Uranyl binding to humic acid under conditions relevant to cementitious geological disposal of radioactive wastes

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ABSTRACT

Few studies have sought to investigate the potential for dissolved organic matter (DOM) to bind (and thus potentially transport) radionuclides under the high pH regimes that are expected in cementitious disposal. We have used equilibrium dialysis to investigate uranyl binding to humic acid over a pH range of ~10 to 13. The experimental results provide evidence that DOM can bind uranyl ions over this pH range, including in the presence of competing ions. There is a general decrease in binding with increasing pH, from ~80% of total uranyl bound at pH 9.8 to ~10% at pH 12.9. Modelling of the system with *WHAM/Model VII* can yield representative results up to pH ~10.5.

Introduction

Strategies for the disposal of intermediate-level radioactive wastes (ILW) in several countries involve geological emplacement, followed by the addition of a cementitious backfill. 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 (Glasser *et al.*, 2008). These reactions result in 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).

Natural dissolved organic matter (DOM) is ubiquitous in aquatic environments and is present in groundwaters with concentrations dependent upon the host rock environment and recharge source and pathway. It exerts a powerful control on chemical conditions in waters and soils, influencing the transport and retention of metals (Tipping *et al.*, 2011). Binding of cationic metals to DOM can result in increased solubility of metal salts and transport of DOM may result in simultaneous transport of bound metals. The influence of these processes on radionuclide migration has been recognized as a significant source of uncertainty in radioactive waste management (Glaus *et al.*, 1997).

Few studies have sought to investigate the potential for DOM to bind (and thus potentially transport) radionuclides under the high pH regimes expected in cementitious disposal. Here, we have used equilibrium dialysis to investigate uranyl binding to humic acid over a pH range of ~9 to 13. We compare the results with predictions from a widely used chemical speciation model to assess the potential for modelling to predict satisfactory results at high pH.

Experimental

Reagents

Solutions were prepared using the following reagents: NaCl and Na_2CO_3 (TraceSelect, Fluka

Analytical), $CuCl_2 \cdot H_2O$ ($\geqslant$99.999%; Aldrich), $CaCl_2$ (99.9%; Alfa Aesar). Humic acid was the reference material Suwanee River humic acid (SRHA) obtained from the International Humic Substances Society. Any 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 vol.% HNO_3) 180 ml polypropylene pots. The ^{238}U was prepared by dissolving $UO_2(NO_3)_2$ in 1 M HCl with subsequent dilution to achieve a 10^{-7} mol l^{-1} stock solution. The ^{232}U, used as a tracer (stock concentration 400 Bq ml^{-1}), was separated from active daughter nuclides using a UTEVA column (Triskem International) by the method reported in (Horwitz et al., 1992).

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. Samples for liquid scintillation counting (Wallac Quantulus 1220 ultra-low level liquid scintillation spectrometer) were prepared by the addition of 1 ml of 1 M HCl to 1 ml of sample, followed by 10 ml of ScintiSafe 3 cocktail (Fisher Scientific).

Equilibrium dialysis procedure

In the dialysis experiments, the outer solution had a total volume of 150 ml, and at the start of the experiment contained the HA and uranyl. The dialysate solution was contained within precleaned 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 volume was 4 ml, and initially the ionic strength and pH were the same as the outer solution, but with no HA or uranyl. 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. 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 as two discrete solutions that were added to the experiment simultaneously. These solutions contained HA or uranyl, 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 uranyl was added to the humic acid. This prevents potential kinetic effects associated with dissociation of uranyl−humic complexes if the pH of a binary mixture is changed. Where Cu, Ca or carbonate were added to experiments, these were included within the uranyl solution, and added so that the final experimental concentrations were 10^{-7}, 10^{-4} and 10^{-4} mol l^{-1}, respectively. Once the solution was added to the airtight pot containing the dialysis bag, the container was additionally sealed with laboratory film to further prevent ingress of CO_2, and left to stand for 7 days. 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 (these effects are quantitatively evaluated in the results and discussion section).

