Sorption of Tc(IV) to Cementitious Materials Associated with a Geological Disposal Facility for Radioactive Waste - 11129

Nicholas D. M. Evans, R. J. Hallam and S. L. Jain
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU, UK

ABSTRACT

Technetium-99 is one of the most important isotopes likely to be disposed of in the proposed UK Geological Disposal Facility (GDF) for higher-activity radioactive wastes. This is due to its long half-life, high fission yield, and its ability to migrate through the geosphere when in its oxidised, pertechnetate form. However, much of the technetium in the GDF is likely to be in the lower oxidation state of Tc(IV) due to the low Eh in the near field caused by the corrosion of the stainless steel canisters. Therefore, an important aspect of the behaviour of technetium in the near- and far-fields of a GDF is its sorption to cementitious materials in this reduced oxidation state. Batch sorption experiments have been performed on technetium in the presence of Ordinary Portland Cement (OPC), Nirex Reference Vault Backfill (NRVB) and Plutonium Contaminated Material Grout (PCMG), all of which may be used in a deep geological disposal facility in the UK.

Tc(IV) solutions were used at trace concentrations from 10^{-9} to 10^{-11} mol dm^{-3} to avoid the possibility of precipitation as TcO$_2$. After equilibration, the technetium concentration in the supernatant solutions was measured using gamma counting. In these studies, the values for the partition coefficient (R$_d$) were found to range from 70 to 5500 cm^3 g^{-1}. It was noticeable that R$_d$ was heavily dependent on pH in all cases.

Surface complexation modelling of the data generated has been performed. In general, using bidentate surface complexation constants in the hyperalkaline region, and a combination of mono- and bidentate ones below $ca.$ pH 11.5 give best agreement between models and data. These data will inform the performance assessment for the behaviour of technetium in the near-field of the UK's planned higher-activity wastes GDF.

INTRODUCTION

The currently preferred UK option for the management of higher-activity radioactive wastes is to store them in a deep underground Geological Disposal Facility (GDF). This may then be backfilled with the cementitious material Nirex Reference Backfill (NRVB). Once closed, the GDF will become saturated with groundwater, and highly alkaline porewater will develop with an initial pH of around 13.3, which will decrease to 12.5 as groundwater flow dissolves, and removes, sodium and potassium hydroxides. The mineral phases in the cement, mainly Portlandite at this stage in its evolution, will act as buffers and maintain the pH at 12.5 for $ca.$ 10^5 years. Corrosion of waste-containing steel canisters will lead to the gradual formation of reducing conditions. Thus, the behaviour of radionuclides in the waste must be understood in the context of this chemistry [1].

The cementitious backfill and grouts within waste containers will chemically condition the porewater to provide a high pH under which the solubility of many radionuclides is low. The backfill will also provide a large surface area for radionuclide sorption. The corrosion of the steel components of the repository, e.g. waste containers and some of the waste itself, will establish widespread anaerobic conditions at an Eh of about -450 mV (at pH 12.5 and 25 ºC), controlled by the Fe(II)/Fe(III) couple [2].

Tc-99, a low energy β emitter (E_{max} = 0.29 MeV), present in some radioactive waste streams from the nuclear industry in the UK as TcO_4^-, is an important species for consideration in the performance assessment of any proposed repository, due to its high yield (6% of fission products) and long half-life (2.1×10^5 years). The aqueous chemistry of technetium is dominated by the highly mobile pertechnetate anion (TcO_4^-) in aerobic waters, and by Tc(IV), as TcO_2(am) solid, in anaerobic [3]. In the past in the UK, technetium was discharged to sea and was thought to disperse widely as it is carried from the Irish Sea by the Gulf Stream which flows past the British Isles to the Arctic and the Barents Sea. *En route*, ^{99}Tc accumulates in seaweed [4] and lobsters [5] along the Norwegian coastline. It was therefore deemed preferable to remove technetium from waste waters prior to their discharge to sea.

During the reprocessing of Magnox fuel, the uranium fuel rods are dissolved in nitric acid. One of the waste streams is an aqueous, acidic Tc-containing medium-active liquor. This is concentrated by evaporation to produce a medium active concentrate (MAC) at Sellafield [6]. Sodium hydroxide and a flocculating agent are added to the MAC, whereupon an insoluble floc forms which contains the main α-emitters. An ion exchange reagent is incorporated into the floc and removes additional species, mainly caesium. The floc is then dewatered by ultrafiltration prior to encapsulation in steel drums. It is at this stage that the Tc is removed, before the permeate is discharged to sea. The MAC floc is now treated with tetraphenylphosphonium bromide (TPPB) to precipitate out the technetium as $TPPTcO_4$, to prevent more marine discharges of technetium [7].

