was performed, using a stirred cell, with Amicon PM30 30,000 nominal molecular weight cut-off (NMWCO) filters.

Chloride and sulfate concentrations were determined by ion chromatography and carbonate by titration. Aluminium, calcium, iron, potassium, silicon and sodium were analysed by inductively-coupled plasma-optical emission spectrometry (ICP−OES). The results of the analyses were used to formulate 'synthetic' cement-equilibrated waters to be used in batch sorption experiments.

## Batch sorption experiments

Batch sorption experiments were carried out in a negative-pressure, nitrogen-filled (<10 ppm oxygen) glovebox. A known mass of crushed NRVB was equilibrated with the known volume of the corresponding synthetic cement-equilibrated water containing the radionuclide of interest in a suitable plastic vessel. An aliquot of a concentrated acidic stock solution of the radionuclide being studied was added to the waters (such that the initial concentration was at least an order of magnitude below the predicted solubility limit) and the pH adjusted to its original value by addition of NaOH. The solutions were then filtered using Millipore HV 0.45 μm filters (as a precaution to ensure that the radionuclides were in solution) and aliquots were then taken to determine the initial concentrations. All experiments were carried out in quadruplicate for each of the four NRVB samples at room temperature, with occasional agitation of the tubes.

During the one month equilibration period solution pH was regularly monitored and adjusted if it had drifted from the original value. At the end of the equilibration period, the experiments were sampled, using two filtration methods for solid/liquid separation: filtration through Millipore Millex HV 0.45 μm filters; and filtration through first a Millipore Millex HV 0.45 μm filter followed by a Millipore TTK 30,000 NMWCO ultrafilter.

Both filters were preconditioned prior to use. Solution samples for radionuclide analysis were filtered into bottles containing a small volume of concentrated acid. Measurements of Eh and pH were made on residual solutions in the vessels after sampling using suitably calibrated electrodes. The vessels were then emptied and washed with the appropriate cement-equilibrated water to remove any remaining solid phase. Sorption to the vessel walls was measured by acid washing with 4 mol dm$^{-3}$ nitric acid for one day and analysing the solution for the appropriate radionuclide.

Values for the sorption distribution ratio, $R_D$, were calculated using the equation:

$$R_D = \frac{V}{m}\left(\frac{C_0 - C_w - C_t}{C_t}\right)$$

where $V$ is the solution volume equilibrated in cm$^3$, with mass, $m$, of solid in g; $C_0$ is the initial concentration of radionuclide (corrected for vessel wall sorption, $C_w$); and $C_t$ the final measured radionuclide concentration. This gives $R_D$ in units of cm$^3$ g$^{-1}$.

The experimental uncertainties in the measured $R_D$ values are based on the analytical errors in measured radionuclide concentrations, which include counting errors and errors associated with internal calibration with yield tracers. The quoted uncertainties are two standard deviations.

Uranium(VI) batch sorption experiments used a liquid:solid ratio of 50:1. The initial $^{233}$U concentration was ~$1 \times 10^{-8}$ mol dm$^{-3}$, at least one order of magnitude below the solubility of uranium(VI) in the pH range $10-13$ (Brownsword et al., 1990). After filtration of the solution, uranium was isolated by anion-exchange chromatography. The purified uranium was then electrodeposited onto stainless steel discs, which were counted by alpha spectrometry. A nationally traceable standard solution of $^{232}$U was used as an internal yield monitor for the analysis procedure.

For neptunium(IV) batch sorption experiments, a liquid:solid ratio of 500:1 was used. This ratio was chosen to increase the likelihood of the final neptunium concentration being above the limit of detection for ICP-MS analysis, which was estimated to be between $10^{-12}$ and $10^{-11}$ mol dm$^{-3}$. The initial neptunium concentration was ~$2.8 \times 10^{-9}$ mol dm$^{-3}$, at least one order of magnitude below the solubility of neptunium(IV) in the pH range $10-13$ (Thomason and Williams, 1992). To maintain the low Eh conditions, a strip of iron foil (99.5% purity Fe foil, supplied by Goodfellow Cambridge Ltd) was contacted with the solution in each experiment. At the end of the experiments filtered samples of solution were evaporated on a low heat to volatilize any organic component, the residue was digested in high purity nitric acid and diluted to a matrix useable for analysis of $^{237}$Np by ICP-MS.

Zirconium batch sorption experiments, used a liquid:solid ratio of 50:1. The solution was

spiked with $^{95}Zr$, at an initial zirconium concentration of $\sim2 \times 10^{-10}$ mol dm$^{-3}$, at least one order of magnitude below the solubility of zirconium in the pH range 12−12.5. (Thomason and Williams, 1992; Baston et al., 1996; Brownsword et al., 2002). Final $^{95}Zr$ concentrations were determined by high-resolution gamma-spectrometry (HRGS).

