Investigating humic substances interactions with Th^{4+} , UO_2^{2+} , and NpO_2^+ at high pH: relevance to cementitious disposal of radioactive wastes

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Abstract

A number of geodisposal concepts for intermediate level radioactive waste involve geological emplacement within cementitious repositories. Such facilities, once rehydrated with groundwater, will create high pH environments due to aqueous phase reaction of the cements. This work focuses on the interactions of several important long-lived radionuclide cations with dissolved organic matter (DOM) constituents (humic and fulvic acids) under high pH conditions. We also sought to test the comprehensive speciation model WHAM/Humic Ion Binding Model VII for these specific conditions. Results for Th demonstrate high fractions present as organic complexes at all pH values. Binding of neptunyl to DOM shows a maximum over the pH range expected within an evolving repository. Uranyl exhibits decreasing binding with pH, however, the majority of metal in solution is present as organic complexes under the lower pH conditions investigated (10-10.5). We have updated the WHAM/Model VII binding values for UO_2^{2+} , and have for the first time added NpO_2^+ values to the database. These updates now allow application of the model for more complex mixtures across the entire repository pH range. Calculations for three simulated cement interstitial waters (representing different degradation phases) suggest U(VI) and Np(V) are not likely to be significantly bound to DOM under these conditions.

1. Introduction

Actinides (particularly Th, U, Np and Pu) may be released to aquatic environments via several different pathways, such as, natural occurrence, intentional discharge (particularly historical), dissolution of mine tailings, or as a result of accidental release. Transport of these metals through the environment is likely to be strongly influenced by the presence of natural dissolved organic matter (DOM), which is ubiquitous in aquatic environments. DOM will also be present in groundwaters with concentrations dependent upon the host rock environment and recharge source and pathway. Binding of cationic metals to DOM exerts a powerful control on chemical conditions in waters and soils, influencing the transport and retention of metals (Tipping et al., 2011). This binding can result in increased solubility of metal salts and transport of DOM may result in simultaneous transport of bound metals. Projects in Europe (e.g., TRANCOM II; Maes et al., 2004) and North America (e.g., Chalk River low level waste disposal sites; Robertson et al., 2000) have sought to investigate specifically the role of DOM on radionuclide transport.

Strategies for disposal of intermediate level radioactive wastes (ILW) in several countries involve geological emplacement, followed by addition of a cementitious backfill (see Crossland and Vines, 2001; for the UK case). The aim is to provide a chemical barrier that retards radionuclide transport from the geological disposal facility (GDF). Aqueous phase reactions, such as dissolution, leaching and associated processes, create a high pH environment within the interstitial waters of the cement (Berner, 1992; Glasser et al., 2008). These reactions induce gradual changes to the composition of the interstitial water, from typical “young” concrete leachate, with a pH above 13, to more evolved leachate with a pH lower than 10 (Jacques et al., 2010). The influence of organic matter on radionuclide migration has been recognised as a significant source of uncertainty in radioactive waste management (Glaus et al., 1997; 2000). A geochemically disturbed zone (GDZ) will evolve at the concrete-host rock interface, and depending on the host rock mineralogy, a high pH

environment may evolve. Thus, there is a pressing need to obtain experimental data and to test models of DOM binding to radionuclides under the high pH conditions that may develop within and around these facilities. The presence of DOM affects not only aqueous radionuclide speciation in the context of geological disposal. A comprehensive review of the influence of DOM of the transport of radionuclides in high pH environments has recently been published (Stockdale and Bryan, 2013) and evidence for wide ranging influences of DOM on radionuclide interactions in relation to mineral sorption, kinetics and redox reactions was evaluated.

The Windermere Humic Aqueous Model (WHAM; <http://www.ceh.ac.uk/products/software/wham/>) is a widely used chemical speciation code used in geochemical and ecotoxicological research and in regulation. The sub-model dealing with natural organic matter binding (Humic Ion Binding Model VII; Tipping et al., 2011) has recently been updated to include the most up to date information on humic and fulvic acid binding of protons and metal cations (40 cationic species). This also includes improved prediction of cation binding at higher pH due to increased numbers of available data and stricter data selection criteria than previously applied. Using established methods based on linear free energy relationships (Carbonaro and Di Toro, 2007), model parameters for several additional actinide cations as well as Pd(II) and Sn(II) have recently been estimated (Stockdale et al., 2011). Despite the inclusion of radionuclides within this and other comprehensive models, they have not yet been significantly exploited in relation to management of radioactive wastes. Continued testing and development of these models, including for geodisposal conditions, should give waste management agencies a greater degree of confidence that such tools can be included in performance assessment calculations.

In this work, we report results of equilibrium dialysis experiments that illustrate the humic substances binding behaviour, in high pH systems, for Th(IV), U(VI) and Np(V). Additionally, we report updates to WHAM/Model VII achieved by incorporating additional datasets for UO_2^{2+} , as well as calculating NpO_2^+ binding constants based on several experimental datasets from the literature, thus, enabling, for the first time, the inclusion of this metal cation in comprehensive speciation modelling.

2. Experimental methods

2.1. Reagents

DOM reference materials (Suwannee River humic acid, SRHA; Suwannee River fulvic acid, SRFA; Suwannee River natural organic matter, SRNOM) were obtained as solid salts from the International Humic Substances Society and once dissolved (initially in MQ water adjusted to pH 10 to aid dissolution, followed by adjustment to pH 6-8 with 0.1 M HCl) were used without any pre-treatment. Final stock concentrations were $\sim 50 \text{ mg L}^{-1}$. Aldrich humic acid was prepared following the procedure outlined in section 2.1.1. Ionic strength was controlled using NaCl (TraceSelect, Fluka Analytical). The pH adjustments were undertaken using 1 M solutions of HCl (prepared from 34% NORMATOM grade, VWR) or NaOH (freshly prepared for each use from 99.99% purity salt; Alfa Aesar). All experiments were performed in acid washed (10% v/v HNO_3) 180 ml polypropylene pots. U-238 was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2$ salt in 1 M HCl and subsequent dilution at the same acid concentration to achieve a $10^{-6} \text{ mol L}^{-1}$ stock. The U-232 stock (1 kBq mL^{-1}), used as a tracer, was separated from daughter nuclides with a UTEVA column (Triskem International) using a previously reported method (Horwitz et al., 1992). The initial product from this process, Th-228 (1.9 kBq mL^{-1} ; including daughter alpha activity), was retained and used to perform Th experiments at very low concentrations. The Np-237 stock was diluted from a more concentrated aqueous solution to give an activity of 344 Bq mL^{-1} .

