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Effects of cellulosic degradation products on uranium sorption in the geosphere

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Abstract

The current design concept for intermediate- and some low-level radioactive waste disposal in the UK involves emplacement in a cementitious repository deep underground. The movement of radionuclides away from such a repository through the host rock formation towards the biosphere is expected to be retarded to a significant degree by sorption processes. One major issue being studied is the effect on uranium sorption of degradation products arising from organic waste matter, especially cellulosic materials. The sorption of uranium could be reduced by degradation products, either because of complexation, or through the organic materials competing for sorption sites. Because of the complexity of authentic degradation products, work has also been carried out using gluconate and iso-saccharinate as well-characterised simulants.

In the presence of high concentrations of either the authentic or simulated degradation products, significant reductions in uranium sorption have been observed. However, in the presence of lower concentrations of these organic materials, such as would be present in the repository, sorption was reduced at most by only a small margin and, in some cases, the results suggested a slight increase.

1. Introduction

The current design concept for intermediate- and some low-level radioactive waste disposal in the UK involves emplacement in a cementitious repository deep underground. The movement of radionuclides away from such a repository through the host rock formation towards the biosphere is expected to be retarded to a significant degree by sorption processes. Therefore, the UK Nirex Ltd Safety Assessment Research Programme includes an investigation into the sorption behaviour of various actinides, under conditions expected to prevail in the geosphere surrounding a cementitious repository [1].

This paper describes a study of uranium(VI) and uranium(IV) sorption onto a red eutaxitic massive tuff sample from the Craghouse Tuff Unit of the Borrowdale Volcanic Group, Borehole 2, at Sellafield, since in the repository uranium may be present in both the VI and IV oxidation states . Apart from investigating sorption under unperturbed far-field conditions, the research programme also includes a study of sorption under conditions where the "normal" chemistry has been affected by the presence of near-field-derived species: organic degradation products from the cellulosic materials within the repository and the alkaline plume from the cementitious near-field barrier.

The products arising from the degradation of cellulosic materials present in low- and intermediate-level radioactive wastes in a cementitious repository are known to decrease the sorption of some important actinides, such as uranium, thorium and plutonium, on a range of rock types such as clay, sandstone and flagstone [2, 3]. Previous studies have also shown that high concentrations of organic materials reduce thorium sorption onto tuff samples, whereas under certain conditions lower concentrations appear to enhance sorption [4].

In the present work, uranium sorption was studied for four different cases: (i) no organic materials present (base-case); (ii) in the presence of authentic degradation products; (iii) in the presence of gluconate (2×10^{-6}–2×10^{-3} M); (iv) in the presence of iso-saccharinate (2×10^{-7}–2×10^{-3} M). Studies were carried out at pH 7 and pH 12.5 to reproduce conditions anticipated to prevail at the extremes of the zone disturbed by the alkaline plume emanating from the repository. The work at high pH was carried out using unaltered samples of tuff as a first stage in the study of sorption on geological materials affected by the alkaline plume.

The authentic degradation products were produced from the accelerated degradation of cellulose at a high

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(10%) cellulose loading in cement. This cellulose loading is very high compared with any likely repository average (less than 1%), although the timescale for degradation in the repository is clearly very much longer than that available for laboratory experiments. Although 2×10^{-3} M gluconate and iso-saccharinate correspond to total organic carbon concentrations less than a hypothetical maximum, they are judged to represent solutions with an effective concentration of complexant at the higher end of the range that might be anticipated in pore fluids emanating from a repository. The lower concentrations of organic species are more likely to represent true repository far-field conditions.