Calculation of humic bound fraction of uranyl

The total uranyl in solution is represented by the sum of the inorganic ($[UO_2']$) and organic fractions, with the concentration of the uranyl humic complex ($[UO_2-HA]$) related to the amount bound (UO_2-HA; mol mg^{-1}) and the humic acid concentration ($[HA]$ 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:

$$A_{bag} \propto [UO_2^{2+}]_{Tot-bag} = UO_2-HA \times [HA]_{bag} + [UO_2'] \quad (1)$$

$$A_{bulk} \propto [UO_2^{2+}]_{Tot-bulk} = UO_2-HA \times [HA]_{bulk} + [UO_2'] \quad (2)$$

where $[HA]_{bag}$ and $[HA]_{bulk}$ 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:

$$A_{UO_2\text{-}HA} = (A_{bulk} - A_{bag})/([HA]_{bulk} - [HA]_{bag}) \quad (3)$$

where $A_{UO_2\text{-}HA}$ can be considered as the tracer activity contribution of the humic bound uranyl per mg l^{-1} of HA in the experiment.

In order to calculate the organic bound fraction of uranyl, 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:

$$A_{inorganic} = A_{bulk} - A_{UO_2\text{-}HA} \times [HA]_{bulk} \quad (4)$$

The fraction of humic bound metal ($f_{organic}$) can then be calculated:

$$f_{organic} = \frac{A_{UO_2HA} \times [HA]_{effective}}{A_{UO_2-HA} \times [HA]_{effective} + A_{inorganic}}$$

$$(5)$$

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

Contribution of regenerated cellulose to the UV measured [HA]

Humic acid is measured using UV−visible spectrophotometry, and the concentrations in this work are 2 mg l^{-1} in the outer solution and typically $\leqslant 0.25$ mg l^{-1} in the dialysate at the end of the experiment (measurements are made on unmodified solutions at the end of the experiments). The presence of low levels of regenerated cellulose degradation products yields absorbance signals in the same range as those used for the determination of humic acid. Where high concentrations of HA are used, this contribution will be negligible, however, this is not the case at the concentrations found within the dialysate (no contribution from these degradation products is detected by UV absorbance increases to the higher volume bulk solution). In order to account for this contribution, experiments in the absence of HA determined the UV−visible absorbance from degradation of regenerated cellulose. A subset of 27 experiments were selected to measure HA absorbance values within the dialysate (due to

the low signals in these dilute HA solutions we used the mean absorbance over the wavelength range 360−410 nm). These data are then used to give a range of values for the HA within the dialysate ($[HA]_{bag}$) which are reflected as error bars where the data are presented.

Speciation modelling

The *Windermere Humic Aqueous Model* (*WHAM*; Tipping, 1994) 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 has recently been updated (*Model VII*; Tipping *et al.*, 2011) 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 than the previous version, due to increased numbers of available data and stricter data selection criteria than previously applied. Proton binding data up to pH ~10.5 are now included. Additional radionuclide cations have also been added to the database (Stockdale *et al.*, 2011). The uranyl binding constant is an average based upon separate values derived from six experimental datasets on a range of humic and fulvic acid types and a reference value based on linear free-energy relationships (Tipping *et al.*, 2011, including supporting information, for full details). It is important to highlight that the humic ion binding models are first parameterized for protons. Only then are the metal datasets fitted using the generic proton conditions (rather than for each specific humic or fulvic acid type). Thus, the aim of the model is to provide a predictive capacity for a 'generic' humic or fulvic acid in a natural system. Binding constants for specific humic or fulvic acid types, if available, can be substituted into the model calculations, depending upon the users requirements. However, there are no data available for the HA used in this work and thus, we use the model generic binding value. The model, subsequently referred to as *WHAM/Model VII*, is used with default values with the exception of the uranyl hydrolysis stability constants that are taken from the compilation of Duro *et al.* (2006). Errors within the model predictions are assessed by varying the humic binding constants by log ±0.3 from their default values (Lofts and Tipping, 2011).