2.1.1. Preparation of purified Aldrich humic acid (PAHA)

In order to ensure the humic acid contained neither fulvic acid (FA) nor insoluble components, we used a slightly revised procedure to that reported in Harbour et al. (2007). Briefly, 600 mg of Aldrich humic acid sodium salt was dissolved into a 1 L solution (using MQ water) of 2.8 mmol L^{-1} NaF (99.99%, Alfa Aesar) that had been adjusted to pH 12. The NaF is used to dissolve silicate impurities (Kim et al., 1990). After being left overnight, the solution was passed through a $0.45 \text{ }\mu\text{m}$ polyethersulfone membrane filter containing a glass microfiber prefilter (Whatman Polydisc AS). In order to remove the FA fraction, the filtrate was then subjected to duplicate purification cycles, i.e., HA precipitation (pH 1), centrifugation, supernatant (FA) removal, and dissolution of the precipitate (0.1 M NaOH). Following the purification process, rather than drying and desiccation, the HA was re-dissolved and the solution pH was adjusted to a circumneutral value and the product stored refrigerated awaiting use. To determine the carbon content of the treated Aldrich HA, we performed total organic carbon (TOC) analysis on diluted aliquots using a Shimadzu TOC 5050A. The concentration of the purified form was 210 mg L^{-1} assuming a carbon content for the purified form of 53% (Kim et al., 1991; Thomsen et al., 2002). This represents a recovery of 35% of the initial concentration of HA. Previous work examining the evolution of DOM properties over long term experiments (up to one year) has demonstrated that oxygen type binding sites are not depleted, and may even be enhanced, during long-term exposure to high pH solutions (Schäfer et al., 2003). Additionally, depending upon the rock type, DOM solution concentrations may be enhanced by desorption processes caused by high alkaline solutions (Claret et al., 2002). These studies suggest that the humic substances typically used for laboratory studies should be suitable proxies for the binding behaviour of material that has had prolonged exposure to alkaline solutions.

2.2. Instrumental analysis

Measurement of pH was performed using a Mettler Toledo Seven Multi meter and a Mettler Toledo InLab Routine Pro electrode. A five point calibration was performed using the following buffers; NIST traceable pH 4, 7 and 10; pH 9 (Scientific Laboratory Supplies, UK), and pH 13 (Fluka Analytical). Calibration slopes below 98% were rejected and the calibration procedure repeated until this value was achieved or exceeded. Calibration was carried out before each set of measurements. This resulted in a maximum uncertainty for pH measurements of approximately 0.1 for pH values ≤ 12.5 and 0.2 for values > 12.5 . Samples for liquid scintillation counting (Wallac Quantulus 1220 ultra-low level liquid scintillation spectrometer) were prepared by addition of 1 mL of 1 M HCl to 1 mL of sample, followed by 10 mL of ScintiSafe 3 cocktail (Fisher Scientific). Th-228 samples were stored for one month prior to analysis in order to ensure secular equilibrium with daughter radionuclides. UV-visible measurements of DOM concentrations were performed on a Cary 500 SCAN spectrophotometer using a 1 cm quartz cuvette. Due to low absorbance values at the experimental HA concentrations and the desire to avoid potential noise related errors caused by using a single wavelength, we used the mean absorbance over the range 360-410 nm to quantify the colour intensity of the DOM in the dialysate relative to that of the bulk solution. We analysed UV-visible absorbance spectra for humic acids at $\leq 5 \text{ mg L}^{-1}$. Over the pH range of our study, we could not establish any statistically significant spectral variations (this work, unpublished results). Previous work by Janot et al. (2010) demonstrated increased absorbance values with increasing pH and using a 5 cm cell. However, convergence is apparent for spectra at pH 10, 10.4 and, the maximum value studied, 10.9. This may explain the lack of any statistical difference in our high pH data.

2.3. Equilibrium dialysis procedure

In the dialysis experiments, the outer solution had a total volume of 149 mL, and at the start of the experiment contained the HA and metal cation. Details of the initial concentrations of electrolyte, metal and humic substance concentration within this solution, along with the pH

measurement at the end of the experiment, are detailed in Table 1. Np(V) and U(VI) experiments were performed in triplicate, Th(IV) experiments were duplicates. The dialysate solution was contained within pre-cleaned regenerated cellulose dialysis membrane tubing, with a molecular weight cut-off of 1000 Da (SpectraPor 7) and sealed with SpectraPor clips at both ends. The upper recommended pH limit for the dialysis membrane is 12. However, one week deployments under our experimental conditions have not resulted in increased absorbance values for UV-visible spectra, which would indicate degradation, from either the presence of cellulose degradation products or an increase in the HA that can pass through the membrane (this work and Stockdale and Bryan, 2012). The dialysate volume was 4 mL, and initially the ionic strength and pH were the same as the outer solution, but with no HA or metal cation. The procedure differs in several ways from previously described methods (e.g., Glaus et al., 1995). The relative volumes of dialysate and bulk solution differed significantly and the total concentration of HA was lower. No additional competing ligands were added as OH^- performs this function at high pH for the majority of radionuclides. This is required for many elements at lower pH values to ensure that there are measurable fractions of radionuclides in both the dialysate and outer fractions.

The outer solution was prepared in two parts of equal volume that were added to the experiment simultaneously. These solutions contained HA or the metal of interest, with the pH and ionic strength adjusted to those required for the experiment. This was done in order to control the pH conditions under which the cation was added to the humic acid. This prevents potential kinetic effects associated with dissociation of cation-humic complexes if the pH of a binary mixture is changed. Once these solutions were added to the airtight vessel containing the dialysis bag, the vessels were then sealed with laboratory film as additional protection against ingress of CO_2 . The prepared experiments were then left to stand for 7 days under dark conditions. At the end of the experiments, we took samples of both bulk solutions and dialysates for liquid scintillation and UV-visible spectrometry

analysis, as outlined in section 2.2. Both dialysate and bulk solutions were prepared under ambient laboratory conditions, but in order to exclude carbonates as much as possible during the preparation, freshly drawn MQ water was used throughout, prepared solutions were stored in air evacuated containers before use, and the experiments were prepared in the shortest time possible. This procedure has been previously demonstrated to exclude any effects of carbonate speciation on the results (Stockdale and Bryan, 2012). This was further validated by repeating experiments at the pH value where ΣCO_3^{2-} was predicted to have the greatest effect on speciation and additionally including $10^{-4} \text{ mol L}^{-1}$ of ΣCO_3^{2-} . No change in speciation was seen between the experiments with and without carbonate, indicating insufficient carbonate dissolution in the experiments to affect uranyl complexation with dissolved organic matter (Stockdale and Bryan, 2012).

Wall sorption was monitored for each of the dialysis experiment (Table 1) by comparing an initial activity measurement with those performed at the end of the experiment. Values were within the range $8 \pm 8\%$. As the amount lost to the walls was within experimental uncertainty of zero, we did not take any further account of this in our calculations.

2.4. Calculation of humic bound fractions of radionuclides

Calculations follow the procedures detailed in Stockdale and Bryan (2012). Here the term 'Me' is used to denote the cation of a radionuclide element. The total radionuclide in solution is represented by the sum of the inorganic ($[\text{Me}^+]$; mol L^{-1}) and organic fractions, with the concentration of the cation humic complex ($[\text{Me-HA}]$; mol mg^{-1}) related to the amount bound (Me-HA) and the humic acid concentration ($[\text{HA}]$; mg L^{-1}). The concentration in the two compartments will be directly related to the measured tracer activity (A_{bag} and A_{bulk} ; Bq) and can be expressed as Equations 1 and 2, assuming equal binding properties of the humic acid within and outside the dialysis membrane (this aspect is discussed further in section 3.4.1.).

$$A_{\text{bag}} \propto [\text{Me}^{x+}]_{\text{Tot-bag}} = \text{Me-HA} \times [\text{HA}]_{\text{bag}} + [\text{Me}'] \quad (1)$$

$$A_{\text{bulk}} \propto [\text{Me}^{x+}]_{\text{Tot-bulk}} = \text{Me-HA} \times [\text{HA}]_{\text{bulk}} + [\text{Me}'] \quad (2)$$

Where $[\text{HA}]_{\text{bag}}$ and $[\text{HA}]_{\text{bulk}}$ represent the humic acid concentration within and outside the dialysis membrane, respectively. Considering measured tracer activity and subtracting Equation 1 from 2, yields Equation 3:

$$A_{\text{Me-HA}} = (A_{\text{bulk}} - A_{\text{bag}}) / ([\text{HA}]_{\text{bulk}} - [\text{HA}]_{\text{bag}}) \quad (3)$$

where $A_{\text{Me-HA}}$ can be considered as the tracer activity contribution of the humic bound cation per mg L^{-1} of HA in the experiment.