Studies [7] have shown that initially, at high pH, TPPB causes a large reduction in the aqueous technetium concentration by precipitating out the pertechnetate anion, but after eight weeks the TcO_4^- solubility reached the inventory concentration of technetium. The increase in aqueous technetium was caused by the alkaline degradation of TPPTc, releasing TcO_4^- into solution. So, if TPPTc floc is introduced to a cementitious environment, TcO_4^- will be re–released into the porewaters. Therefore, the reduction of Tc(VII) to Tc(IV) will be crucial in restricting technetium escape to the far-field of the repository. Should this reduction take place, the mobility of technetium in the porewaters and backfill of the GDF will be controlled by the sorption of technetium(IV) to the main cementitious materials used.

The purpose of this research was to ascertain the sorption behaviour of reduced technetium in the presence of two important cementitious materials used, or likely to be used' in a UK GDF. These materials are NRVB and Plutonium Contaminated Materials Grout (PCM Grout). Ordinary Portland Cement (OPC) was also used as a reference

material for comparison purposes. Although the initial pH of the GDF will be high, as mentioned above, the pH will gradually decrease with time due to groundwater ingress altering the chemistry of the cementitious phases. Thus, the sorption of Tc(IV) to NRVB and PCM was studied across a wide range of pH values. This is also important as some waste packages will contain sufficient acid to partly neutralise the grouts which have been added to immobilise the wastes.

OPC consists of around 60-65% calcium oxide (CaO), 20-25% silicon oxide (SiO_2) and small quantities of alumina (Al_2O_3), ferric oxide (Fe_2O_3) and gypsum ($CaSO_4$). The PCM Grout used in this study was a 3:1 mixture of pulverised fuel ash (PFA) and OPC. NRVB is a more complex material, a high porosity cementitious material based on a mixture of ordinary Portland cement (OPC), hydrated lime (calcium hydroxide), limestone flour ($CaCO_3$) and water [8].

EXPERIMENTAL

Ammonium pertechnetate (2 cm^3) was placed in a three-necked round bottomed flask and made up to 200 cm^3 with de-ionised water producing a pertechnetate concentration of 6.79×10^{-7} mol dm^{-3}. Sodium hydroxide was then added to produce solutions of the required pH. The solution was then purged for two hours with oxygen free nitrogen to remove dissolved oxygen from the solution. A vitreous carbon cathode and a platinum wire anode were then placed into the cell in a nitrogen glove box with oxygen content less than 1 ppm. An electropotential (6 V) was then used to reduce the pertechnetate to Tc(IV). It was found that the complete reduction of technetium from Tc(VII) to Tc(IV) could be completed overnight. This has allowed production of Tc(IV) aqueous solutions at a concentration $\sim 1 \times 10^{-9}$ mol dm^{-3}. Solutions with Tc(IV) concentrations of 1×10^{-10} and 1×10^{-11} were also prepared, to ensure that precipitation of TcO_2 did not occur in any of the experiments. At this concentration Tc-99 does not have a high enough specific activity to be measured by liquid scintillation counting, so the solutions were spiked with Tc-95m which had been prepared by the University of Wisconsin. Tc-95m is a gamma emitter with a half life of 61 days, and with measurable gamma photon energies of 204.1 and 582.1 keV.

The ground cements (0.1 g, <180 μm) were weighed into 20 cm^3 polypropylene vials. The Tc(IV) solutions were added and left for at least one week to equilibrate on a flatbed stirrer in the nitrogen glove box. This was done in at least triplicate for each solid, at each pH. pH was measured at the end of the equilibration phase. After the equilibration phase, a 5 cm^3 sample of the supernatant was removed from the vials through a 0.22 μm syringe filter with approximately 2 cm^3 being weighed into a gamma vial, and counted using a Cobra II Autogamma counter. The remaining solution was discarded to waste. No evidence of wall sorption or sorption to the filters was detected.

For the surface area measurements, approximately 1 g of each cementitious material was dried at 60 ^{o}C under vacuum overnight. The solid was then weighed accurately to 4 decimal places. The BET surface area was then measured on a Micromeritics Gemini VI physisorption system [9] at the British Geological Survey. Gemini software was used to

obtain the BET surface areas. The surface areas were determined to be; NRVB = 24.733 ± 0.0654 m² g^{-1}; OPC = 0.9898 ± 0.0099 m² g^{-1} and PCM grout = 23.087 ± 0.2350 m² g^{-1}.

The cation exchange capacities of each cementitious material were determined by titration using a Metrohm Titrando 857 with a Metrohm Dosino 800 dosing unit. 0.3 g of solid was suspended in 60 cm^3 of de-ionised water (18 MΩ) to keep the solid solution ratio the same as in the sorption experiments, and allow the solution level to sufficiently cover the pH probe. The solution was stirred and 2 mol dm^{-3} hydrochloric acid added drop-wise until the pH stabilised at roughly pH 2 - 3 (fully protonated). 0.1 mol dm^{-3} sodium hydroxide solution was added at a rate of 0.1 cm^3 min^{-1} until the pH had risen and stabilised above 11 - 12.