2. Principle of batch sorption experiments

In batch sorption experiments – the technique used throughout the present work – a known weight M of crushed rock is contacted with a solution of known volume V containing the radionuclide of interest at concentration c_o. The rock is crushed to allow diffusion into the particles in convenient times. As sorption proceeds, the concentration in the solution falls to a final steady value c_t, which is determined after filtering or centrifuging to remove any suspended material. The sorptivity (R_d value) can then be calculated using:

$$R_d = \{(c_o - c_t)/c_t\}(V/M)$$

3. Experimental details

All the experiments were carried out in nitrogen atmosphere glove-boxes to prevent reactions of aqueous species with carbon dioxide and, where relevant, the oxidation of uranium(IV) to uranium(VI). A further precaution used to prevent uranium(IV) oxidation was the presence of 0.0025 M sodium hydrosulphite ($Na_2S_2O_4$) as a holding reductant [5].

^{232}U and ^{233}U were obtained from Actinide Chemistry and Analysis Department, AEA Fuel Services, Harwell, as calibrated acidic uranyl chloride stock solutions. The uranium concentration was determined by α-spectrometry (Canberra S100). The initial concentration was $\sim 8\times10^{-8}$ M. The errors (2 sigma) quoted on the values of the distribution ratio R_d are based on counting statistics only.

3.1. Preparation of starting materials

The sample of tuff was crushed until less than 425 μm in size, with 95% of the sample being less than 300 μm. The whole rock fraction was used to prevent the selective removal of certain mineral phases. The approximate mineralogy of the geological material used is listed in Table 1.

TABLE 1. Approximate mineralogy of the tuff sample

Mineral	Tuff
Quartz	Dominant
K-feldspar	Present
Plagioclase	Minor
Calcite/dolomite	Major
Clays + amorphous material	Present

TABLE 2. Groundwater compositions [10][a]

Ion	Far-field groundwater	Evolved near-field groundwater
Na^+	3.44×10^{-1}	3.88×10^{-1}
K^+	2.80×10^{-3}	3.94×10^{-3}
Ca^{2+}	1.76×10^{-2}	5.42×10^{-2}
Mg^{2+}	3.42×10^{-3}	1.08×10^{-7}
Sr^{2+}	1.77×10^{-4}	2.96×10^{-4}
Ba^{2+}	1.04×10^{-6}	–
Cl^-	3.65×10^{-1}	4.34×10^{-1}
Br^-	2.94×10^{-4}	3.21×10^{-4}
HCO_3^-	2.21×10^{-3}	7.52×10^{-6}
SO_4^{2-}	1.11×10^{-2}	1.14×10^{-2}
pH	6.9	12.4

[a] All concentrations are given in units of mol dm^{-3}.

For the experiments under far-field conditions, synthetic groundwater was used (Table 2). The authentic degradation product leachate was prepared by heating tissues (1 kg), cement (10 kg Nirex reference vault backfill) and water (10 kg) in an autoclave to 80 °C for 30 days. The concentrations of inorganic species in this leachate were then increased until they equalled those of the equilibrated groundwater.

For the near-field experiments, an evolved near-field groundwater was used (Table 2). The same authentic degradation products were used as described above, except that the concentrations of the ions in the leachate were increased to those of the evolved near-field groundwater.

The acidic radionuclide stock solution was used to spike the appropriate solution, following which, the pH was adjusted to its original value using a small volume of 1 M sodium hydroxide. This did not significantly affect the groundwater compositions.

3.2. Batch sorption methodology

The batch sorption experiments were carried out in triplicate. One tube was monitored regularly over a period of 100–120 days to test for a steady final concentration of uranium and pH drift. If necessary, the pH of the liquid in this tube was adjusted using hydrochloric acid or sodium hydroxide. The same volume of acid or alkali was then added to the other tubes in the set (this dilution was allowed for when the final R_d values were calculated). The redox potential Eh was also monitored during the uranium(IV) experiments, the least negative values measured being −530 mV at pH 12.4 and −280 mV at pH ~7 (both with respect to the standard hydrogen electrode (SHE)). Typical E_h values measured in the uranium(VI) experiments ranged from +150 mV (pH ~12.2) to +300 mV (pH ~7). All the tubes were gently agitated continuously.