In order to calculate the organic bound fraction of Me, it is first necessary to calculate the tracer activity of the inorganic fraction (Equation 4). Using data from either the bulk solution or the dialysate results in the same value.

$$A_{\text{inorganic}} = A_{\text{bulk}} - A_{\text{Me-HA}} \times [\text{HA}]_{\text{bulk}} \quad (4)$$

The fraction of humic bound metal (f_{organic}) can then be calculated from Equation 5.

$$f_{\text{organic}} = A_{\text{Me-HA}} \times [\text{HA}]_{\text{effective}} / (A_{\text{Me-HA}} \times [\text{HA}]_{\text{effective}} + A_{\text{inorganic}}) \quad (5)$$

Where $[\text{HA}]_{\text{effective}}$ is the effective mean concentration of HA when the total experimental volume is considered.

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2.4.1. Determination of upper limits for cation-reactive DOM in the dialysate

Measurements using UV absorbance yield the relative fractions of coloured DOM in the two fractions. However, early results indicated that not all of the dialysate DOM had the sorption behaviour of the bulk solution, and this was revealed from results where the bound fractions were calculated to be greater than 100% of the total radionuclide concentration. This is likely

to be caused by preferential diffusion across the membrane of HA in the lower molecular weight range, with a corresponding lower reactivity towards cations. Tetravalent actinides have been shown to bind strongly to humic acids in solution over a wide range of pH values (e.g., Warwick et al., 2005, for U-IV; and Benes, 2009, for Th-IV), thus, in the absence of competing ligands, such as carbonate, tetravalent actinides will exist in solution mainly as complexes with HA. This behaviour can be exploited in order to determine an upper limit for the fraction of HA within the dialysate that is reactive to radionuclides (relative to the bulk HA). Thus, for each DOM type (except SRNOM), we performed additional dialysis experiments with Th, and used the results to estimate the maximum value (fraction relative to the bulk solution) of reactive DOM within the dialysate. This was achieved by assuming 100% of the Th is present as organic complexes (discussed in section 4.1.1.) and using Excel[®] Solver to calculate the dialysate HA or FA fraction that results in a calculation of 100% Th complexation with DOM.

3. Humic Ion Binding Model VII; theory and methods

The Windermere Humic Aqueous Model combines the WHAM inorganic speciation program (Tipping, 1994) with Humic Ion Binding Model VII, which is described in more detail in Tipping et al. (2011). The combination of the organic and inorganic codes is referred to here as WHAM/Model VII. The model uses a structured formulation of discrete, chemically-plausible, humic binding sites for protons, in order to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. Metal ion binding at the type A (carboxylic acid type groups) and B (weaker acids, such as phenolic acids) sites is described with average intrinsic equilibrium constants (K_{MA} and K_{MB} , which are interrelated). High values of K_{MA} mean that the metal ion is strongly bound at the high abundance “weak” (carboxylic and/or phenolic) sites. A low density of “strong” binding sites are defined and are postulated to be associated with nitrogen groups in the model (represented by ΔLK_2). Only the free ion

and first hydrolysis products are considered to bind to organic matter and have the same equilibrium constant for any given metal.

For Model VII, metal binding data were fitted by optimising $\log K_{MA}$, using the default parameters obtained for proton-binding, and with ΔLK_2 related to the stability constant for the ammonia-metal ion complex ($\Delta LK_2 = 0.58 \times K_{NH_3}$). Parameter estimation was then performed by minimizing the sum of the squared differences between observed and calculated values of $\log v$, where v is the moles of metal bound per gram of humic matter (Tipping et al., 2011). Hydrolysis reactions of metal ions were taken into account, using equilibrium constants from Guillaumont et al. (2003). Here, we used the same fitting program as used for the previous Model VII parameter fitting, which were carried out by the Nelder-Mead polytope method (Nash and Walker-Smith, 1987). Following calculation of $\log K_{MA}$ values for individual datasets, the default values for a 'generic' fulvic and humic acid are calculated according to equations 6 and 7 (Tipping et al., 2011), where n_{FA} and n_{HA} refers to the number of datasets for FA and HA and α_O is the Irving-Rossotti slope (defined below).

$$\begin{aligned} \log K_{MA,FA,def} = & \{n_{FA} \log K_{MA,FA,mean} \\ & + (n_{HA} \log K_{MA,HA,mean}/1.11) \\ & + (3.81\alpha_O + 0.37)\}/(n_{FA} + n_{HA} + 1) \end{aligned} \quad (6)$$

$$\begin{aligned} \log K_{MA,HA,def} = & \{n_{HA} \log K_{MA,HA,mean} \\ & + 1.11n_{FA} \log K_{FA,HA,mean} \\ & + (3.51\alpha_O + 0.74)\}/(n_{HA} + n_{FA} + 1) \end{aligned} \quad (7)$$

Two aspects of these equations are included to reduce the possibility of excessive outliers. Firstly, Tipping et al. (2011) observed a linear relationship between the HA and FA values with a slope of 1.11, this relationship is included in the second line of these equations. This allows values for both organic acids to be used in the calculation of both HA and FA default values. Secondly, a correlation is observed between $\log K_{MA}$ and α_O (the slope of the

equation of Irving and Rossotti for ligands with oxygen donor atoms, described further in section 4.1.3.; Carbonaro and Di Toro, 2007). In equations 6 and 7, the third line includes this relationship. This combination of procedures improves on earlier model versions through more internally consistent parameter values. This method also allows calculation of default Model VII binding parameters in the absence of data for both HA and FA binding (e.g., Stockdale et al., 2011). Clearly, the larger the number of HA and FA datasets, the more weight the experimental data will provide to the overall calculation of the default log K_{MA} values. Tipping et al. (2011) calculated log K_{MA} values for uranyl binding of 2.61 for HA and 2.38 for FA. No previous work has calculated binding values for Np(V).

In selecting suitable datasets from the literature, we required several data (or data from which the required inputs could be calculated). These included: pH, ionic strength, the metal free ion concentration and the corresponding amount of metal bound per gram of organic acid. The studies also need to be performed in solutions in the absence of competition from other cations. Thus, due to the potential for competitive effects, those experiments performed using natural waters cannot be used in the determination of log K_{MA} values. Such studies (e.g., Zeh et al., 1997) can yield interesting insights into metal complexation behaviour. Readers are referred to the review of Stockdale and Bryan (2013) for further discussion of these datasets in relation to high pH geodisposal environments.