RESULTS AND DISCUSSION

The aqueous chemistry of Tc(IV) is dominated, in all but highly acidic solutions, by the species $TcO(OH)_2$ [10] (figure 1). This species is capable of surface complexation reactions by exchange of one or two of the hydroxyl groups. Hence, the sorption behaviour observed in this study has been modelled on the basis of mono- or bidentate surface complexes. The surface complexation modelling was performed using the geochemical speciation code JCHESS [11].
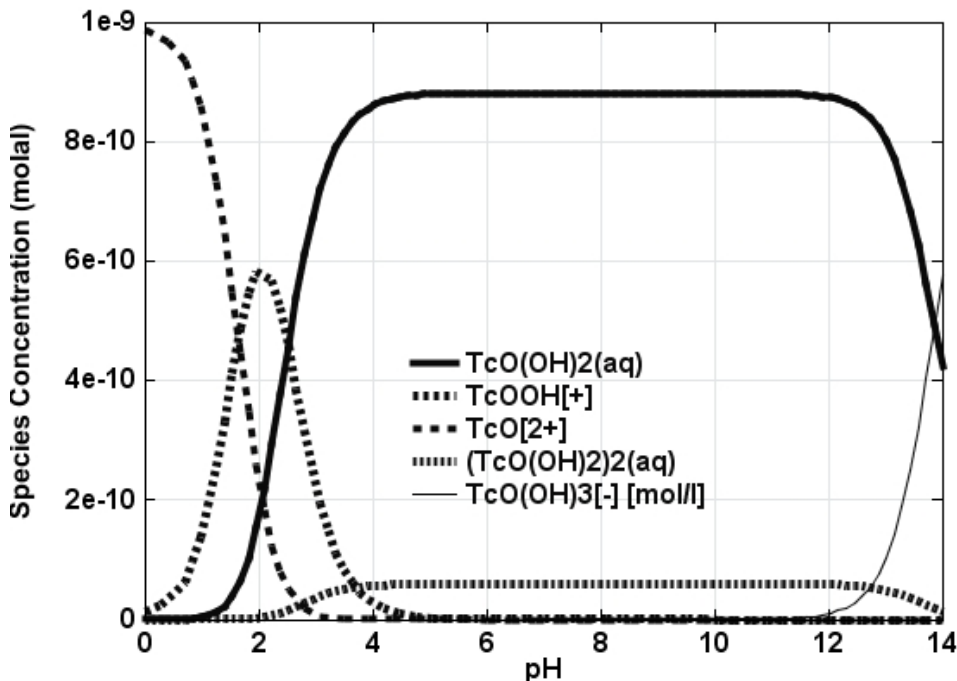

Fig. 1. The speciation of Tc(IV) as a function of pH, using the JCHESS code [11]. (Total Tc(IV) concentration 10^{-9} mol dm^{-3}). Thermodynamic data used as in Warwick *et al.* [10].
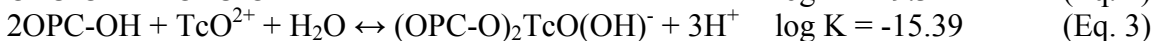
Sorption to OPC

Sorption onto OPC in the hyperalkaline range (pH = 12 - 13.3) was found to increase with pH with R_d values being typically in the range 50 to 270 cm^3 g^{-1}. This indicates some degree of surface complexation of Tc(IV) species to the cement phases in OPC in the hyperalkaline region (Table I). Relating this to the speciation of Tc(IV) at high pH

(figure 1), shows that this increase in sorption to the solid phases occurs at the same pH values at which the anionic $TcO(OH)_3^-$ species begins to become more significant, and the neutral $TcO(OH)_2(aq)$ less so. The surmised ligand exchange reactions occurring to form the bidentate complex are a significant competitor to the two main aqueous species above pH 13. The cement phases will thus provide some retardation of Tc(IV) migration in the early stages of the evolution of the GDF.