Results and discussion

Contribution of regenerated cellulose to the UV measured [HA]

The upper recommended pH limit for the dialysis membrane is 12. However, no increased absorbance (indicating degradation of the cellulose) was seen within the dialysate volume when exposed to pH 13 solutions for the same time interval as the HA experiments. Based upon the results of the UV−visible spectrophotometry study on the dialysate membrane only samples and the 27 HA dialysate and bulk solution samples, a mean concentration of dialysate HA was determined, as well as a 90% confidence interval. The HA concentration within the bag had a mean of 4.2% of the bulk solution value and a range of 0−13.3%. To illustrate the uncertainty in the presented data, the upper and lower limits were used to obtain error ranges and these data presented as error bars. Uncertainty from the HA concentration within the dialysate typically results in ranges of bound metal that are within <10% of the mean value. No statistically significant variations in the shape of the absorbance profiles was observed for the different samples over the pH range of the experiment, nor between the bulk solution and dialysate samples.

Uranyl binding to humic acid in a binary system

The majority of studies of natural organic matter binding to trace cations present results in the form of complexation constants that relate the humic bound metal to the free ion concentration of the cation and the concentration or proton exchange capacity of the organic matter. For uranyl in the circumneutral and slightly acidic range, the organic bound fraction will dominate and reporting of experimental results in terms of log complexation constants enables small variations caused by different experimental conditions (e.g. ionic strength) to be assessed quantitatively. As the pH increases, hydrolysis product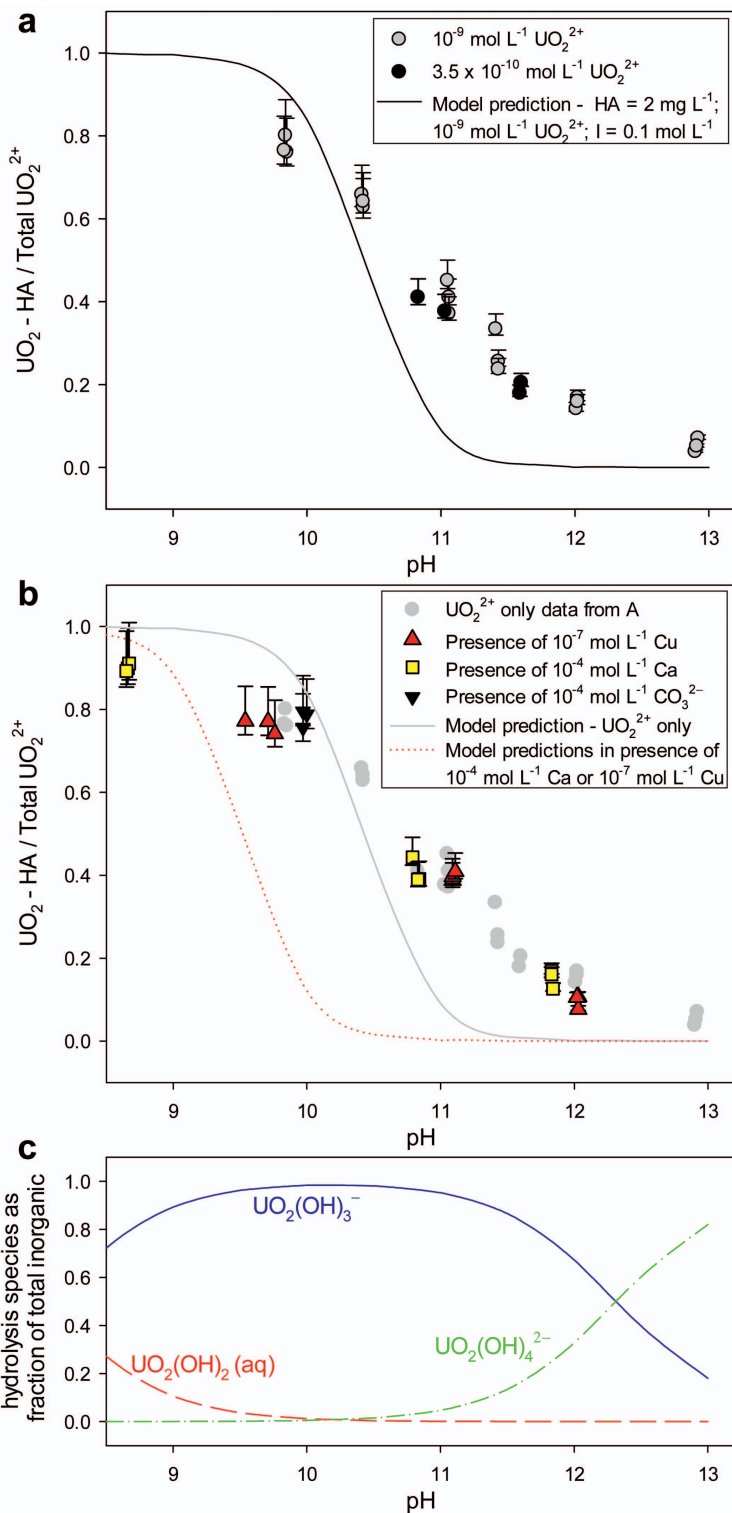s of metal ions become more prevalent and consequently decrease the free ion concentration. Changes in complexation constants due to hydrolysis induced changes to the free ion concentrations may obfuscate variations caused by subtle changes in organic bound metal in high pH systems. For example, if the free ion decreases by orders of magnitude but the organic bound changes by a factor of <10, changes to the complexation constant will largely reflect the changes to the free ion concentrations. With this in mind, we report results in terms of the percentage of total metal or the concentration that is bound to the humic acid. Equations 1−5 reflect the fact that we are considering inorganic components of the system as a whole, rather than the constituent complexes as is the case in other studies (Glaus et al., 1997).