Once a final steady concentration of uranium was established in the periodically monitored tube, the remaining two unperturbed tubes were analysed. Three liquid/solid separation techniques were used: (i) unfiltered (left standing for 72 h for uranium(VI), or centrifuged for uranium(IV)), with aliquots being removed from near the surface of the supernatant liquid; (ii) filtration through a 0.45 μm filter (Millipore "Millex"® HV 0.45); (iii) filtration through a 30 000 MWCO filter (Millipore "TTK"®). In the tables of results, since there was little variation in the R_d values with the liquid/solid separation technique, the six R_d values obtained have been averaged. Final pH measurements were also taken. The results from experiments where 1 M nitric acid was used to leach any sorbed radioactivity off the containers walls, along with analysis of solutions from the tubes containing no rock, indicated that in the presence of rock the loss of uranium onto the vessel walls was minimal. These procedures have been described in more detail elsewhere [6, 7].

4. Uranium(VI)

4.1. Uranium(VI) results

The results of the experiments investigating uranium(VI) sorption onto the tuff are given in Tables 3–6. In the absence of organic materials, uranium(VI) sorption was found to decrease from ~110 cm^3 g^{-1} at pH ~7 to ~20 cm^3 g^{-1} at pH ~10.7, before increasing again to ~400 cm^3 g^{-1} at pH ~12.8.

Table 4 shows the effect of high concentrations of organic materials on uranium(VI) sorption. At pH ~7, the presence of organic materials reduces uranium(VI) sorption from ~110 cm^3 g^{-1} for the base-case to ~15 cm^3 g^{-1} in the presence of 2×10^{-3} M gluconate, 2×10^{-3} M iso-saccharinate or neat authentic degradation products. However, at a pH ~12.8, R_d for the base-case < authentic degradation products, ≃R_d iso-saccharinate, <R_d for gluconate.

TABLE 3. Effect of pH on uranium(VI) sorption

Final measured pH	R_d (cm^3 g^{-1})
7.0	110±10
7.5	65±10
10.7	18±5
12.3	60±10
12.8	420±40

The dependence of uranium(VI) sorption on the initial gluconate concentration is given in Table 5. At pH ~7, in the presence of gluconate concentrations above 2×10^{-6} M, the extent of uranium(VI) sorption falls steadily as the gluconate concentration is increased further. However, at pH ~12.8, even in the presence of 2×10^{-6} M gluconate, uranium(VI) sorption is four times that for the base-case, as the gluconate concentration increases, so does the extent of uranium(VI) sorption.

The results of the experiments at different iso-saccharinate concentrations are given in Table 6. At pH ~7, uranium(VI) sorption is reduced in the presence of iso-saccharinate concentrations above 2×10^{-5} M, with the overall drop in R_d value being very similar to that for gluconate. However, at pH ~12.8, the presence of iso-saccharinate appears to enhance sorption by approximately a factor of five, even at 2×10^{-7} M, and this enhancement increases to an order of magnitude in the presence of 2×10^{-3} M iso-saccharinate.

4.2. Discussion of results for uranium(VI) sorption

For uranium(VI), gluconate, iso-saccharinate and authentic degradation products all affect sorption in similar ways. At pH ~12.8, the extent of sorption is apparently increased in the presence of organic degradation products, relative to the base-case, whereas sorption at pH ~7 is decreased. At the higher pH, gluconate exerts the strongest effect on sorption, whereas the reduction of sorption in the presence of organic materials at pH ~7 is very similar for all three organic materials studied.

5. Uranium(IV)

5.1. Uranium(IV) results

The results of the experiments investigating uranium(IV) sorption onto the tuff are given in Tables 7 and 8. In the absence of organic degradation products, uranium(IV) sorption was observed to be strong. R_d values >10^5 cm^3 g^{-1} and 3×10^4 cm^3 g^{-1} were obtained at pH ~7 and pH ~12.2 respectively.