Table I. Partition coefficients, R_d, $(cm^3 \ g^{-1})$ for the sorption of Tc(IV) in hyperalkaline conditions to Ordinary Portland Cement (OPC) at ambient temperature in an oxygen-free atmosphere (< 1 ppm). Initial Tc(IV) concentrations range between 10^{-9} and 10^{-11} mol dm^{-3}. Solid to liquid ratio 1:200). Data uncertainties shown as plus/minus one standard deviation.

pH	R_d $(cm^3 \ g^{-1})$
12.17 ± 0.015	55.6 ± 25
12.21 ± 0.006	86 ± 24
12.27 ± 0.012	105 ± 1
12.41 ± 0.006	125 ± 105
12.50 ± 0.012	71 ± 14
12.72 ± 0.006	153 ± 25
13.05 ± 0.006	242 ± 28
13.28 ± 0.033	270 ± 38

It proved possible to model the sorption of Tc(IV) to OPC in the hyperalkaline region using a bidentate binding model, for the surface complexation reactions occurring. These are described in equations 1 to 3. The model provides a good fit for both the maximum R_d values measured and also the trend of increasing complexation with pH towards 13.3. The model is shown in figure 2, along with the data and models for NRVB and PCM grout which are included for comparison purposes. Error bars have been left out of this figure for clarity. Indications of the spread of data can be seen in tables I to III).

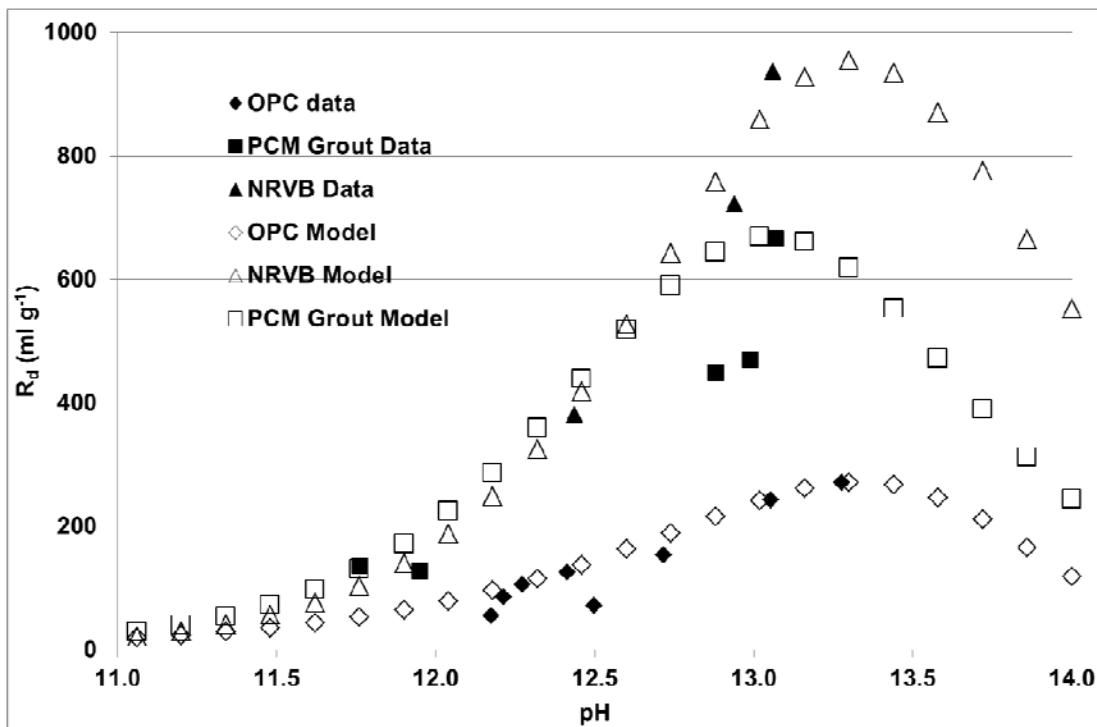|		
$OPC\text{-}OH + H^+ \leftrightarrow OPC\text{-}OH_2^+$	log K = 4.5	(Eq. 1)
$OPC\text{-}OH \leftrightarrow OPC\text{-}O^- + H^+$	log K = -9.3	(Eq. 2)
$2OPC\text{-}OH + TcO^{2+} + H_2O \leftrightarrow (OPC\text{-}O)_2TcO(OH)^- + 3H^+$	log K = -15.39	(Eq. 3)

Fig. 2. The sorption of Tc(IV) as a function of pH to OPC, NRVB and PCM grout in the hyperalkaline region described using bidentate surface complexation models. (Initial Tc(IV) concentrations 10^{-9} to 10^{-11} mol dm^{-3}, ambient temperature, < 1 ppm oxygen atmosphere, solid to liquid ratio 1:200). Error bars plus/minus one standard deviation.
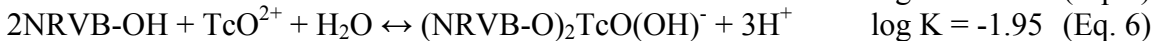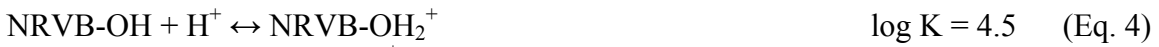
Sorption to NRVB

Sorption onto NRVB in the hyperalkaline range (pH = 12.44 - 13.06) was found to increase with pH with R_d values being typically in the range 380 to 950 cm^3 g^{-1} (Table II). This behaviour is similar to OPC with slightly higher R_d values being measured. This suggests that sorption in this pH range is being controlled by similar phases to those present in OPC.