For tin batch sorption experiments a liquid:solid ratio of 50:1 was used. The initial tin concentration in solution was $\sim1 \times 10^{-8}$ mol dm$^{-3}$ ($^{113}Sn$, with a stable tin carrier), at least one order of magnitude below the lowest solubility measured of tin at pH 12 (Thomason and Williams., 1992; Baston et al., 1996; Brownsword et al., 2002). Final $^{113}Sn$ concentrations were determined by high-resolution gamma spectrometry.

### Characterization of aged NRVB

The X-ray diffraction (XRD) analysis was carried out on samples of the NRVB of <250 μm particle size prepared using a mortar and pestle mill. A fully automated Siemens D500 powder diffractometer was used, employing CuKα radiation (λ = 0.15406 nm) and a secondary monochromator. The samples were continuously spun during data collection and scanned using a step size of 0.05º 2θ in the range 5−75º 2θ at a count time of 12 s per step. The sample holder was a single crystal silicon disc, cut in such a way that it gives rise to no diffraction peaks. The sample powder was held to the disc by smearing with a very small quantity of grease, which also does not produce diffraction peaks. Phase identification achieved using search and match software, which compares combinations of d spacings obtained from the sample to a standard database, compiled by the International Centre for Diffraction Data (ICDD)

Differential scanning calorimetry (DSC) analysis was carried out using a NETZSCH DSC 204 Instrument, over a temperature range of 20ºC to 1000ºC at a heating rate of 10ºC per minute; 20−30 mg samples of the crushed NRVB (<250 μm) were used. Energy required to raise the sample temperature is expressed in units of W g$^{-1}$. The specific heat of sapphire was used as a standard.

The specific surface area of crushed NRVB samples was measured by nitrogen gas adsorption using the BET method. The samples were first dried by out-gassing at 100ºC with nitrogen for 2 hours. Surface area measurements were then made using a Quantachrome Quantasorb instrument.

## Results and Discussion

### Composition of leachate solutions

Results of leachate analyses are given in Table 1. For the sample leached for 541 days, the pH of the final solution was 10.5 with a calcium concentration of 60 mg dm$^{-3}$. This compares to a pH of ~10.8 and a calcium concentration of ~40 mg dm$^{-3}$ for the final leachate of NRVB leached for 1272 days. The lower calcium concentration is consistent with incongruent dissolution of C-S-H phases, resulting in lower calcium to silicon ratios in the solid as leaching progressed. However, this is at odds with the higher pH observed after further leaching. The reason for this rise in pH is not entirely clear, but it is noted that it is accompanied by a lower sulfate concentration (thus maintaining the anion/cation charge balance). This suggests that the pH buffering of the aged NRVB cannot be fully explained by C-S-H dissolution.

The leachate solution prior to hydrothermal treatment had a pH of 11.3 and a calcium concentration of 44 mg dm$^{-3}$ (not shown in Table 1). The pH was higher than for solutions after 541 and 1272 days leaching, due to the lower NRVB to cumulative leachate ratio. After hydrothermal treatment the pH value had risen to 11.9 and the calcium concentration had changed to 259 mg dm$^{-3}$. It is known that, at a temperature of 70−90ºC, there is a drop in the thermodynamic stability of ettringite in favour of monosulfate, but ettringite may start to form on cooling. Thermodynamic modelling, using PHREEQC (Parkhurst and Appelo., 1999), with the HATCHES database version nea19 (Heath et al., 2012), indicates that after hydrothermal treatment the solution was super-saturated with respect to ettringite. This suggests that the high pH and ionic strength may be due to increased mineral solubility under hydrothermal treatment, which is then kinetically slow to re-equilibrate when the temperature is lowered.

Comparing aged- with untreated-NRVB-equilibrated water the significant differences were: (1) lower pH values and calcium concentrations in the aged-NRVB-equilibrated solutions, due to portlandite being removed during leaching; and (2) higher concentrations of some ions in the aged NRVB equilibrated solution, particularly sulfate and silicon.

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TABLE 1. Chemical composition of NRVB-equilibrated waters.