The following inorganic U(VI) species were included in the model for the example application; UO_2OH^+ , $UO_2(OH)_2$, $UO_2(OH)_3^-$, $UO_2(OH)_4^{2-}$, UO_2CO_3 , $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, UO_2Cl^+ , UO_2Cl_2 , $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_2(OH)_3CO_3^-$, $(UO_2)_2OH^{3+}$, $(UO_2)_3(CO_3)_6^{6-}$, $(UO_2)_3(OH)_4^{2+}$, $(UO_2)_3(OH)_5^+$, $(UO_2)_3(OH)_7^-$, $(UO_2)_3(OH)_3CO_3^+$, $(UO_2)_4(OH)_7^+$, $CaUO_2(CO_3)_3^{2-}$ and $Ca_2UO_2(CO_3)_3$. These thermodynamic data were largely from the recent Nuclear Energy Agency (NEA) database publication (Guillaumont et al., 2003), which is an update of the original NEA review of Grenthe et al., (1992). Exceptions were $UO_2(OH)_4^{2-}$ (from Duro et al.,

2006) and the calcium-uranyl-carbonate species (Bernhard et al., 1996; Kalmykov and Choppin, 2000; Bernhard et al., 2001). The following Np(V) species from Guillaumont et al. (2003) were included; NpO_2OH , $\text{NpO}_2(\text{OH})_2^-$, $\text{NpO}_2\text{OH}(\text{CO}_3)_2^{4-}$, $\text{NpO}_2\text{CO}_3^-$, $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2(\text{CO}_3)_3^{5-}$.

4. Results and discussion

4.1. Dialysis experiments

This section details the results of the dialysis experiments, and presents data in terms of the fractions of the metals that are bound to DOM ligands. The full data set is provided as electronic supporting information for those wishing to perform additional data analysis, for example, calculation of conditional stability constants. The formation of organic complexes will, in part, be a function of the inorganic complexes in solution due to competition with inorganic ligands. Figure 1 illustrates the inorganic complexation of U(VI) and Np(V), calculated for a simple solution in both the presence and absence of carbonates. This figure shows the increased formation of multi-hydroxide complexes as the pH increases over the range covered in our experimental work.

4.1.1. Using Th data to determine maximum values for reactive HA within the dialysate

We performed dialysis experiments with Th across the pH range 10.4 to 13.1 (data are included in the supporting information). Table 2 shows the calculated fraction of Th bound to DOM assuming different values for the quantity of 'speciation active' DOM within the dialysate (i.e., that fraction of the humic that plays a significant role in radionuclide complexation within the dialysate solution). The second column shows Th binding values when it is assumed that the UV measured fraction represents the 'speciation active' DOM. This assumption yields values for metal bound to DOM vastly in excess of 100%, demonstrating that this value over predicts the binding capacity of the DOM measured in the

dialysate. The third column shows the predicted Th binding under the assumption that there is no DOM in the dialysate. This yields values of 98-99%, demonstrating that there is very little 'speciation active' DOM in the dialysate. The forth column of Table 2 indicates the calculated values for the fraction of 'speciation active' DOM in the dialysate under the assumption that 100% of the Th is present in solution as organic complexes (using the methods reported in section 2.4.1.). Thus, we calculated a maximum possible value for $[HA]_{bag}$ relative to $[HA]_{bulk}$ and this value was then applied to the results for the other radionuclides for each of the DOM types. We recognise that the HA within the dialysate is likely to contain a continuum of binding strengths across the entire HA fraction. However, following this procedure allows us to define the dialysate HA operationally with respect to the bulk solution HA, and thus calculate the relative organic and inorganic fractions of the metals. Whilst we have used these values in the calculations for the dialysis experiments of other metals, it is worth noting that due to the low values for $[HA]_{bag}$, if we had assumed that no 'speciation active' DOM were present in the dialysate, percentage binding values would be lower by only 4% or less.

The strong association of thorium with organic acids is consistent with other studies. Beneš (2009) used free-liquid electrophoresis techniques to examine the complexation of thorium with purified Aldrich humic acid over the pH range 2 to 11. In the absence of other strongly complexing ligands, it was found that Th-humic complexes represent close to 100% of the total solution concentration. This behaviour was observed up to the maximum pH studied of 11. Although studied over a narrower pH range, tetravalent uranium speciation has also been investigated. Warwick et al. (2005) studied U^{4+} binding to boom clay and Aldrich humic acids over the pH range 6-9. For Aldrich HA, the median value of the U – HA complex was >95% of the total dissolved metal, with a range of 46.4-99.8%. For boom clay HA, organic complexes represented >99.7% for all measurements.

4.1.2. Uranyl binding to humic substances: effect of pH and ionic strength

The distribution of U(VI) in the presence of PAHA as a function of pH is presented in Figure 2. These data show decreasing organic complexation as pH increases. Organic complexes represent ~60-70% of the total UO_2^{2+} at pH ~10.5. This falls rapidly as the pH increases due to the inorganic speciation shifting as a result of increased formation of hydrolysis products, particularly the third and fourth uranyl hydrolysis species (Figure 1). However, organic complexes are still observed, albeit at a lower concentration, at pH >12. Previous work that investigated the addition of carbonate (as discussed in section 2.3.), and the low calculated values for carbonate species as shown in Figure 1, suggest that carbonate complexes will not be a significant factor in the distribution of species across the pH range and experimental conditions studied here.

Figure 2 presents the fractions bound at different PAHA concentrations at various concentrations of the background electrolyte (NaCl). These concentrations will approximate the ionic strength up to pH ~12.1, where the ionic strength will have a contribution from NaOH of ~0.01 mol L⁻¹, and at pH 13 it will contribute 0.1 mol L⁻¹. No clear ionic strength dependence can be demonstrated from these data. This is consistent with Glaus et al. (1997), who observed only weak correlations with ionic strength, which were not statistically significant when considered against the ranges of values obtained from replicate experiments. The ionic strengths in this work and the Glaus et al. (1997) study were < 0.3 mol L⁻¹ and the humic acid concentrations were ≤500 mg L⁻¹ (≤16 mg L⁻¹, this work; ≤500 mg L⁻¹, Glaus et al., 1997). Greater ionic strengths or high DOM concentrations may result in increased DOM coagulation. This may alter their interactions with metal ions, and therefore this may require further consideration if data are required for geodisposal in saline or high DOM concentration environments.

We performed additional dialysis experiments in the absence of HA in order to check that equal concentration values were obtained for dialysate and bulk solution after the duration of the experiment. Whilst this was the case for all pH values less than ~12.3, experiments at pH ~13 resulted in dialysate concentrations that were typically 10% lower than those of the bulk solution (this behaviour was not seen for neptunyl). In the presence of HA the relative concentrations of the dialysate and bulk solutions also yielded the same result at pH ~13. These results suggest that there is no significant binding of uranyl by organic matter at this pH, or that binding is at levels that are too low to be detected using dialysis techniques. For this reason, data obtained for uranyl at pH values >12.5 are excluded from the presented results and associated modelling.