Table II. Partition coefficients, R_d, (cm^3 g^{-1}) for the sorption of Tc(IV) to Nirex Reference Vault Backfill (NRVB) at ambient temperature in an oxygen-free atmosphere (< 1 ppm). Initial Tc(IV) concentrations 10^{-9} to 10^{-11} mol dm^{-3}. Solid to liquid ratio 1:200). Data uncertainties shown as plus/minus one standard deviation.
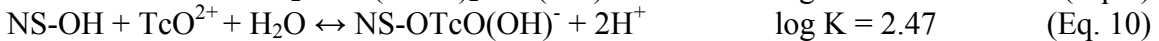
pH	R_d (cm^3 g^{-1})
3.58 ± 0.05	1573 ± 203
6.85 ± 0.10	2704 ± 370
7.60 ± 0.04	5332 ± 1166
8.95 ± 0.00	3864 ± 10
12.44 ± 0.03	382 ± 25
12.94 ± 0.00	723 ± 237
13.06 ± 0.03	937 ± 251

It proved possible to model the sorption of Tc(IV) to NRVB in the pH region 11-14 in a similar way to that used for OPC by using a bidentate binding model for the proposed surface complexation reactions occurring (Equations 4 to 6, and figure 2).

$$NRVB\text{-}OH + H^+ \leftrightarrow NRVB\text{-}OH_2^+ \qquad\qquad \log K = 4.5 \quad \text{(Eq. 4)}$$
$$NRVB\text{-}OH \leftrightarrow NRVB\text{-}O^- + H^+ \qquad\qquad \log K = -13.3 \quad \text{(Eq. 5)}$$
$$2NRVB\text{-}OH + TcO^{2+} + H_2O \leftrightarrow (NRVB\text{-}O)_2TcO(OH)^- + 3H^+ \qquad \log K = -1.95 \quad \text{(Eq. 6)}$$

The designation NRVB-OH indicates the surface groups controlling the sorption in the hyperalkaline region for the NRVB system.

At lower pH values (9 to 3.6) similar behaviour is seen to that observed by Grambow *et al.* [12], who studied the sorption of Tc(IV) to bentonite from pH 3.5 to 9.5. This behaviour manifests itself in a sorption edge from pH 6-7, with maximum sorption occurring in the region just above neutral pH. It has not been possible to analyse the exact phases to which the Tc(IV) is sorbing, but it has been possible to model its behaviour using two surface complexation constants, one monodentate and one bidentate (Equations 7 – 10). The relevant equations are shown below. The designation NS-OH indicates the surface groups controlling the sorption to NRVB in the pH region 9 to 3.6.

$$NS\text{-}OH + H^+ \leftrightarrow S\text{-}OH_2^+ \qquad\qquad\qquad \log K = 8.72 \qquad \text{(Eq. 7)}$$
$$NS\text{-}OH \leftrightarrow S\text{-}O^- + H^+ \qquad\qquad\qquad \log K = -8.3 \qquad \text{(Eq. 8)}$$
$$2NS\text{-}OH + TcO^{2+} + H_2O \leftrightarrow (NS\text{-}O)_2TcO(OH)^- + 3H^+ \qquad \log K = 3.81 \qquad \text{(Eq. 9)}$$
$$NS\text{-}OH + TcO^{2+} + H_2O \leftrightarrow NS\text{-}OTcO(OH)^- + 2H^+ \qquad \log K = 2.47 \qquad \text{(Eq. 10)}$$

Sorption is described by the monodentate surface complex from pH 3 to 6.5, (figure 3) after which the bidentate complex becomes predominant. The maximum R_d observed was 5332 ± 1166 cm^3 g^{-1}, measured at pH 7.6, although the modelling suggests maximum sorption would occur at around pH 8.5. The maximum values measured by Grambow *et al.* [12] for sorption of Tc(IV) to bentonite were around 10^5 cm^3 g^{-1}, but the majority of values were *ca.* 10^4 cm^3 g^{-1}. Hence, it can be seen that sorption to these particular cementitious phases is not quite as strong as to a clay, but the values are not too dissimilar; which lends credence to the view that the binding mechanism is similar. Grambow *et al.* also found the same pattern of a monodentate complex being predominant in the lower part of this range, with the bidentate one best describing