| | Units | Untreated | Leached 541 days | Leached 1272 days | Hydrothermally treated |
|---|---|---|---|---|---|
| pH | | 12.2 | 10.5 | 10.8 | 11.9 |
| Eh | mV | − | 370 | 390 | 370 |
| Chloride | mol l$^{-1}$ | $<3 \times 10^{-6}$ | $5.6 \times 10^{-5}$ | $5.4 \times 10^{-5}$ | $6.2 \times 10^{-4}$ |
| Sulfate | mol l$^{-1}$ | $2.1 \times 10^{-5}$ | $9.9 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $3.2 \times 10^{-3}$ |
| Carbonate | mol l$^{-1}$ | $<7 \times 10^{-4}$ | $<2 \times 10^{-4}$ | $2.0 \times 10^{-4}$ | $<2 \times 10^{-4}$ |
| Aluminium | mol l$^{-1}$ | $7 \times 10^{-6}$ | $2.5 \times 10^{-5}$ | $1.9 \times 10^{-5}$ | $4.2 \times 10^{-5}$ |
| Calcium | mol l$^{-1}$ | $1.5 \times 10^{-2}$ | $1.5 \times 10^{-3}$ | $9.7 \times 10^{-4}$ | $6.5 \times 10^{-3}$ |
| Iron | mol l$^{-1}$ | | $2.1 \times 10^{-5}$ | $<4 \times 10^{-7}$ | $<2 \times 10^{-7}$ |
| Potassium | mol l$^{-1}$ | $6.4 \times 10^{-4}$ | $<3 \times 10^{-5}$ | $7.7 \times 10^{-5}$ | $1.5 \times 10^{-3}$ |
| Silicon | mol l$^{-1}$ | $3.9 \times 10^{-5}$ | $8.2 \times 10^{-4}$ | $1.0 \times 10^{-3}$ | $5.0 \times 10^{-4}$ |
| Sodium | mol l$^{-1}$ | $1.9 \times 10^{-4}$ | $4.3 \times 10^{-5}$ | $4.3 \times 10^{-5}$ | $4.3 \times 10^{-5}$ |

## X-ray diffraction

The XRD powder diffraction patterns are shown in Fig. 1. The dominant phase in untreated NRVB was identified as calcite (added as limestone aggregate in the NRVB formulation). A lesser but significant amount of portlandite was also identified. Portlandite is derived from the hydrated lime aggregate and also a product OPC hydration. Minor quantities of a calcium alumi-nium oxide carbonate hydrate, $Ca_4Al_2O_6CO_3 \cdot 11H_2O$ and magnesium aluminium hydroxide carbonate hydrate, $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$ (hydrotalcite) were observed. Some of the minor lines are indicative of $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ (ettringite) but this identification is only tentative.

In samples of NRVB after 541 and 1272 days leaching, the powder diffraction patterns were
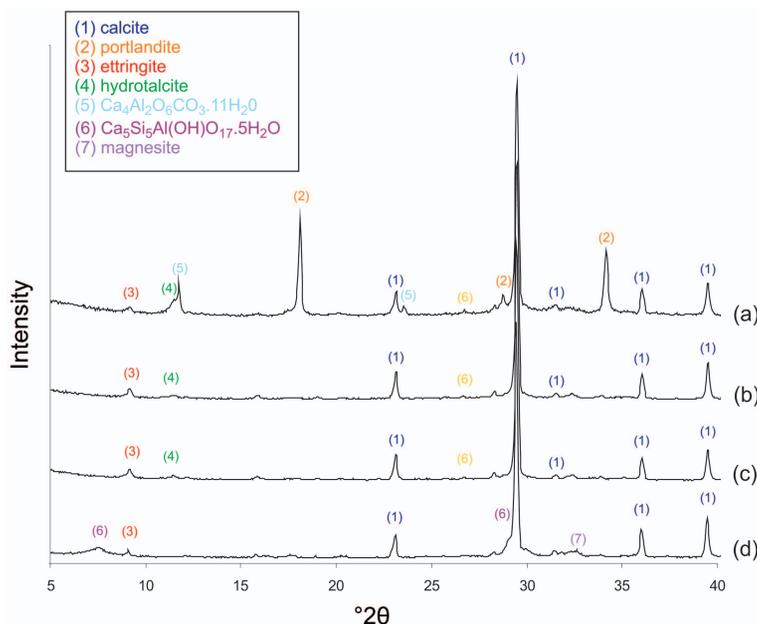


FIG. 1. X-ray diffraction patterns for (a) untreated NRVB; (b) NRVB leached for 541 days; (c) NRVB leached for 1272 days; and (d) NRVB subjected to leaching followed by hydrothermal treatment, with principal peaks indicated.

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dominated by calcite, with minor amounts of ettringite and hydrotalcite detected in both. Portlandite was shown to have been completely removed by leaching.

In the hydrothermally aged NRVB sample, calcite was again the dominant phase and a minor quantity of ettringite was observed. Some of the minor peaks indicate the presence of $Ca_5Si_5Al(OH)O_{17}\cdot 5H_2O$ (calcium aluminium silicate hydroxide hydrate) and $MgCO_3$ (magnesite).

The C-S-H phases were not identified by XRD in any of the samples. This is probably due to the large amounts of calcite, added as limestone aggregate in the NRVB formulation, because the dominant calcite peak at $2\theta = 29°$ coincides with the main peak for tobermorite-type C-S-H (Chen et al., 2004; Garbev et al., 2008).