Table 7 compares the effects of 2×10^{-3} M gluconate, 2×10^{-3} M iso-saccharinate and authentic degradation products on uranium(IV) sorption. At pH ~7, sorption in the presence of 2×10^{-3} M iso-saccharinate or authentic degradation products is significantly reduced compared with the base-case, whereas the presence of 2×10^{-3} M gluconate has a smaller effect on reducing

TABLE 4. Effect of organic degradation products on uranium(VI) sorption

Organic materials present	Final measured pH	R_d (cm^3 g^{-1})
None	7.0	110±10
2×10^{-3} M gluconate	7.0	13±6
2×10^{-3} M iso-saccharinate	7.1	19±5
Authentic degradation products	7.1	19±4
None	12.8	420±40
2×10^{-3} M gluconate	12.7	$(1.3\pm0.1)\times10^4$
2×10^{-3} M iso-saccharinate	12.6	3700±200
Authentic degradation products	12.7	5600±600

TABLE 5. Effect of gluconate concentration on uranium(VI) sorption

Organic materials present	Final measured pH	R_d (cm^3 g^{-1})
None	7.0	110±10
2×10^{-6} M gluconate	6.9	150±20
2×10^{-4} M gluconate	6.9	30±8
2×10^{-3} M gluconate	7.0	13±6
None	12.8	420±40
2×10^{-6} M gluconate	12.7	1800±200
2×10^{-4} M gluconate	12.7	2600±300
2×10^{-3} M gluconate	12.7	$(1.3\pm0.1)\times10^4$

TABLE 6. Effect of iso-saccharinate concentration on uranium(VI) sorption

Organic materials present	Final measured pH	R_d (cm^3 g^{-1})
None	7.0	110±10
2×10^{-7} M iso-saccharinate	7.2	140±20
2×10^{-6} M iso-saccharinate	7.2	95±10
2×10^{-5} M iso-saccharinate	7.2	130±10
2×10^{-4} M iso-saccharinate	7.1	55±8
2×10^{-3} M iso-saccharinate	7.1	19±5
None	12.8	420±40
2×10^{-7} M iso-saccharinate	12.8	2600±200
2×10^{-6} M iso-saccharinate	12.8	980±110
2×10^{-5} M iso-saccharinate	12.9	2100±200
2×10^{-4} M iso-saccharinate	12.5	3200±300
2×10^{-3} M iso-saccharinate	12.6	3700±200

the extent of sorption, with the R_d values being $>10^5$ cm^3 g^{-1}, ~4000 cm^3 g^{-1}, ~700 cm^3 g^{-1} and ~600 cm^3 g^{-1} for the base, gluconate, iso-saccharinate and authentic degradation products cases respectively. A similar trend was observed at pH ~12.2, except in the presence of 2×10^{-3} M iso-saccharinate, where uranium(IV) sorption was reduced ~24 cm^3 g^{-1}.

The effects of lower concentrations of iso-saccharinate on uranium(IV) sorption are presented in Table 8. The extent of uranium(IV) sorption in the presence of 2×10^{-7} and 2×10^{-5} M iso-saccharinate is very similar to that for the base-case. However, as the iso-saccharinate concentration is increased beyond this level, the extent of uranium(IV) sorption falls sharply, with similar trends observed at pH ~12.2 and ~7. For example, at pH ~12.2, R_d values of 3×10^4 cm^3 g^{-1}, 4×10^4 cm^3 g^{-1}, ~7000 cm^3 g^{-1} and ~25 cm^3 g^{-1} were obtained for the base case and in the presence of 2×10^{-5} M, 2×10^{-4} M and 2×10^{-3} M iso-saccharinate respectively.