sorption at neutral and higher pH values. Unfortunately, there is no comparison available in the literature, known to the authors, for the hyperalkaline region.
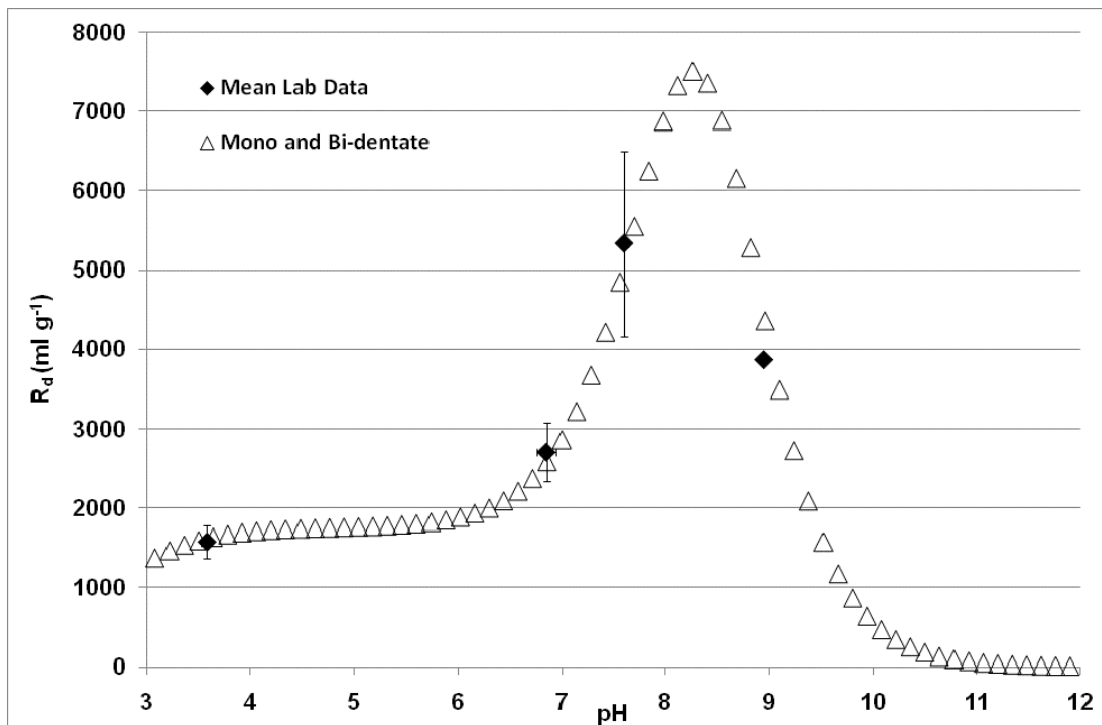

Fig. 3. The sorption of Tc(IV) to NRVB from pH 3.5 to 12 described using a mono- and bidentate surface complexation model. Initial Tc(IV) concentrations 10^{-9} to 10^{-11} mol dm^{-3}, ambient temperature, < 1 ppm oxygen atmosphere, solid to liquid ratio 1:200). Error bars plus/minus one standard deviation.
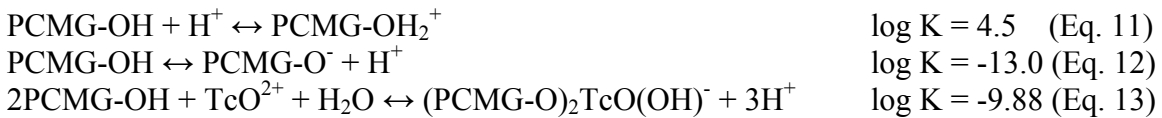
Sorption to PCM grout

Sorption onto PCM grout in the hyperalkaline range (pH = 11.7 - 13.1) was again found to increase as a function of pH, with R_d values being typically in the range 120 to 660 cm^3 g^{-1} (Table III). This behaviour is similar to both the OPC and NRVB systems with slightly higher R_d values than for OPC, but lower than NRVB, being measured. This also suggests that sorption in this pH range is being controlled by the same phases as are present in OPC.
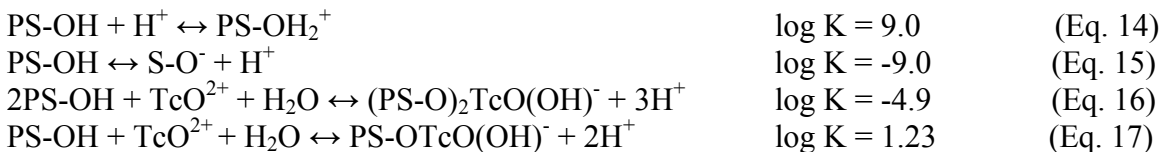
Table III. Partition coefficients, R_d, (cm^3 g^{-1}) for the sorption of Tc(IV) to Plutonium Contaminated Material grout (PCMG) at ambient temperature in an oxygen-free atmosphere (< 1 ppm). Initial Tc(IV) concentrations 10^{-9} to 10^{-11} mol dm^{-3}, solid to liquid ratio 1:200). Data uncertainties shown as plus/minus one standard deviation.