### Differential scanning calorimetry

The DSC results confirm some of the features found from XRD analysis (Fig. 2). The major peak in all cases is calcite decomposition at around 800ºC. Untreated NRVB gives a peak for portlandite at around 450ºC, which is not seen in the other three samples. The temperature at which the calcite peak occurs is slightly higher in the aged samples, but this may be a result of physical differences between samples (e.g. particle size), rather than differences in the mineral.

Peaks at around 100ºC are due to removal of water. The general trend in this region is of a wide peak from C-S-H gels, with the aged material showing additional, more distinct peaks. In untreated NRVB the peak in the 100ºC region is fairly broad and undefined indicating the amorphous nature of the C-S-H gels. For NRVB leached for 541 days, there are two distinct low-temperature peaks, the second of which could be attributed to the ettringite (Sha et al., 1999) detected by the XRD analysis. The trace from the 1272-day-leached NRVB showed only a single peak, suggesting that further alteration has occurred in these phases with continued ageing. The hydrothermally aged NRVB also gave one low-temperature peak, but this is larger and more clearly defined than in the other samples, suggesting that more crystallization may have occurred.

### Specific surface area

The specific surface area, for untreated NRVB was determined as 14 $m^2$ $g^{-1}$. Leaching for 541 days increased this to 61 $m^2$ $g^{-1}$, probably due in part to the removal of low-surface-area portlandite. The effect of leaching of cements producing an increase in surface area has been reported elsewhere and was attributed variously to alteration from a high density C-S-H structure to lower density calcium silicoaluminate gels (Hidalgo et al., 2007) or the transformation of the higher density inner product C-S-H gel into forms with a high specific surface area (Thomas et al., 2004). After further leaching for a total of 1272 days the surface area decreased to 44 $m^2 g^{-1}$. In comparison, after hydrothermal ageing of the leached NRVB, the surface area was 25 $m^2$ $g^{-1}$ possibly due to more crystalline forms of C-S-H being present.

### Sorption

In some cases there was some drift in solution pH values and although adjustments were made during the course of the experiments, the final pH values were considerably different to the original solutions. This indicates that, despite the solution compositions being prepared from analyses of NRVB leachates, they did not fully equilibrate with the solids over the 30 days duration. In future, this may be avoided by first equilibrating the NRVB with the solution, adding the acidic stock solution and adjusting the pH if necessary. However, the method used in these experiments of preparing the radionuclide solution at the required pH, filtering then sampling to determine initial concentrations, has the advantage of ensuring the radionuclides are below the solubility limit. The effects that the variation in pH may have had on sorption properties of each of the radionuclides are discussed below.

### Uranium (VI)

Results from uranium(VI) batch sorption experiments onto untreated and aged NRVB samples are listed in Table 2. Sorption is strong for both aged and untreated NRVB. Distribution ratios ($R_D$ values) for uranium(VI) sorption onto untreated NRVB are in the range $4(\pm 1) \times 10^4$ to $10(\pm 2) \times 10^4$ $cm^3$ $g^{-1}$, with a mean value of $7(\pm 2) \times 10^4$ $cm^3$ $g^{-1}$. These values are approximately an order of magnitude higher than those reported in previous work (Bayliss et al., 1996), but are similar to values of $3 \times 10^4$ $cm^3$ $g^{-1}$ measured by Pointeau et al. (2004) for OPC
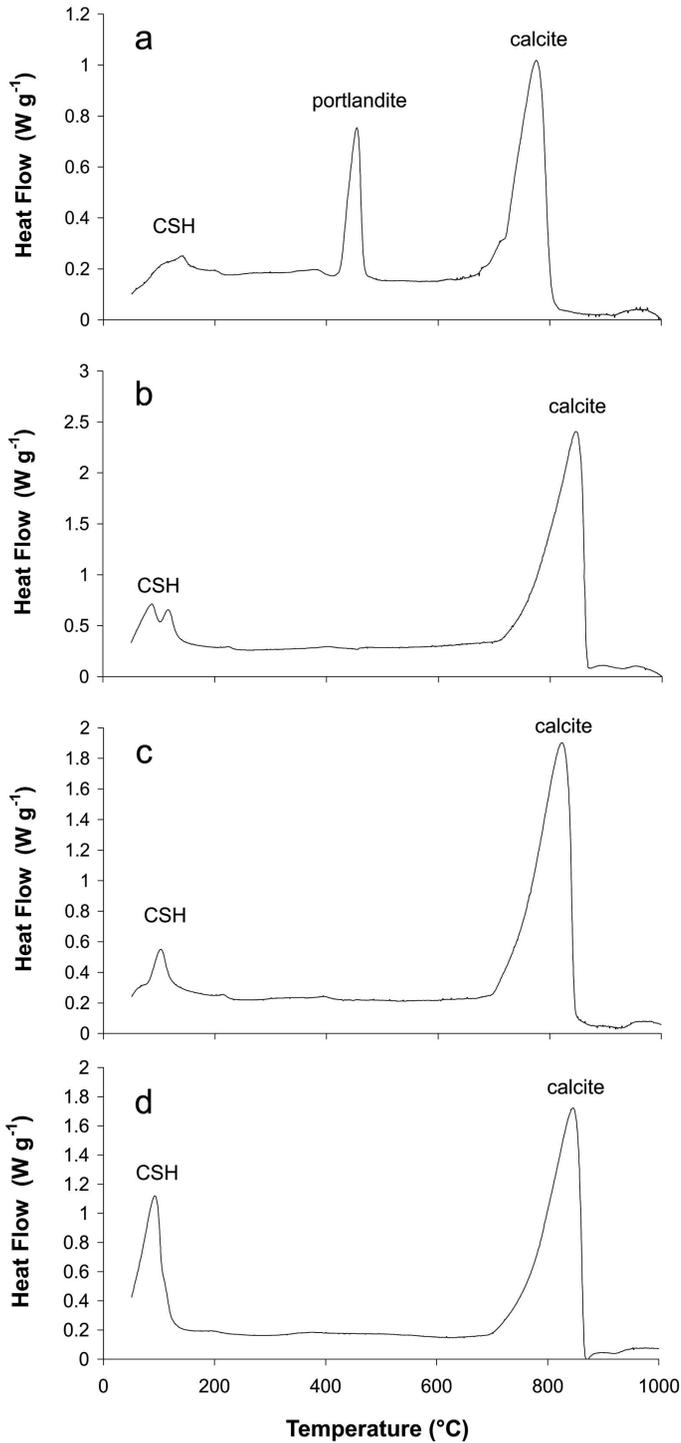
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FIG. 2. Differential scanning calorimetry traces for (*a*) untreated NRVB; (*b*) NRVB leached for 541 days; (*c*) NRVB leached for 1272 days; and (*d*) NRVB subjected to leaching followed by hydrothermal treatment.