4.1.3. Neptunyl binding to humic substances: effect of pH and ionic strength

The distribution of Np(V) in the presence of PAHA as a function of pH is presented in Figure 3. Neptunyl binding differs from uranyl due to the dual factors of lower binding strength of DOM for neptunyl ions, and that neptunyl does not undergo hydrolysis until a much higher pH than uranyl. This is evident in comparative studies that included U(IV) and Np(V) complexation on the same organic acids (Glaus et al., 1997) or by comparison of independent complexation studies, as referenced in Tables 3 and 4. Neptunyl exhibits increasing binding as the pH increases to ~12, after which the fraction bound decreases. The increase in binding can be attributed to increasing deprotonation of phenolic sites on the HA as the pH increases, while the decrease is due to increasing competition for organic binding sites with the hydrolysis product $\text{NpO}_2(\text{OH})_2^-$, as shown by the inorganic speciation in Figure 1. This figure suggests that the potential presence of carbonates in our experiments will have a greater effect on Np(V) organic binding than on uranyl at the same carbonate concentration. However, modelling with the inclusion of organic matter suggests that at this carbonate concentration, the organic binding will dominate, and carbonate species will contribute to less than 3% of the total Np(V). The majority of the data suggest

that there is no ionic strength dependence of binding. However, data at pH 10.5 and 12.9 show increased binding when the electrolyte concentration is 0.2 mol L^{-1} , compared to the other concentrations. This is not expected and other work at lower pH values (Glaus et al., 1997) shows very little ionic strength dependency.

4.1.4. Effect of humic acid concentration on neptunyl and uranyl binding

Figures 4 and 5 show the effect of increasing the humic acid concentrations under conditions of equal uranyl and neptunyl concentration, respectively (i.e., decreasing the ratio of metal to humic acid). The majority of the data show the fraction bound increasing as the HA concentration doubles or triples, the trend in binding then continues to show increases, but to a lesser extent with the addition of more HA. These data demonstrate that across all pH values analysed for Np(V) and at pH 11.3 and 12.3 for U(VI), the humic acid concentrations would need to be greater than the highest values ($\sim 16 \text{ mg L}^{-1}$), for humic substances to bind sufficient metal to cause order of magnitude changes in the concentration of inorganic species in solution. It is effects in this range (i.e., 90, 99, 99.9% etc.) that would potentially enhance the solubility of metals in environments where a pool of solid phase material exists (Stockdale and Bryan, 2013).

4.1.5. Differences in neptunyl and uranyl binding between organic acid types

Figures 6 and 7 show results for binding experiments using various DOM types for uranyl and neptunyl, respectively. Contrasting behaviour is observed in the presence of different organic acid types. SRHA exhibits stronger binding than the other DOM types analysed. This is more evident for Np(V), as the U(VI) results are less distinct due to the inflection of the curve in the data. The differences across the pH range are not equal, and this is probably due to functional and structural differences between the various humic materials. The results for uranyl are similar to previous results presented by Stockdale and Bryan (2012), where

binding to SRHA decreased sharply from ~80% bound to organic matter at pH ~10 to <20% at pH 12. Our results show SRHA exhibits stronger binding than SRFA. SRNOM binding (results for uranyl only) does not differ significantly from SRFA suggesting FA is the major component of this DOM. PAHA exhibits very similar binding to that observed for SRHA.

4.2. Modelling uranyl and neptunyl data using WHAM/Model VII

4.2.1. Uranyl (UO_2^{2+})

WHAM/Model VII, as presented by Tipping et al. (2011), included a default value for binding for U(VI), including ΔLK_2 . Previous work has presented model fits for uranyl binding to humic acid (e.g., Tipping, 1993; using Model V and Tipping, 1998; for Model VI). These comparisons focus on the data available at the time of publication and include data obtained from studies at relatively low pH only, i.e., of five datasets, only the work of Glaus et al. (1997) covers pH values above 5, and this work included experiments performed up to pH 10.1. Here, we focus our comparisons of measurements and modelling on the high pH data presented here and in Stockdale and Bryan (2012). Firstly, we conducted a literature search for additional data using the selection criteria defined in section 3. and have calculated log K_{MA} values for further datasets, including, Pompe et al. (1998; 2 HA types), Montavon et al. (2000), Lubal et al. (2000; 5 HA types), Saito et al., (2004) and Stockdale and Bryan (2012), as well as the data presented here. Table 3 shows the values calculated from these datasets and the source of the DOM materials studied. Incorporating these data with those previously presented by Tipping et al. (2011), and using Equations 6 and 7, we have calculated updated default parameters for WHAM/Model VII. These new log K_{MA} values, incorporating values from 21 HA and FA datasets, are 2.61 for FA (log $K_{MA,FA,def}$) and 2.89 for HA (log $K_{MA,HA,def}$). Data used for the fitting procedure are included in the electronic supporting information. These values are approximately 0.3 units higher than the previous default values presented in Tipping et al. (2011), where a total of 8 HA and FA datasets were used. We emphasise that these new datasets are not exclusively from studies at high pH (Table

3), and thus these changes in values are not as a result of incorporating high pH datasets. The updated default value can be considered as a representative for all pH values up to ~12 (see section 4.2.1.1. for recommendations for modelling at higher pH values). The uncertainties in the $\log K_{MA}$ values (root mean square deviations, RMSD; Table 3) appear to have some correlation with pH. However, there is a clearer relationship between larger RMSD values and the maximum values for p_v (the negative logarithm of the metal bound per gram of organic acid; $-\log \text{mol g}^{-1}$). This also accounts for the relatively large RMSD for the Montavon et al. (2000) dataset that contains experiments performed at pH 4-5 and at relatively low metal loading.

4.2.1.1. Comparison of measurements versus modelling

Figure 8 shows comparisons of measured and modelled values for uranyl – organic complexation, calculated using the $\log K_{MA}$ values for the specific humic acid, as presented in Table 3. The data that fall below the 1:1 line are for experiments at the higher end of the pH range (>12). Previous work by Stockdale and Bryan (2012) applied the WHAM/Model VII default binding values when comparing the measured values with modelling. This resulted in poor fits for all data obtained for pH values of over ~10.5. Clearly, the improvement in model fits for a wider pH range (as shown in Figure 8) is related to the use of the specific $\log K_{MA}$ value of 2.93, which is very similar to the newly calculated default value of 2.89.

The data for all DOM types show that the model gives poor predictions only at the highest pH values studied. Stockdale and Bryan (2012) suggested that this may be due to binding of higher hydrolysis products, such as $\text{UO}_2(\text{OH})_2$, which is not captured by the model assumption that only the free ion and first hydrolysis products bind to DOM binding sites. Previous work has determined that the apparent positive charge of the uranyl ion can be considered to be greater than 2 (2.1 to 4; Perez-Bustamante, 1971; Rao and Choppin, 1984). Thus, uranyl species with an apparent positive charge may exist at a higher pH than

that predicted from formation of nominally zero or negatively charged hydrolysis species and it is possible that these as well as UO_2^{2+} and UO_2OH^+ , are able to bind to humic substances (Stockdale and Bryan, 2012). The U(VI) ion is larger than many other cationic metal ions included in the model and can accommodate more ligand groups. This lends support to the hypothesis that higher hydrolysis products may be capable of binding to DOM. Further investigation is desirable, so that this behaviour can be considered in a future iteration of the speciation model. However, it is important to note, that based on the experimental evidence in this study, the degree of complexation over this pH range is low (typically <20%).