pH	R_d (cm^3 g^{-1})
3.35 ± 0.03	758 ± 54
6.17 ± 0.03	1374 ± 365
6.71 ± 0.05	3871 ± 920
8.33 ± 0.00	2817 ± 1192
11.23 ± 0.03	550 ± 137
11.52 ± 0.00	330 ± 9
11.76 ± 0.00	136 ± 7
11.95 ± 0.00	127 ± 1
12.88 ± 0.02	449 ± 18
12.99 ± 0.01	470 ± 16
13.07 ± 0.00	666 ± 55

It proved possible to model the sorption of Tc(IV) to PCM in this region using a bidentate binding model, for the surface complexation reactions occurring (Equations 11 -13, and figure 2). The designation PCMG-OH indicates the surface groups controlling the sorption in the hyperalkaline region for the PCM grout system.

$PCMG\text{-}OH + H^+ \leftrightarrow PCMG\text{-}OH_2^+$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ log K = 4.5 (Eq. 11)
$PCMG\text{-}OH \leftrightarrow PCMG\text{-}O^- + H^+$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ log K = -13.0 (Eq. 12)
$2PCMG\text{-}OH + TcO^{2+} + H_2O \leftrightarrow (PCMG\text{-}O)_2TcO(OH)^- + 3H^+$ $\quad$ log K = -9.88 (Eq. 13)

The data are more scattered for PCM grout than for NRVB and proved more difficult to interpret, perhaps due to a large influence of the PFA over the cement phases. However, at pH values below the hyperalkaline region (11.5 - 3.6) similar behaviour is seen to that observed for NRVB. This behaviour again manifests itself in a sorption edge, in this case from pH 5-6.5. The best fit model (Equations 14-17 and figure 4) again uses two surface complexation constants, one monodentate and one bidentate; log K values are given below. The designation PS-OH indicates the surface groups controlling the sorption of Tc(IV) to PCM grout in the pH region 9 to 3.6.

$PS\text{-}OH + H^+ \leftrightarrow PS\text{-}OH_2^+$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ log K = 9.0 $\quad\quad\quad$ (Eq. 14)
$PS\text{-}OH \leftrightarrow S\text{-}O^- + H^+$ $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ log K = -9.0 $\quad\quad$ (Eq. 15)
$2PS\text{-}OH + TcO^{2+} + H_2O \leftrightarrow (PS\text{-}O)_2TcO(OH)^- + 3H^+$ $\quad\quad$ log K = -4.9 $\quad\quad$ (Eq. 16)
$PS\text{-}OH + TcO^{2+} + H_2O \leftrightarrow PS\text{-}OTcO(OH)^- + 2H^+$ $\quad\quad\quad$ log K = 1.23 $\quad\quad$ (Eq. 17)

Sorption again appears to be controlled by the monodentate surface complex at lower pH values, with the bidentate complex more significant above pH 9. The fit of model to data is less convincing than for NRVB, with the maximum measured sorption occurring at pH 6.7, but being predicted by the model to occur at *ca.* pH 10. However, the measured and predicted R_d values are not dissimilar.
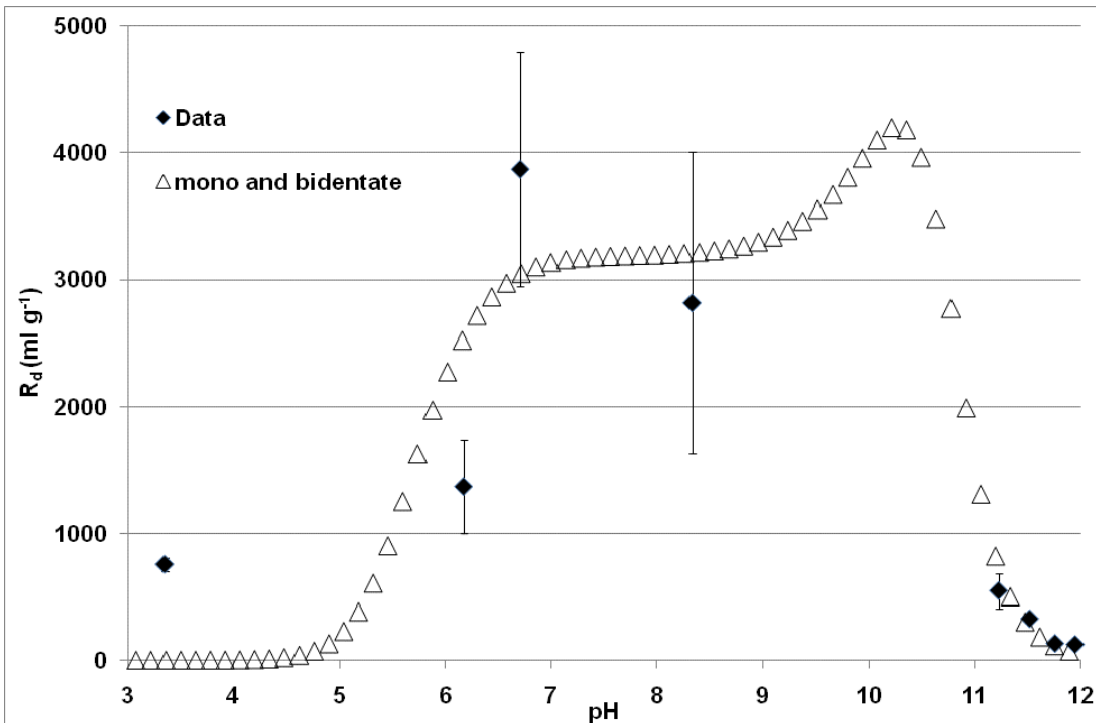
Fig. 4. The sorption of Tc(IV) to PCM grout from pH 3.5 to 12 described using a mono- and bidentate surface complexation model. Initial Tc(IV) concentrations 10^{-9} to 10^{-11} mol dm^{-3}, ambient temperature, < 1 ppm oxygen atmosphere, solid to liquid ratio 1:200. Error bars plus/minus one standard deviation.

