Application of DGT to high pH environments: uptake efficiency of radionuclides of different oxidation states onto Chelex binding gel[†]

[†]This manuscript is dedicated to Professor Bill Davison on the occasion of his retirement

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Summary

The DGT Chelex binding phase has not been tested for binding efficiency over the extreme high pH range (i.e., 10 to 13). Here, we examined the uptake efficiency of the gel-encapsulated Chelex cation exchange resin binding phase when in direct contact with solutions of radionuclides of different oxidation states over the circumneutral to high pH range (~7 to 13). Results show that the Chelex binding gel is suitable for Eu^{3+} for circumneutral pH, for UO_2^{2+} up to at least pH 10.7 and for NpO_2^{2+} up to at least pH 11.7. Application may be appropriate at higher pH values but testing of complete solution deployment units will be required. This work provides the framework to use DGT as a tool for the study of high pH radionuclide systems.

Introduction

The technique of diffusive gradients in thin films (DGT)¹ uses a selective binding layer behind a permeable gel diffusion layer of known thickness. Following deployment, concentration analysis is performed on the binding layer and Fick's law of diffusion is used to calculate a time averaged solute concentration or flux. DGT has been applied in a large variety of research areas. Examples include geochemical cycling,^{2,3} kinetic behaviour of metal-natural organic carbon complexes,⁴ solute behaviour in marine^{1,5} and freshwaters,⁶ sediments⁸⁻¹¹ and soils¹². These studies span a large range of analytes including, cationic trace metals,^{1-6,8,9,13} major cations,¹⁴ anionic metals^{10,11} and nutrients,^{15,16} sulfide,⁷ rare earth elements^{13,17} and radionuclides.^{11,13,18-24}

In recent work by Hartland et al.,²⁵ DGT was used as part of an investigation into colloid-metal interactions in hyperalkaline cave waters. The studied site, Poole's Cavern, Buxton, UK,²⁶ had drip waters of pH 11.7 ± 0.4 . These deployments were under the assumption that DGT efficiency was the same as expected under circumneutral pH values. DGT gels and the various binding phases have not yet been tested for suitability under high pH conditions. Such environments are rare in nature, but may potentially prove to be useful proxy study sites for the conditions expected to evolve within a cementitious radioactive waste repository. Strategies for disposal of intermediate level radioactive wastes (ILW) in several countries involve geological emplacement, followed by addition of a cementitious backfill.²⁷ 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.²⁸ These reactions induce gradual changes to the composition of the interstitial water (leachate), from typical "young" cement leachate, with a pH above 13, to more evolved leachate with a pH lower than 10.²⁹

To date there has been no testing of the Chelex resin phase for the uptake of radionuclides at high pH values. This work aims to test the efficiency of the Chelex binding gel for the binding of Eu^{3+} , NpO_2^+ and UO_2^{2+} over a large pH range (7-13). Recently new binding phases have been developed for uranyl.^{23,24} We chose to focus on the Chelex gel due to its utility for a large range of cationic metals and its commercial availability. Having data available from a larger range of analytes is more likely to provide insights into biogeochemical processes than if only single analyte data are available. The elements tested were Eu^{3+} , Np(V)O_2^+ and U(VI)O_2^{2+} and these may be considered to exhibit resin binding behaviour that is largely representative of other trivalent, pentavalent and hexavalent radionuclide cations, respectively.

Methods

Equipment and reagents

The Chelex resin discs (cation exchange resin encapsulated within polyacrylamide gel) were obtained from DGT Research Ltd. (Lancaster, UK). Ionic strength was controlled using NaCl (TraceSelect, Fluka Analytical). Any pH adjustments were undertaken using 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) 30 ml Nunc universal tubes. U-238 was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2$ salt into 1 M HCl and subsequent dilution to achieve a $10^{-6} \text{ mol L}^{-1}$ stock solution. U-232, used as a tracer, was separated from daughter nuclides with a UTEVA column (Triskem International) using a previously reported method (1 kBq mL^{-1}).³⁰ The very low activity of the natural uranium at the final solution concentration means that it does not contribute to the liquid scintillation activity measurement, only the U-232 activity is measurable over the time period of the analysis. Np-237 was used directly from a $5.5 \times 10^{-5} \text{ mol L}^{-1}$ stock solution in 1 M HCl. Eu solution was prepared by dissolving $\text{Eu}(\text{NO}_3)_3$ salt into 1 M HCl and subsequent dilution to achieve a $10^{-6} \text{ mol L}^{-1}$ stock, and a solution of Eu-152 was used as a tracer (1 kBq mL^{-1}).