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pastes and of ~$10^5$ cm$^3$ g$^{-1}$ by Zhao *et al.* (2000) for Portland cement with limestone aggregate. The two NRVB samples treated by leaching only, gave distribution ratios similar to or higher than untreated NRVB. Mean distribution ratios for backfill leached for 541 days and 1272 days were $1.6(\pm0.3)\times10^5$ cm$^3$ g$^{-1}$ and $8(\pm2)\times10^4$ cm$^3$ g$^{-1}$, respectively. Distribution ratios for hydrothermally treated NRVB were slightly lower, in the range $1.9(\pm0.2)\times10^4$ to $6.0(\pm0.9)\times10^4$ cm$^3$ g$^{-1}$ with a mean value of $4(\pm2)\times10^4$ cm$^3$ g$^{-1}$. Washing of the vessel walls with acid at the end of the sorption experiments indicated that less than 1% of the uranium had sorbed onto the plastic container.

These data show that there was an approximate two fold increase in uranium(VI) sorption onto NRVB leached after 541 days compared to untreated NRVB. An increase in U(IV) sorption onto cements following leaching has been reported by Pointeau *et al.* (2004). Studies using pure C-S-H phases have also measured higher $R_D$ values at pH values of $10.5-12.5$ than in highly alkaline systems with pH values above 13.0 and have attributed this to changes in the aqueous speciation of U(IV) (Tits *et al.*, 2008; Gaona, 2012). The buffering of the solution pH from 12.2 to 12.9 by the untreated NRVB may therefore have an effect of U(IV) sorption. The hydrothermally treated NRVB data are slightly lower (by a factor of 2) than for the untreated NRVB, though it should be noted that there is an overlap in these data when the uncertainties are considered. Zhao *et al.* (2000) have reported a decrease in $R_D$ values of one order of magnitude, following hydrothermal treatment of concrete at 200ºC.

### Neptunium

Neptunium was strongly sorbing onto all four NRVB samples; $R_D$ values were above $10^4$ cm$^3$ g$^{-1}$ in all cases (Table 3). In most of the experiments, the final neptunium concentrations were close to or below the limit of detection. As many $R_D$ values were greater than the maximum measureable value of $10^5$ cm$^3$g$^{-1}$ it is not possible to distinguish any significant differences in neptunium sorption behaviour between the untreated NRVB and the aged materials. No significant differences were found

TABLE 2. Distribution ratios for uranium(VI) sorption.