Figure 1a shows the change in relative concentrations of humic bound uranyl with pH. There is a general decrease in binding with increasing pH from ~80% of the total bound at pH 9.8 to ~10% at pH 12.9. Previous data have been obtained for uranyl binding at pH $\leqslant$ 10 in the presence of competing ligands (Glaus et al., 1997). However, this is the first time that it has been practically demonstrated that binding can be significant over the pH 10 to 13 range. These are the conditions that are expected during the evolution of a cementitious GDF.

Previous studies have examined uranyl complexation with HA up to pH 10 (Zeh et al., 1997; Glaus et al., 1997). Zeh et al. (1997) performed experiments on pH adjusted natural Gorleben groundwaters to which additional uranyl was added. They observed binding in the absence of carbonate of 5.9% at pH 8.8 and 1% at pH 10.1. Glaus et al. (1997) reported results of 60 binding experiments at a range of ionic strengths, organic acid types (purified Aldrich humic acid, Laurentian soil fulvic acid and Suwannee River fulvic acid), and ratios of uranyl to humic/fulvic acid, performed in the presence of $0.2-1 \times 10^{-3}$ mol l^{-1} CO_3^{2-}. The fraction of uranyl bound increases with the ratio of uranyl to organic acid, from $7.5 \pm 2\%$ at 3×10^{-8} mol U mg^{-1} HA/FA to $28 \pm 11\%$ at 1.2×10^{-9} mol mg^{-1}. The

FIG. 1 (facing page). Complexation of UO_2^{2+} with Suwannee River humic acid (SRHA). (a) The fraction of total uranyl bound to SRHA in a solution containing 2 mg l^{-1} SRHA (added electrolyte, 0.1 mol l^{-1} NaCl), the solid line represents the predicted values using WHAM/Model VII. (b) The fraction of uranyl bound to SRHA in the presence of competing metal ions or carbonate. Only one model prediction line is shown for both the Cu^{2+} and Ca^{2+} systems due to very similar effects at the metal ion concentrations considered. (c) The modelled changes to the hydrolysis in the inorganic system over the pH range considered in the experiments and modelling.