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 (Eu^{3+} and UO_2^{2+} ; 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). Samples for ICP-MS analysis (NpO_2^+) were acidified with nitric acid and a small volume of non-active Eu internal standard was introduced.

Experimental procedure

Experiments were performed in the presence of 0.005 mol L^{-1} NaCl and at a metal concentration of $1.24 \times 10^{-9} \text{ mol L}^{-1}$ ($\times 10$ for Np). If 100% of this is bound this represents a concentration per disc of $3.09 \times 10^{-11} \text{ mol}$ ($\times 10$ for Np; based on immersion into 25 mL of solution). This corresponds to the accumulation that would occur during a 48 hour DGT solution deployment in a solution of constant concentration of $10^{-9} \text{ mol L}^{-1}$ ($\times 10$ for Np; assuming a 0.94 mm diffusive layer thickness and calculated using the diffusion coefficient for Eu at 25 °C of $5.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)¹³. Neptunium concentrations were 10 times that of the other elements to ensure that the sample concentrations were sufficiently above the method detection limits. Experiments were performed in groups of four replicates (triplicates for Np). Uptake was quantified by taking an aliquot of solution before commencement of the experiment and at each time interval following addition of the gel discs. Solutions were prepared for analysis as outlined above.

Theoretical modelling

In order to compare experimental results with model predictions, we conducted modelling of radionuclide interactions with the methyl iminodiacetate (MIDA) ligand. The Chelex resin is a styrene divinylbenzene co-polymer with iminodiacetate functional groups (see Stockdale, 2005 and references therein³¹). As the resin contains a known amount of equivalents of binding sites per gram, it is possible to calculate the equivalent concentration of MIDA. Using the speciation model WHAM VII³² and stability constant data from the NIST database,³³ we calculated speciation for the experimental conditions across the range pH 7-13 and under the assumption that MIDA speciation approximates that of the IDA ligands within the Chelex. This yields theoretical selectivity factors, that can be compared to experimental results.

Results and discussion

Binding efficiency at high pH

Prior to their addition to the experiment, the solution containing the Chelex discs was at pH ~7. No attempt was made to adjust the pH prior to experimental addition due to the potential complexation effects of buffers. Following the experiments, the pH of each individual solution was measured. The addition of the Chelex discs had a buffering effect on some solutions and all those originally in the range 7 to 10 were 7.5 ± 0.2 at the end of the 7 day experiment. This effect results in 16 replicates (12 for Np) at this pH value and further data between pH 10.5 and 13.1.

Figures 1 to 3 show the results for measured uptake of Eu^{3+} , NpO_2^+ and UO_2^{2+} onto Chelex resin discs. Error bars show $\pm$ one standard deviation from the mean of replicate measurements. Rapid uptake is seen at pH 7.4 for all radionuclides, up to pH 10.7 for UO_2^{2+} and up to pH 11.7 for NpO_2^+ . Uranyl uptake is slower at pH 11.7 and neptunyl uptake is slower at pH 12.8, potentially due to kinetic limitations caused by slower penetration of larger multiple hydroxide species into the resin matrix. No sorption of uranyl to the resin is seen at pH 13. Europium is slowly sorbed to the resin at all of the pH values studied, however, >30% still remains in solution after 7 days at all pH values studied, except 7.4. Uptake of NpO_2^+ is

rapid for up to pH 11.7. Whilst, data for pH 12.8 show slower uptake kinetics, after 7 days most of the initial solution metal is bound to the resin. The stark difference in binding to Chelex at pH values of ~13 between U(VI)O_2^{2+} and Np(V)O_2^{2+} could be exploited for the separation of penta- and hexa-valent actinides. We did observe a greater variability across replicate experiments for europium compared to the other two elements, and this may be attributed to small pH variations between replicates that will have a greater effect for this element than the others, or higher variability from low tracer concentrations that are compounded for this element by the lower counting efficiency for this isotope, because a significant fraction decays by electron capture.