CONCLUSIONS

The sorption of Tc(IV) to three cementitious materials has been measured. The values for the partition coefficient (R_d) were found to range from 70 to 5500 cm^3 g^{-1}. It was noticeable that R_d was heavily dependent on pH in all cases, with a maximum sorption occurring in the near-neutral pH range and an increase in sorption above pH 13. In general, modelling using bidentate surface complexation constants in the hyperalkaline region, and a combination of mono- and bidentate ones below *ca.* pH 11.5 give best agreement between models and data. These data will inform the performance assessment for the behaviour of technetium in the near-field of the UK's planned higher-activity wastes GDF.

REFERENCES

1. "Generic Repository Studies: The Nirex Phased Disposal Concept", United Kingdom Nirex Ltd, Nirex Report N/074, (2003).
2. S. BAKER, G.M.N. BASTON, M.C. MANNING, R. McCROHON and S. WILLIAMS, "The Aqueous Solubility Behaviour of Selenium, Technetium and Tin", AEAT/R/ENV/0233, AEA Technology, Harwell, Didcot (2000).
3. D. CUI AND T.E. ERIKSEN, "Reduction of Pertechnetate by Ferrous Iron in Solution: Influence of Sorbed and Precipitated Fe(II)", Environmental Science and Technology 30(7), 2259 (1996).
4. J.L. MAS, K. TAGAMI and S. UCHIDA, "Method for the detection of Tc in seaweed samples coupling the use of Re as a chemical tracer and isotope dilution inductively coupled plasma mass spectrometry", Analytica Chimica Acta, 509, 83, (2004).
5. D. COPPLESTONE, D. JACKSON, R.G. HARTNOLL, M.S. JOHNSON, P. McDONALD and N. WOOD, "Seasonal variations in activity concentrations of Tc-99 and Cs- 137 in the edible meat fraction of crabs and lobsters from the central Irish Sea", Journal of Environmental Radioactivity, 3, 29, (2004).
6. J. REED, "Technetium to go", Nuclear Engineering International, 49, 14, (2004).
7. S. ALDRIDGE, P. WARWICK, N. EVANS and S. VINES, "Degradation of tetraphenylphosphonium bromide at high pH and its effect on radionuclide solubility", Chemosphere, 66(4), 672, (2007).
8. "Development of the Nirex Reference Vault Backfill; Report on Current Status in 1994", United Kingdom Nirex Limited, Science Report S/97/014, (1997).
9. S.J. KEMP, G. TURNER and D. WAGNER, "Initial testing and a laboratory manual for the Micromeritics Gemini VI physisorption system", British Geological Survey Internal Report, IR/08/086, (2009).
10. P. WARWICK, S. ALDRIDGE, N. EVANS and S. VINES, "The Solubility of Technetium(IV) at High pH", Radiochimica Acta, 95(12), 709, (2007).
11. J. VAN DER LEE, "Jchess 2.0", Ecole des Mines de Paris, Centre d'Informatique Géologique, http://chess.ensmp.fr jchess (2000).
12. B. GRAMBOW, M. FATTAHI, G. MONTAVON, C. MOISAN, and E. GIFFAUT, "Sorption of Cs, Ni, Pb, Eu(III),Am(III), Cm, Ac(III), Tc(IV), Th, Zr, and U(IV) on MX 80 Bentonite: An Experimental Approach to Assess Model uncertainty", Radiochimica Acta, 4, 627, (2006).

ACKNOWLEDGEMENTS