For the purposes of performance assessment, we can produce conservative estimates for DOM complexation by considering ranges for the $\log K_{\text{MA}}$ values. In the case of the data at high pH (>12), better predictions will only be obtained when an adjusted $\log K_{\text{MA}}$, $\log K_{\text{MA}}' = \log K_{\text{MA}} + \text{RMSD}$ (Table 3), is used. Use of this higher value will then result in over prediction of organic binding for data at lower pH values, but will yield data that is conservative for performance assessment purposes. Binding data sets that include data for high pH experiments tend to result in much higher root mean square deviation (RMSD) values for $\log K_{\text{MA}}$. This is shown in Table 3 for datasets HUO2_A07-9 and FUO2_A01 that include data involving experiments up to pH 12.4, additionally, the data for PAHA of Glaus et al. (1997) results in a calculated value of 2.64 ± 0.78 for experiment in the pH range 5.0 to 10.1 (Tipping et al., 2011). These large RMSD values may be as a result of significant measureable organic bound uranyl (i.e., detectable by dialysis experiments), potentially due to the reasons discussed above. Although, as previously discussed (Section 4.2.1.), low metal loading (high p_v) values can also result in greater RMSD values.

4.2.2. Neptunyl (NpO_2^+)

Several studies have examined Np(V) binding by humic and fulvic acids (references listed in Table 4). These data, plus the data presented here, have been used to determine $\log K_{\text{MA}}$

values for Model VII. Equations 6 and 7 include the Irving-Rossotti slope (α_O) as part of the calculation of the default Model VII parameters. The value of α_O is calculated from data of stability constants for monodentate binding of both protons and metal cations to simple organic ligands (Irving and Rossotti, 1956). Figure 9A shows the calculation of the α_O value based on ligands and conditions included in the data search of Carbonaro and Di Toro (2007), and data available in the NIST stability constant database (Martell et al., 2004). The line of best fit is forced through the origin, based on the procedures of Carbonaro and Di Toro (2007). The value for ΔLK_2 is required as an input value for the fitting programme. As the equilibrium constant for complex formation with NH_3 is not directly available we used a linear free energy relationship (LFER) to calculate the value (using a method described by Mulla et al., 1985). This calculation was performed for the LFER between the ligand pair aminoacetic acid/hydroxyacetic acid and NH_3 . Figure 9B shows the data used in the calculation. We used data for divalent cations for this calculation, owing to data availability. The calculated value for ΔLK_2 used in the fitting program was 0.70.

Table 4 shows the calculated $\log K_{\text{MA}}$ values for each of the individual datasets. Using these data and Equations 6 and 7 we determined default WHAM/Model VII values for NpO_2^+ of 1.34 for FA ($\log K_{\text{MA,FA,def}}$) and 1.49 for HA ($\log K_{\text{MA,HA,def}}$). Data used in the fitting program are included in the electronic supporting information.

Figure 10 shows the results of the comparisons of the measured and modelled values for neptunyl binding to humic and fulvic acid for data presented here as well as other studies cited in Table 4 (Tochiyama et al., 2000 excluded from the Figure 10 comparison as not all the required WHAM/Model VII input data were available). These data cover over 10 orders of magnitude in the metal to DOM ratios and cover a pH range of 4.9 to 13.0. The fits for these datasets over a large range of pH conditions and metal loadings demonstrate the utility of the model over a very large range of conditions. The Glaus et al. (1997) data fall into

three distinct groups. Firstly, those that fall largely within the shaded area (which represents data within ± 0.5 of the 1:1 line). These data are for experiments at pH values from 6.8 to 9.8. The second and third groups fall approximately 0.8 and 1.3 units from the 1:1 line respectively. These data are for experiments performed at pH 5.8 and 4.9 respectively. The datasets of Marquardt et al. (1996), for the same HA, and Kim and Sekine (1991), for Gorleben HA, cover similar pH ranges (5.0-9.0 and 6.0-9.0, vs. 4.9-9.8 for Glaus et al., 1997), yet do not exhibit the same anomalous behaviour.

4.2.3. Application of the WHAM/ModelVII, including uncertainty analysis

Cementitious repositories, once hydrated with groundwater, will yield high pH conditions (>13) during the early stages of their evolution (Jacques et al., 2010). Containment failure, resulting in release of radionuclides into the aqueous environment, is more likely to occur during the later evolutionary stages of the repository, rather than in the early stages (recognising that the timing of the various evolutionary stages will ultimately depend upon groundwater flow rates as well as other factors). This work demonstrates that the model can yield representative results over much of the pH range expected within these geodisposal environments and by adjusting $\log K_{MA}$ the model can potentially be used to yield more conservative values (or ranges of values) for use in performance assessment.

To demonstrate the utility of the model, we ran simulations for aqueous systems under four distinct conditions, the chemistries of which are defined in Table 5. These represent three conditions for evolving cement interstitial waters, 'young' with a pH of 13.1, 'intermediate' with a pH of 12.3 and 'old' with a pH of 10.5. A fourth simulation is included for a neutral pH water. In addition to major ions we also include a range of trace metals to allow for the effect of complex solution compositions to be assessed. We include DOM in the modelling as HA, both to be consistent with our experimental data, and also to give conservative results, as HA binding strengths are greater than FA. To demonstrate the uncertainties in the model

outputs, we use the in-built Monte Carlo function in the Graphical User Interface version of WHAM 7.0. We allow trace metal concentrations to vary from 10^{-11} to 2×10^{-9} mol L⁻¹, and allow an uncertainty for log K_{MA} values of ± 0.3 , except for uranyl at pH values greater than 12, where a uncertainty in log K_{MA} of ± 0.8 is applied. The advantages of using a Monte Carlo approach include the rapid and robust generation of many 'scenarios' (samples) by statistical sampling from parameter and input variable distributions. Each input parameter (or input variable), for which uncertainty is to be considered, is assigned an absolute or relative uncertainty factor. Sample sets of 2000 values of each variable are then generated by random sampling, each model calculation using one set of the sampled variables, producing for each output a population of values. (Lofts and Tipping, 2011). From these values uncertainty ranges for the ranges of output variables can be calculated (as percentiles). See Lofts and Tipping (2011) for further details and application of the Monte Carlo function.

The results of our simulation are presented in Figure 11. This shows that, under conditions more representative of evolving cement interstitial waters, U(VI) and Np(V) are not predicted to bind significantly to DOM. This contrasts significantly to the binding behaviour in neutral water. Figure 11 also show the outputs available for Monte Carlo uncertainty analysis, with the extents of the grey lines showing the 2.3 and 97.7 percentiles.

5. Conclusions

This study has given further insight into the organic matter binding of Th, U(VI) and Np(V) under alkaline conditions. Results for Th, consistent with previous studies for tetravalent actinides, demonstrate high fractions present as organic complexes and this behaviour has been exploited to aid data calculation for the other metal ions. Binding of neptunyl to DOM show a maximum over the pH range expected within an evolving repository. Uranyl exhibits decreasing binding with pH, however, the majority of metal in solution is present as organic complexes under the lower pH conditions investigated (10-10.5).

Whilst these data for simple systems are not directly representative of behaviour under repository conditions (they do not, for example, include the competitive effects of Ca), they can be used to determine binding parameters for comprehensive speciation modelling. We have updated the WHAM/Model VII binding values for UO_2^{2+} , and have for the first time added Np(V)O_2^+ values to the database (only Np(VI)O_2^{2+} was included previously). These updates now allow application of the model for more complex mixtures across the entire repository pH range. Example simulations, containing more representative water chemistries, suggest that binding to DOM will not be significant under some high pH conditions and demonstrates the model utility for predicting binding under these conditions, including the determination of uncertainly values.