| NRVB type | pH | Eh (mV) | $R_D$ (cm$^3$ g$^{-1}$)* 30,000 MWCO filtration |
|---|---|---|---|
| Untreated | 12.9 | 403 | $4.2\pm0.5\times10^4$ |
| Untreated | 12.9 | 405 | $8.3\pm1.4\times10^4$ |
| Untreated | 12.9 | 407 | $9.5\pm1.8\times10^4$ |
| Untreated | 12.9 | 409 | $7.7\pm1.2\times10^4$ |
| Leached 541 days | 10.5 | 407 | $1.2\pm0.3\times10^5$ |
| Leached 541 days | 10.5 | 405 | $1.6\pm0.4\times10^5$ |
| Leached 541 days | 10.6 | 405 | $1.5\pm0.3\times10^5$ |
| Leached 541 days | 10.6 | 405 | $1.9\pm0.5\times10^5$ |
| Leached 1272 days | 11.2 | 411 | $8.8\pm1.8\times10^4$ |
| Leached 1272 days | 11.2 | 411 | $6.1\pm0.9\times10^4$ |
| Leached 1272 days | 11.3 | 409 | $1.0\pm0.2\times10^5$ |
| Leached 1272 days | 11.3 | 409 | $5.0\pm0.7\times10^4$ |
| Hydrothermally treated | 12.1 | 396 | $6.0\pm0.9\times10^4$ |
| Hydrothermally treated | 12.1 | 399 | $5.6\pm0.7\times10^4$ |
| Hydrothermally treated | 12.1 | 399 | $1.9\pm0.2\times10^4$ |
| Hydrothermally treated | 12.1 | 401 | $3.6\pm0.4\times10^4$ |

* The ±2 sigma uncertainties for distribution ratios are based on the combination of the uncertainties in the counting statistics only.

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between samples filtered through 0.45 μm filters alone and those also filtered through 30,000 NMWCO ultrafilters. The Eh values in all experiments remained below −300 mV. Under these conditions neptunium is predicted to be present predominantly as neptunium(IV), by the available thermodynamic data (Guillamont et al., 2003). Up to 2% of the neptunium inventory was found to be sorbed on the vessel walls.

The high $R_D$ values measured are similar to those reported previously for neptunium(IV) onto cementitious materials. Using 0.45 μm filtration for phase separation, these ranged from $4 \times 10^4$ cm$^3$ g$^{-1}$ for NRVB (Bayliss et al., 1996) to $2 \times 10^5$ cm$^3$ g$^{-1}$ for BFS/OPC (blast furnace slag/ ordinary Portland cement) (Bayliss et al., 2000). In both sets of previous experiments, no chemical reducing agents were added to the batch sorption experiments, to control Eh. Instead, neptunium was reduced prior to addition and then main-tenance of low Eh conditions relied on a low-oxygen atmosphere and in the case of BFS/OPC, the reducing properties of the solid. These previous neptunium sorption studies used the relatively short-lived isotope $^{235}$Np. However, a source of this isotope was not available and so

$^{237}$Np was used in the current study. The isotope $^{235}$Np has a significantly higher specific activity so that its use allowed the achievement of lower detection limits for neptunium and consequently higher $R_D$ values to be measurable. Measurements of Np(IV) sorption onto C−S−H phases have reported distribution ratios of $3 \times 10^5$ cm$^3$ g$^{-1}$ (Gaona et al., 2012).

### Zirconium

For all of the NRVB samples, sorption of zirconium was very strong, with all $R_D$ values greater than $10^5$ cm$^3$ g$^{-1}$ (Table 4). The $R_D$ values were slightly higher for untreated NRVB. However, there is a large scatter on the results, so this is not considered to be strong evidence of a reduction in sorption capacity with respect to zirconium, caused by leaching. Wall washes showed up to 2% of the zirconium to have been sorbed onto vessel walls.

The $R_D$ values measured were approximately an order of magnitude higher than those reported by Brownsword et al. (2002) for sorption onto NRVB ($1 \times 10^5$ cm$^3$ g$^{-1}$). The reasons for these differ-ences are not clear, but the high degree of variation

TABLE 3. Distribution ratios for neptunium(IV) Sorption.