a

Legend:
- ○ 10^{-9} mol L^{-1} UO_2^{2+}
- ● 3.5×10^{-10} mol L^{-1} UO_2^{2+}
- Model prediction - HA = 2 mg L^{-1}; 10^{-9} mol L^{-1} UO_2^{2+}; I = 0.1 mol L^{-1}

y-axis: UO_2 - HA / Total UO_2^{2+}
x-axis: pH

b

Legend:
- ○ UO_2^{2+} only data from A
- ▲ Presence of 10^{-7} mol L^{-1} Cu
- ■ Presence of 10^{-4} mol L^{-1} Ca
- ▼ Presence of 10^{-4} mol L^{-1} CO_3^{2-}
- Model prediction - UO_2^{2+} only
- Model predictions in presence of 10^{-4} mol L^{-1} Ca or 10^{-7} mol L^{-1} Cu

y-axis: UO_2 - HA / Total UO_2^{2+}
x-axis: pH

c

Labels: $UO_2(OH)_3^-$, $UO_2(OH)_2$ (aq), $UO_2(OH)_4^{2-}$

y-axis: hydrolysis species as fraction of total inorganic
x-axis: pH

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results from these two studies contrast somewhat with our experimental observations. These discrepancies may be the result of the presence of a cocktail of competing metals in the case of the natural Gorleben groundwater and, for the Glaus *et al.* (1997) study, the presence of high carbonate concentrations and the comparatively higher uranyl/HA ratios than in our work. There also likely to be variations in binding strengths between humic acid types, which could be a further reason for differences between the datasets.

Uranyl binding to humic acid in the presence of Ca or Cu

Competitive reactions with other cationic metals may influence the concentration of humic bound uranyl. In order to quantify such effects, we performed experiments where either Cu^{2+} (10^{-7} mol l^{-1}) or Ca^{2+} (10^{-4} mol l^{-1}) were added. These metal ions were chosen due to their relative binding strengths and typical concentrations in natural waters. The concentrations of these metals will be controlled by various mineral solubility controls within a cement matrix. However, here we are studying only the competition effects in the simple aqueous system. The Cu^{2+} typically binds very strongly to organic matter and is present in trace concentrations in groundwater (mean European groundwater value $\sim 5 \times 10^{-8}$ mol l^{-1}; Shand and Edmunds, 2008). The Ca^{2+} typically has weaker binding to organic matter, but is present at greater concentrations (mean European groundwater (~ 1.6 mmol l^{-1}). Competition from these metal ions in the europium–humic acid system at pH 5.5 has been assessed previously (Marang *et al.*, 2008, 2009). Figure 1*b* shows that, in the presence of either metal, uranyl is not significantly displaced from humic acid. For Cu^{2+}, only a small reduction in bound uranyl is observed at pH 12 and 10. This may be attributed to an excess of humic binding sites available for both metals. However, this is unlikely to be the case for Ca^{2+}, where the results suggest that uranyl is able to compete for the available binding sites. Further work is required to test the scale of these effects over different relative metal concentrations and should also be performed on a range of HA types.

Comparison of measured and modelled data

In order to test the measurements against a comprehensive speciation model we modelled the exact experimental conditions using *WHAM/Model VII* (Tipping *et al.*, 2011). Figure 1 shows the model predictions in terms of the fraction of uranyl present as humic complexes *vs*. pH. Figure 2 shows the data expressed in terms of the log concentration of the humic bound uranyl. Error bars for the modelled values are determined by variation of the humic binding constants by a fixed value of log ±0.3 (Lofts and Tipping, 2011). In the uranyl only system, the model gives reasonable predictions up to pH ~10.5. Greater deviation from measured values is then observed as the pH increases. The data, as presented in Fig. 2, shows clearly that even in the case where the binding strength is varied to be higher by log 0.3 units, the model still significantly underestimates binding at pH 13. Predictions of binding to organics will also be affected by the accuracy of the data for the speciation of the inorganic complexes.