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Supporting information

A complete data file for the dialysis experiments is available as electronic supporting information. This file includes; concentrations of added electrolyte, metal and DOM (including type); activity measurements for the bulk solution and dialysate at the end of the experimental procedure; temperature and pH at the end of the experiments (including slope value for the pH meter calibration); the measured and calculated (from Th data) values for the HA dialysate fractions; and also includes calculation steps and the final calculated values for the fractions bound, as presented in the manuscript figures. Data used in the calculation of Model VII parameters for U(VI) and Np(V) are also included.

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771

772 **Tables**

773 Table 1. Initial conditions for the concentrations of humic substance and metal in the bulk solutions in all
 774 experiments. The pH values represent the measured values at the end of the experiment. For the dialysate,
 775 the initial electrolyte concentration was the same as for the bulk solution and the DOC and metals
 776 concentrations were zero.

Element	Humic type	pH	Electrolyte concentration (NaCl; mol L ⁻¹)	Humic concentration (mg L ⁻¹)	Element concentration (mol L ⁻¹)	Element to humic ratio (mol mg ⁻¹)
U(VI)	SRHA	10.0, 11.0, 12.0, 13.0	0.1	5.0	10 ⁻⁹	2.00 × 10 ⁻¹⁰
	SRFA	9.6, 11.0, 12.0, 12.8	0.1	5.0	10 ⁻⁹	2.00 × 10 ⁻¹⁰
	SRNOM	9.8, 11.0, 12.0, 12.9	0.1	5.0	10 ⁻⁹	2.00 × 10 ⁻¹⁰
	PAHA	10.6, 11.5, 12.4, 13.1	0.01	2.6	10 ⁻⁹	3.82 × 10 ⁻¹⁰
		10.6, 11.4, 12.3, 13.0	0.05	2.6	10 ⁻⁹	3.82 × 10 ⁻¹⁰
		10.4, 11.3, 12.2, 13.0	0.1	2.6	10 ⁻⁹	3.82 × 10 ⁻¹⁰
		10.4, 11.2, 12.2, 13.1	0.2	2.6	10 ⁻⁹	3.82 × 10 ⁻¹⁰
		10.5, 11.3, 12.3, 13.1	0.05	5.2	10 ⁻⁹	1.91 × 10 ⁻¹⁰
		10.4, 11.3, 12.3, 13.1	0.05	7.9	10 ⁻⁹	1.27 × 10 ⁻¹⁰
		10.4, 11.2, 12.2, 13.1	0.05	15.7	10 ⁻⁹	6.36 × 10 ⁻¹¹
Np(V)	SRHA	9.7, 10.9, 12.0, 12.9	0.1	5.0	7.0 × 10 ⁻⁹	1.40 × 10 ⁻⁹
	SRFA	10.4, 11.2, 12.2, 13.0	0.05	5.0	5.0 × 10 ⁻⁸	10 ⁻⁸
	PAHA	10.6, 11.4, 12.3, 13.0	0.01	2.4	4.5 × 10 ⁻⁸	1.91 × 10 ⁻⁸
		10.3, 11.3, 12.2, 12.9	0.05	2.6	5.0 × 10 ⁻⁸	1.91 × 10 ⁻⁸
		10.3, 11.2, 12.1, 12.9	0.1	2.6	5.0 × 10 ⁻⁸	1.91 × 10 ⁻⁸
		10.4, 11.2, 12.2, 12.9	0.2	2.6	5.0 × 10 ⁻⁸	1.91 × 10 ⁻⁸
		10.3, 11.1, 12.1, 12.9	0.05	5.2	5.0 × 10 ⁻⁸	9.54 × 10 ⁻⁹
		10.3, 11.2, 12.1, 12.9	0.05	7.9	5.0 × 10 ⁻⁸	6.35 × 10 ⁻⁹
		10.4, 11.2, 12.2, 12.9	0.05	15.7	5.0 × 10 ⁻⁸	3.18 × 10 ⁻⁹
Th(IV)	SRHA	10.4, 11.2, 12.3, 13.1	0.05	5.0	~2 × 10 ⁻¹³	~4 × 10 ⁻¹⁴
	SRFA	10.5, 11.3, 12.2, 12.9	0.05	5.0	~2 × 10 ⁻¹³	~4 × 10 ⁻¹⁴
	PAHA	10.4, 11.2, 12.2, 12.9	0.01	2.6	~2 × 10 ⁻¹³	~7.6 × 10 ⁻¹⁴
		10.4, 11.2, 12.1	0.2	2.6	~2 × 10 ⁻¹³	~7.6 × 10 ⁻¹⁴

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778 Table 2. Calculations of the fractions of Th binding to DOM under different assumptions for the
 779 'speciation active' dialysate DOM and the calculated fraction of DOM (relative to the bulk
 780 solution) assuming 100% of Th is present as organic complexes.

DOM type	Calculated fraction bound		Fraction of 'speciation active' dialysate DOM assuming 100% Th binding
	<i>If active DOM = UV measured</i>	<i>If active DOM = 0</i>	
PAHA	1.37 ± 0.22	0.99 ± 0.01	0.015 ± 0.015
ESHA	1.30 ± 0.06	0.99 ± 0.02	0.012 ± 0.014
SRHA	1.33 ± 0.15	0.98 ± 0.02	0.017 ± 0.021
SRFA	1.73 ± 0.28	0.99 ± 0.01	0.009 ± 0.009

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Table 3. Supplementary datasets and calculated Model VII binding constants (including root-mean-square deviation; RMSD) for U(VI) binding to humic and fulvic acids. The code denotes the numerical assignment as used in the supporting information, n denotes the number of individual data in the dataset, $\log K_{MA}$ is the calculated WHAM/Model VII binding constant.

Code	n	Log K_{MA}	RMSD	DOM type	pH range	Reference
Humic acid						
HUO2_A01	69	3.13	0.11	Coal HA	3.0-5.0	Lubal et al., 2000
HUO2_A02	19	2.88	0.06	Peat HA	3.5	Lubal et al., 2000
HUO2_A03	19	3.89	0.04	Coal HA	3.5	Lubal et al., 2000
HUO2_A04	19	3.58	0.02	Tschernozem Soil HA	3.5	Lubal et al., 2000
HUO2_A05	19	3.24	0.02	Fluka HA	3.5	Lubal et al., 2000
HUO2_A06	10	3.09	0.08	PAHA	4.0	Saito et al., 2004
HUO2_A07	19	2.93	0.75	SRHA	9.8-12.0	Stockdale and Bryan, 2012
HUO2_A08	9	2.96	0.87	SRHA	9.9-12.0	This work
HUO2_A09	63	2.98	0.99	PAHA	10.4-12.4	This work
HUO2_A10	55	2.64	0.55	PAHA	4.0-5.0	Montavon et al., 2000
HUO2_A11	9	2.90	0.07	Fluka HA	3.9	Pompe et al., 1998
HUO2_A12	11	2.84	0.17	PAHA	4.0	Pompe et al., 1998
Fulvic acid						
FUO2_A01	9	2.61	0.97	SRFA	9.4-12.0	This work

Table 4. Datasets and calculated Model VII binding constants (including root-mean-square deviation; RMSD) for Np(V) binding to humic and fulvic acids. The code denotes the numerical assignment as used in the supporting information, n denotes the number of individual data in the dataset, $\log K_{MA}$ is the calculated WHAM/Model VII binding constant.