| NRVB type | pH | Eh (mV) | $R_D$ (cm$^3$ g$^{-1}$)* | |
|---|---|---|---|---|
| | | | 0.45 μm filtration | 30,000 MWCO filtration |
| Untreated | 12.5 | −520 | $>1 \times 10^5$ | $>1 \times 10^5$ |
| Untreated | 12.4 | −300 | $>1 \times 10^5$ | $>1 \times 10^5$ |
| Untreated | 12.4 | −330 | $7\pm4 \times 10^4$ | $7\pm4 \times 10^4$ |
| Untreated | 12.6 | −300 | $5\pm3 \times 10^4$ | $>1 \times 10^5$ |
| Leached 541 days | 10.3 | −300 | $5\pm2 \times 10^4$ | $7\pm4 \times 10^4$ |
| Leached 541 days | 10.2 | −300 | $>1 \times 10^5$ | $>1.3 \times 10^5$ |
| Leached 541 days | 10.5 | −280 | $9\pm5 \times 10^4$ | $9\pm5 \times 10^4$ |
| Leached 541 days | 10.6 | −290 | $>1 \times 10^5$ | $>1 \times 10^5$ |
| Leached 1272 days | 10.3 | −320 | $>1 \times 10^5$ | $>1 \times 10^5$ |
| Leached 1272 days | 10.7 | −340 | $>1 \times 10^5$ | $7\pm3 \times 10^4$ |
| Leached 1272 days | 10.6 | −340 | $>1 \times 10^5$ | $>1 \times 10^5$ |
| Leached 1272 days | 10.5 | −300 | $5\pm3 \times 10^4$ | $7\pm4 \times 10^4$ |
| Hydrothermally treated | 12.6 | −545 | $2\pm1 \times 10^4$ | $>1 \times 10^5$ |
| Hydrothermally treated | 11.8 | −300 | $9\pm5 \times 10^4$ | $>1 \times 10^5$ |
| Hydrothermally treated | 12.0 | −290 | $>1.4 \times 10^5$ | $>1 \times 10^5$ |
| Hydrothermally treated | 12.0 | −280 | $5\pm2 \times 10^4$ | $>1 \times 10^5$ |

* The ±2 sigma uncertainties for distribution ratios are based on the combination of the uncertainties in the counting statistics only.

in the quadruplicate sets of results suggests that $R_D$ values greater than $10^5$ cm$^3$ g$^{-1}$ should be treated with some caution. Therefore, these results are interpreted as showing $R_D$ values of greater than $10^5$ cm$^3$ g$^{-1}$ for both untreated and aged NRVB.

*Tin*

In common with uranium, zirconium and neptunium, tin was found to be strongly sorbing onto all of the NRVB samples, irrespective of ageing treatment applied. All $R_D$ values were in the range $7 \times 10^4$ to $7 \times 10^5$ cm$^3$ g$^{-1}$ (Table 5). Average $R_D$ values for untreated NRVB and 541-days-leached NRVB were approximately twice those for the 1272-days-leached and hydrothermally aged material. However, given the high degree of variation in some sets of results, as reflected in the calculated standard deviation, there is no strong evidence for suggesting that the ageing treatments had an effect on the sorption of tin. The shifts in pH from their original values to as low 9.6 may have influence tin sorption, due to changes in aqueous speciation, from $Sn(OH)_6^{2-}$ at higher pH to $Sn(OH)_5^-$. Up to 0.5% of the tin was found to be sorbed on vessel walls. The results are similar to experimental measurements of tin sorption onto NRVB carried out previously, which reported $R_D$ values of $9 \times 10^4$ to $>3 \times 10^5$ cm$^3$ g$^{-1}$ (Bayliss et al., 1996).

## Conclusions

In terms of composition, the major difference between the leached and untreated NRVB was the absence of portlandite in the aged samples, as shown by XRD and DSC analysis. The removal of portlandite is consistent with a drop in leachate pH and lower calcium concentration observed with the leached NRVB. Leaching followed by hydrothermal treatment gave a higher pH value and calcium concentration in solution, than leaching only. Calcite remained a dominant mineral in both untreated and aged samples. Analysis by XRD showed some alteration in the minor phases. Hydrotalcite was detected in all NRVB except the hydrothermally aged sample, where magnesium was possibly present as magnesite. There is evidence from DSC of C$-$S$-$H crystallization induced by hydrothermal treatment. Leaching for 541 days had the effect of increasing the specific surface area of the NRVB

TABLE 4. Distribution ratios for zirconium sorption.