5.2. Discussion of results of uranium(IV) sorption

In the absence of organic degradation products, uranium(IV) sorption was observed to be very strong. However, the presence of organic degradation products reduced the extent of uranium(IV) sorption significantly; this was particularly so for high concentrations of iso-saccharinate (above 2×10^{-4} M). This reduction in uranium(IV) sorption in the presence of organic degradation products could be caused either by complexation or through the organic materials competing for sorption sites. Also, there was no marked difference between the sorption behaviour in the two pH ranges investigated.

6. Comparison of uranium(IV) and uranium(VI) behaviours

In the absence of organic degradation products, uranium(IV) sorption is three orders of magnitude stronger than that of uranium(VI) at pH ~7 and two orders of magnitude stronger at pH ~12.5. This weaker sorption of uranium(VI) could be attributed to the formation of uranium(VI)-carbonate species, which sorb less strongly. This suggestion has been supported by the results of thermodynamic modelling of sorption onto clay [8, 9]. The uranium(IV) speciation across the pH range studied was predicted to be almost totally dominated by the hydroxide species $U(OH)_4$.

TABLE 7. Effect of organic degradation products on uranium(IV) sorption

Organic materials present	Final measured pH	Final *E*h (mV *vs.* SHE)	R_d (cm^3 g^{-1})
None	7.1	−330	$>10^5$
2×10^{-3} M gluconate	7.2	−330	3500 ± 100
2×10^{-3} M iso-saccharinate	7.1	−350	680 ± 30
Authentic degradation products	7.1	−270	610 ± 30
None	12.3	−590	$(3.1\pm0.2)\times10^4$
2×10^{-3} M gluconate	12.1	−640	7100 ± 300
2×10^{-3} M iso-saccharinate	12.2	−590	24 ± 3
Authentic degradation products	12.1	−670	170 ± 10

TABLE 8. Effect of iso-saccharinate concentration on uranium(IV) sorption

Organic materials present	Final measured pH	Final *E*h (mV *vs.* SHE)	R_d (cm^3 g^{-1})
None	7.1	−330	$>10^5$
2×10^{-7} M iso-saccharinate	7.1	−350	$(7.9\pm0.8)\times10^4$
2×10^{-5} M iso-saccharinate	6.9	−330	$(5.9\pm0.5)\times10^4$
2×10^{-4} M iso-saccharinate	7.0	−330	$(1.5\pm0.1)\times10^4$
2×10^{-3} M iso-saccharinate	7.1	−350	680 ± 30
None	12.3	−590	$(3.1\pm0.2)\times10^4$
2×10^{-7} M iso-saccharinate	12.1	−600	$(3.1\pm0.1)\times10^4$
2×10^{-5} M iso-saccharinate	12.3	−590	$(4.0\pm0.3)\times10^4$
2×10^{-4} M iso-saccharinate	12.2	−600	7400 ± 300
2×10^{-3} M iso-saccharinate	12.2	−590	24 ± 3

The effect of the presence of organic degradation products on uranium sorption at pH ~7 is independent of the oxidation state. For both uranium(IV) and uranium(VI), sorption is reduced in the presence of any of the organic degradation products studied, compared with the base case. However, at pH ~12.5, the presence of organic degradation produces affects the sorption of the two uranium oxidation states in very different ways. For uranium(IV), sorption is reduced in the presence of organic degradation products – particularly iso-saccharinate and authentic degradation products – whereas uranium(VI) sorption is enhanced by the presence of any of the organic materials investigated.

7. Conclusions

The results show that at pH ~7, high concentrations of organic degradation products are able to reduce the sorption of uranium(VI) and uranium(IV) onto tuff samples, whereas the presence of lower concentrations of these organic materials reduces sorption at most by only a small margin. Similarly, at pH ~12.2, the extent of uranium(IV) sorption is only significantly reduced in the presence of high concentrations of organic materials. However, at very high pH values (pH ~12.8), under certain conditions, the sorption of uranium(VI) appears to be enhanced by the presence of organic materials.

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