We stress the fact that the model is parameterized using proton binding data only up to the same pH value (i.e. 10.5), and that for the majority of metal ions in the database, binding data are calculated from experimental data at much lower pH values (for example four of five uranyl humic acid binding datasets contain data at pH <5, with the other dataset at pH ~5−10 and all Cu humic binding datasets fall in the pH range 2.0 to 8.3). Moreover, as detailed in the theory section, we use the generic *Model VII* value for binding of the uranyl ion. Should SRHA bind stronger than the average value, this will result in experimental binding values higher than predictions. Preliminary results from the authors for neptunyl binding show SRHA binds more strongly than purified Aldrich humic acid under the same aqueous conditions (Stockdale and Bryan, unpublished data). The higher complexation capacity of the SRHA could also partly explain why no competition effects are observed in the presence of Cu^{2+}. The high pH range is of interest in geodisposal environments, but the model has the majority of its applications in natural waters where such pH regimes rarely exist. The model operates on the basis that only the free ion and first hydrolysis product can bind to organic matter. Increasing competition between organic binding and hydrolysis will operate as the pH increases, and higher hydrolysis products that may bind are not captured by the model. Figure 1*c* shows the inorganic speciation in the modelled system of Fig. 1*a*. This illustrates the increased hydrolysis over the experimental range and the
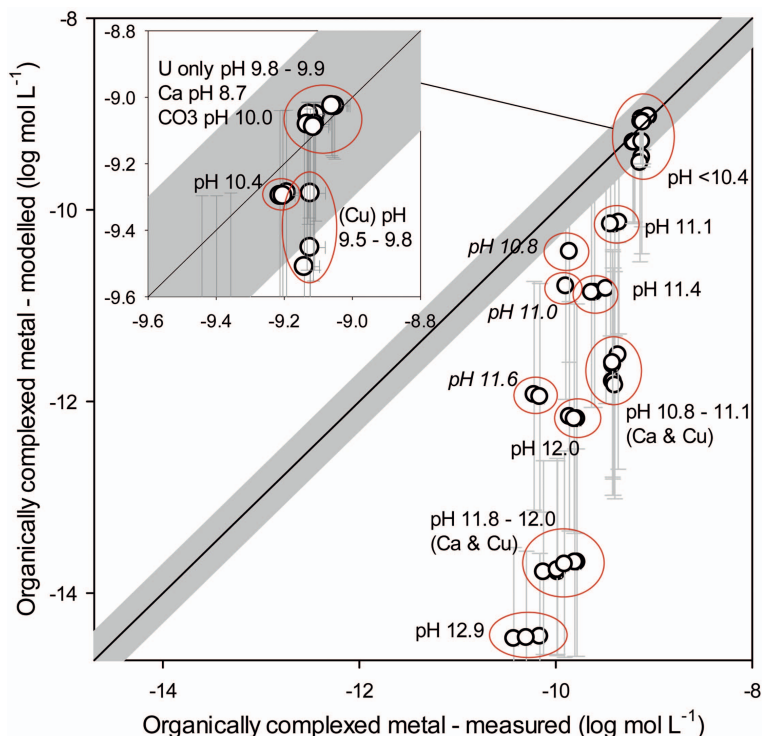
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FIG. 2. Comparison of *WHAM/Model VII* calculated concentrations of organically complexed metal and those derived from experimental data. The solid line represents the 1:1 line and the grey area shows those points that fall within 0.3 of a log unit from this line. Experimental conditions are defined in Fig. 1. Italicized data indicate those points in Fig. 1*a* where a UO_2^{2+} concentration of 3.5×10^{-10} mol l^{-1} was used.

dominance of negatively charged species throughout. Previous work has determined that the apparent 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. Experimental data of the type presented here will enable further considerations of high pH systems when fitting and testing humic binding models for high pH.