| NRVB type | pH | Eh (mV) | $R_D$ (cm$^3$ g$^{-1}$)* 0.45 μm filtration | 30,000 MWCO filtration |
|---|---|---|---|---|
| Untreated | 12.4 | 40 | $1.0 \pm 0.4 \times 10^7$ | $>4.9 \times 10^7$ |
| Untreated | 12.4 | 50 | $1.2 \pm 0.5 \times 10^7$ | $>1.6 \times 10^7$ |
| Untreated | 12.3 | 50 | $>1.5 \times 10^7$ | $>6.2 \times 10^7$ |
| Untreated | 12.4 | 50 | $1.3 \pm 0.6 \times 10^7$ | $>8.2 \times 10^7$ |
| Leached 541 days | 10.7 | 0 | $5.3 \pm 0.5 \times 10^5$ | $7.5 \pm 1.6 \times 10^6$ |
| Leached 541 days | 10.2 | 20 | $8.3 \pm 3.3 \times 10^6$ | $3.7 \pm 0.4 \times 10^6$ |
| Leached 541 days | 11.2 | 0 | $>1.9 \times 10^7$ | $>2.7 \times 10^7$ |
| Leached 541 days | 11.4 | −20 | $>1.9 \times 10^7$ | $>1.8 \times 10^7$ |
| Leached 1272 days | 11.0 | −20 | $2.2 \pm 0.1 \times 10^5$ | $2.1 \pm 1.7 \times 10^7$ |
| Leached 1272 days | 10.6 | −110 | $>1.8 \times 10^7$ | $>1.7 \times 10^7$ |
| Leached 1272 days | 9.7 | −90 | $1.5 \pm 0.1 \times 10^5$ | $1.4 \pm 0.1 \times 10^5$ |
| Leached 1272 days | 10.3 | −120 | $>1.2 \times 10^7$ | $1.4 \pm 0.6 \times 10^7$ |
| Hydrothermally treated | 11.8 | −80 | $7.6 \pm 1.6 \times 10^6$ | $>2.6 \times 10^7$ |
| Hydrothermally treated | 11.9 | −80 | $1.3 \pm 0.5 \times 10^6$ | $1.7 \pm 1.1 \times 10^7$ |
| Hydrothermally treated | 11.9 | −80 | $1.3 \pm 0.6 \times 10^6$ | $>1.2 \times 10^7$ |
| Hydrothermally treated | 11.6 | −70 | $2.1 \pm 1.3 \times 10^7$ | $>3.8 \times 10^7$ |

* The ±2 sigma uncertainties for distribution ratios are based on the combination of the uncertainties in the counting statistics only.

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TABLE 5. Distribution ratios for tin sorption.

| NRVB type | pH | Eh (mV) | $R_D$ (cm$^3$ g$^{-1}$)* | |
|---|---|---|---|---|
| | | | 0.45 μm filtration | 30,000 MWCO filtration |
| Untreated | 12.3 | −90 | $6.7{\pm}0.6 \times 10^5$ | $3.5{\pm}0.3 \times 10^5$ |
| Untreated | 12.2 | −90 | $5.9{\pm}0.5 \times 10^5$ | $5.0{\pm}0.6 \times 10^5$ |
| Untreated | 12.2 | −80 | $4.2{\pm}0.3 \times 10^5$ | $1.3{\pm}0.1 \times 10^5$ |
| Untreated | 12.2 | −90 | $6.9{\pm}0.8 \times 10^5$ | $5.5{\pm}0.5 \times 10^5$ |
| Leached 541 days | 9.9 | 100 | $4.1{\pm}0.4 \times 10^5$ | $4.2{\pm}0.3 \times 10^5$ |
| Leached 541 days | 9.8 | 110 | $4.3{\pm}0.4 \times 10^5$ | $4.5{\pm}0.5 \times 10^5$ |
| Leached 541 days | 9.6 | 110 | $3.9{\pm}0.3 \times 10^5$ | $3.8{\pm}0.3 \times 10^5$ |
| Leached 541 days | 9.9 | 90 | $3.9{\pm}0.3 \times 10^5$ | $4.3{\pm}0.4 \times 10^5$ |
| Leached 1272 days | 10.5 | 140 | $2.6{\pm}0.2 \times 10^5$ | $2.6{\pm}0.2 \times 10^5$ |
| Leached 1272 days | 10.6 | 140 | $2.9{\pm}0.3 \times 10^5$ | $2.9{\pm}0.2 \times 10^5$ |
| Leached 1272 days | 10.8 | 130 | $1.8{\pm}0.1 \times 10^5$ | $1.5{\pm}0.1 \times 10^5$ |
| Leached 1272 days | 10.5 | 130 | $1.8{\pm}0.1 \times 10^5$ | $1.3{\pm}0.1 \times 10^5$ |
| Hydrothermally treated | 11.9 | 160 | $1.7{\pm}0.1 \times 10^5$ | $9.0{\pm}0.6 \times 10^4$ |
| Hydrothermally treated | 11.5 | 100 | $3.4{\pm}0.3 \times 10^5$ | $2.5{\pm}0.2 \times 10^5$ |
| Hydrothermally treated | 11.5 | 100 | $7.2{\pm}0.5 \times 10^4$ | $1.4{\pm}0.1 \times 10^5$ |
| Hydrothermally treated | 11.3 | 120 | $3.3{\pm}0.3 \times 10^5$ | $2.1{\pm}0.2 \times 10^5$ |

* The ±2 sigma uncertainties for distribution ratios are based on the combination of the uncertainties in the counting statistics only.

samples, although further leaching then led to a decrease. However, the surface area of the untreated NRVB was lower than that of any of the aged samples.

This study has shown that these alterations have very little effect on the sorption of uranium(VI), neptunium(IV), zirconium and tin onto NRVB. The most probable explanation for these findings is that, even after the 'ageing' treatments, C−S−H gel still constitutes a large fraction of the NRVB and after its conversion to more crystalline forms it retains a high sorption capacity.

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