Comparison of experimental and modelling results

Each resin disc contains approximately the equivalent of 10.4 μmol of iminodiacetate (IDA) chelating sites. One disc was added to 25 mL of radionuclide in solution, corresponding to an equivalent molar concentration of $\sim 0.42 \text{ mmol L}^{-1}$ IDA sites per experiment. We modelled the speciation using this IDA concentration and the experimental radionuclide and NaCl concentrations as defined in the methods. Table 1 shows the selectivity factors (i.e., ratio of bound to inorganic metal in solution) for radionuclide binding onto methyl IDA at several pH values. These calculated values are for equilibrium ratios (i.e., bound relative to solution concentration). In contrast, the experimental data are dependent upon the kinetics of uptake, and this will be affected by diffusion into the hydro-gel and diffusion into the gel matrix, which contains the majority of the binding sites. However, we can compare modelled equilibrium data with experimental data at the end of the experiment to see if the experimental results are approaching what we would expect from free binding sites in equilibrium with the dissolved elements.

The modelling results for uranyl predict that it will not significantly sorb to the resin at pH values of 9 and higher (Figure 2, Table 1). This contrasts with the experimental results that show significant sorption occurring up to pH 11.7. This may be related to higher

complexation constants for the Chelex IDA sites than free MIDA or due to stronger binding due to complexation by multiple ligands or electrostatic effects. Europium is predicted to partition strongly to MIDA at pH values up to 10 (Figure 1, Table 1). However, whilst sorption is seen at all pH values, there appears to be slow binding kinetics at all pH values except 7.4. DGT application relies on the fact that the binding layer creates an effectively zero concentration of the analyte at the binding layer side of the diffusive gel, thus it may be unsuitable for europium at these pH values. Formation of neptunyl hydroxide complexes only becomes significant at the higher of the pH values in this study. Due to the lack of competition from the hydroxide ligand, it is predicted to partition strongly onto MIDA across the pH range (Figure 3, Table 1).

Gel swelling at high pH

We observed significant swelling of the Chelex discs at some of the high pH values studied. These effects have been observed in previous work. Swelling has been observed to occur in gels immersed in solution of pH values ≥ 11 ⁽³⁴⁾ and gels immersed in high pH solutions continue to hydrate over time.^{34,35} In our work hydrated disc diameters (initially ~2.5 cm) remained unchanged at pH ~7, swelling to 2.9 cm at pH 10.7 (32% increase in area), and 3.9 cm at pH 11.7 and 13 (134% increase in area). This will need to be considered when deploying DGT in high pH environments. This could be accounted for using several approaches; short deployment times, as was the case for the Poole's Cavern application,²⁵ careful monitoring that potential swelling is not affecting the physical shape of the diffusive interface with the solution; pre-treating to the pH of interest and accounting for potential changes to gel thickness, resin distribution and diffusion coefficients; increasing the concentration of cross-linker in the preparation of the gel to decrease the scale of any swelling and assessing any potential resulting changes to diffusion coefficients; or use of an alternative resin with different hydration properties.

Conclusions

This study provides DGT practitioners with guidance for the use of Chelex binding in deployment within high pH solutions, including suggestions for avoiding problems associated with physical changes to the hydro-gels. Experimental evidence for high pH systems is essential for any safety case for cementitious geodisposal and this work extends the available 'toolbox'. In terms of binding capacity, the Chelex binding gel is suitable for Eu^{3+} for circumneutral pH, for UO_2^{2+} up to at least pH 10.7 and for NpO_2^+ up to at least pH 11.7. Application may be appropriate at higher pH (11.7 for UO_2^{2+} ; and 12.9 and for NpO_2^+) but testing of complete solution deployment units will be required to ensure uptake is quantitative.

Acknowledgements

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298 **Tables**

299 Table 1. Theoretical selectivity factors of radionuclides binding onto
300 methyl iminodiacetate (bound ÷ solution metal concentrations).

pH	Eu ³⁺	NpO ₂ ⁺	UO ₂ ²⁺
7	7364	17	81
8	40515	199	11
9	11443	1833	<1
10	105	9549	<<1
11	<1	11545	<<1
12	<<1	2028	<<1
13	<<1	33	<<1

302 **Figures**

Figure 1. Uptake of Eu³⁺ onto DGT Chelex resin discs. The horizontal lines with the pH values denote the theoretical solution fractions for equilibrium with MIDA.

Figure 2. Uptake of UO_2^{2+} onto DGT Chelex resin discs. The horizontal lines with the pH values denote the theoretical solution fractions for equilibrium with MIDA.

Figure 3. Uptake of NpO_2^+ onto DGT Chelex resin discs. The horizontal lines with the pH values denote the theoretical solution fractions for equilibrium with MIDA.