Effect of carbonate on the uranyl-humic system

An important consideration in the speciation of UO_2^{2+} is the formation of carbonate complexes. Our experiments were conducted in such a way as to

minimize CO_2 dissolution, but were not performed in CO_2 free conditions. It is therefore necessary to evaluate the potential of CO_3^{2-} species to affect the humic binding results. Figure 3 shows modelling results for organically complexed uranyl in the presence of varying concentrations of CO_3^{2-}. Predicted values at 0.1 mmol l^{-1} are within log <0.005 of the values where CO_3^{2-} is absent. Increasing concentrations from 1 mmol l^{-1} to 3 mmol l^{-1} results in a marked reduction in humic bound uranyl at all the pH values considered. This is consistent with the experimental procedure of Glaus *et al*. (1997), where concentrations in this range were used in competition equilibrium dialysis experiments for a fulvic acid uranyl system and at similar DOM:uranyl ratios. The predictions suggest that lower CO_3^{2-} concentrations (from 0.1 to 1 mmol l^{-1}) only significantly decrease the humic bound uranyl concentration at pH 10. The fact that the model underestimates uranyl binding to humic acid means that these
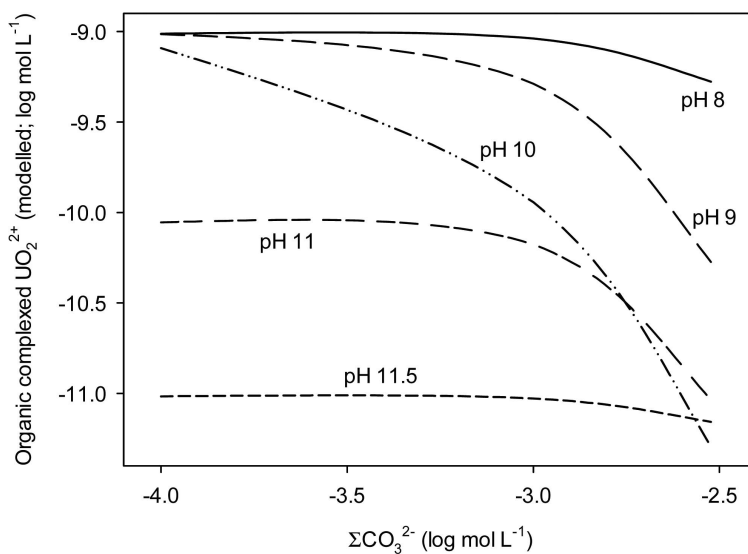
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FIG. 3. Modelled humic complexation of uranyl in the presence of varying concentrations of carbonate. Concentrations are the same as the grey circles in Fig. 1a. See text for discussion.

results will be conservative as it will underestimate competition between the carbonate ligand and humic binding sites. Experiments performed at pH 10 with addition of 0.1 mmol l^{-1} CO$_3^{2-}$ (Fig. 1b) demonstrate that no decrease of humic bound uranyl is observed. We therefore conclude that any CO$_3^{2-}$ present in the experiment is insufficient to suppress humic binding. We recognize that the binding to HA of mixed uranyl-carbonate complexes could also partly explain the apparent lack of competition in this system. Such mixed complexes for europium speciation have been identified by Dierckx et al. (1994).

Conclusions

The experimental results presented here provide evidence that within simple high pH environments dissolved organic matter can bind uranyl ions, including in the presence of competing ions. The results therefore suggest that DOM has the potential to be important in the transport of uranium from a cementitious (alkali) geological disposal facility, despite formation of highly hydrolysed species.

Using the default *Model VII* uranyl binding values we cannot accurately predict uranyl humic interactions for the HA used in this work at pH values above ~10.5. The reason for the discrepancies may be due to a possible underestimation of the binding of more hydrolysed species, or be related to higher binding strengths for the specific HA used in this work. Further experimental work of the type presented here, and on a range of HA types, will enable further considerations of high pH environments when fitting and testing humic binding models for such pH systems.

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