Code	n	Log K_{MA}	RMSD	DOM type	pH range	Reference
Humic acid						
HNpO2_01	214	1.35	0.78	PAHA	4.9-9.8	Glaus et al., 1997
HNpO2_02	26	1.33	0.30	GoHA	7.0-9.0	Marquardt and Kim, 1998a
HNpO2_03	87	1.75	0.40	PAHA	6.0-7.1	Tochiyama et al., 2000
HNpO2_04	85	1.74	0.64	PAHA	5.0-9.0	Marquardt et al., 1996
HNpO2_05	28	1.20	0.13	GoHA	6.0-9.0	Kim and Sekine, 1991
HNpO2_06	12	1.50	0.50	SRHA	9.6-12.9	This work
HNpO2_07	84	1.46	0.45	PAHA	10.3-13.1	This work
Fulvic acid						
FNpO2_01	30	1.10	0.07	GoFA	6.0-8.0	Marquardt and Kim, 1998b
FNpO2_02	12	1.25	0.25	SRFA	10.4-13.0	This work

797 Table 5. Input variables for example application of WHAM/Model VII.

	Cement evolution phase			Neutral natural water
	Young	Intermediate	Old	
pH	13.1	12.3	10.5	7.0
[HA] (mg L ⁻¹)	5	5	5	5
Na ⁺ (mol L ⁻¹)	9.5×10^{-2}	1.8×10^{-4}	4.3×10^{-5}	1.0×10^{-5}
K ⁺ (mol L ⁻¹)	9.2×10^{-2}	4.0×10^{-3}	1.0×10^{-5}	1.0×10^{-5}
Ca ²⁺ (mol L ⁻¹)	1.4×10^{-3}	1.6×10^{-2}	2.2×10^{-4}	1.0×10^{-6}
F ⁻ and (Mg, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb) ²⁺ (mol L ⁻¹)	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}
UO ₂ ²⁺ and NpO ₂ ⁺ (mol L ⁻¹)	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}	1.0×10^{-9}
Cl ⁻ , (mol L ⁻¹)	1.0×10^{-6}	4.2×10^{-3}	1.0×10^{-6}	2.0×10^{-5}
CO ₃ ²⁻ , (mol L ⁻¹)	1.4×10^{-4}	5.7×10^{-6}	2.2×10^{-5}	1.0×10^{-6}

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799 **Figures**

Figure 1. Inorganic speciation of U(VI) and Np(V) in the absence (A and B) and presence of carbonate ($\Sigma\text{CO}_3^{2-} = 10^{-4} \text{ mol L}^{-1}$; C and D). Minor species are excluded for clarity. $\Sigma\text{UO}_2^{2+} = 10^{-9} \text{ mol L}^{-1}$; $\Sigma\text{NpO}_2^+ = 5 \times 10^{-8} \text{ mol L}^{-1}$; and the background electrolyte $\text{NaCl} = 0.05 \text{ mol L}^{-1}$.

Figure 2. Fraction of uranyl bound to purified Aldrich humic acid with changing pH for four electrolyte (NaCl) concentrations. Ratios of uranyl to PAHA $3.82 \times 10^{-10} \text{ mol mg}^{-1}$.

809

810 Figure 3. Fraction of neptunyl bound to purified Aldrich humic acid with changing pH for four
 811 electrolyte (NaCl) concentrations. Ratios of neptunyl to PAHA $1.91 \times 10^{-8} \text{ mol mg}^{-1}$.

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813

814 Figure 4. Fraction of uranyl bound to purified Aldrich humic acid with changing humic acid
 815 concentrations and for different experimental pH values. Ratios of uranyl to PAHA 3.82,
 816 1.91, 1.27 and 0.64×10^{-10} mol mg⁻¹. Error bars represent two standard deviations from the
 817 mean of triplicate measurements. The concentration of the added electrolyte (NaCl) was
 818 0.05 mol L^{-1} .

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Figure 5. Fraction of neptunyl bound to purified Aldrich humic acid with changing humic acid concentrations and for different experimental pH values. Ratios of neptunyl to PAHA are 19.1, 9.54, 6.35 and $3.18 \times 10^{-9} \text{ mol mg}^{-1}$. Error bars represent two standard deviations from the mean of triplicate measurements. The concentration of the added electrolyte (NaCl) was 0.05 mol L^{-1} .

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828 Figure 6. Fraction of uranyl bound to different types of DOM with changing pH. Ratios of
 829 uranyl to DOM were $2 \times 10^{-10} \text{ mol mg}^{-1}$ for SRFA, SRNOM and SRHA; and $1.91 \times 10^{-10} \text{ mol}$
 830 mg^{-1} for PAHA. The concentration of the added electrolyte (NaCl) was 0.1 mol L^{-1} for SRFA,
 831 SRNOM and SRHA, and 0.05 mol L^{-1} for PAHA.

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834 Figure 7. Fraction of neptunyl bound to different types of DOM with changing pH. Ratios of
 835 neptunyl to DOM were $1.4 \times 10^{-9} \text{ mol mg}^{-1}$ for SRHA, $10^{-8} \text{ mol mg}^{-1}$ for SRFA; and $9.54 \times$
 836 $10^{-9} \text{ mol mg}^{-1}$ for PAHA. The concentration of the added electrolyte (NaCl) was 0.1 mol L^{-1}
 837 for SRHA, and 0.05 mol L^{-1} for SRFA and PAHA.

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Figure 8. Comparison of measured and modelled values for organically bound uranyl. Modelled data are calculated using the $\log K_{MA}$ values for each individual DOM type.

Figure 9. Calculation of supplementary thermodynamic data for NpO_2^+ . Panel A shows the determination of the Irving-Rissotti slope (α_0 , using data for the ligands OH^- and ethanoate). Panel B shows the linear free energy relationship between stability constants of the ligand pair aminoacetic acid (AAA)/hydroxyacetic acid (HAA) and NH_3 , allowing estimation of the $\log K_{\text{NH}_3}$ value for NpO_2^+ (data shown are for divalent cations). Confidence bands (95%) are shown by the checked lines.

Figure 10. Comparison of ν values (moles bound per gram of humic/fulvic acid) for NpO_2^+ experimental and modelled data (moles of metal per gram of organic acid; log mol g⁻¹). Organic acid types are; this work, as specified in the figure legend; Marquardt and Kim (1998a and b) and Kim and Sekine (1991) Gorleben groundwater humic acid (or fulvic acid denoted as FA in the figure legend); and Glaus et al (1997) and Marquardt et al (1996), purified Aldrich HA. Note the different scales for each plot. The shaded grey area highlights those data that fall within log ± 0.5 of the 1:1 line.

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861 Figure 11. Fraction of metal bound to HA under different aqueous conditions of varying pH
 862 as calculated by WHAM/Model VII using the input parameters of Table 5. Young,
 863 intermediate and old represent three different evolving cement degradation phases. Red
 864 lines are the median calculated values. The extent of the grey lines show the 2.3- and 97.7
 865 percentile values. The median for the neutral pH U(VI) calculation is 0.9968, with 2.3 and
 866 97.7 percentile of 0.9719 and 0.9996 respectively.