

1 **The influence of natural organic matter on radionuclide mobility under conditions**
2 **relevant to cementitious disposal of radioactive wastes: a review of direct evidence**

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14
15 **Abstract**

16 A concept for the disposal of intermediate level radioactive wastes involves emplacement
17 within a geological disposal facility, followed by backfilling of the facility with cement. When
18 the closed facility is re-saturated with groundwater, this will create a high pH environment
19 due to dissolution of the cement minerals. Dissolved organic matter (DOM; defined here as
20 naturally occurring organic acids and humin) will be present in the groundwater at a
21 concentration that reflects the host rock environment and the recharge source and pathway.
22 Interactions between DOM and radionuclides may enhance transport away from the facility
23 and are an important consideration in safety performance assessments. This review
24 specifically focuses on studies of DOM - radionuclide interactions at the high pH range that
25 is expected during a repository lifetime. Whilst the vast majority of available data cover
26 binary (DOM - radionuclide) and batch ternary systems (mineral - radionuclide - DOM), this
27 review also covers other potentially important areas, such as reversibility kinetics and redox
28 processes that can be mediated by DOM.

29 **Keywords:** Radioactive waste; geodisposal; humic substances; radionuclides; cement

30

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82 **1.Introduction**

83 Strategies for geological disposal of intermediate level radioactive wastes (ILW) in multiple
84 countries involve emplacement, followed by addition of a cementitious backfill. The aim is to
85 provide a chemical barrier that retards radionuclide transport from the geological disposal
86 facility (GDF). Due to chemical degradation of the cements, migration of plumes of interstitial
87 water away from the engineered barrier system and into the surrounding host rock will create
88 a geochemically disturbed zone (GDZ), with large chemical gradients particularly in pH,
89 electrolyte composition and ionic strength (and possibly redox potential). These conditions
90 will evolve over the lifetime of the repository and will depend on flow rates, groundwater
91 composition and the formulation of the cement barrier.

92
93 Dissolved organic matter (DOM; defined here as naturally occurring organic acids and
94 humin; see section 1.3 for a more detailed description) is ubiquitous in aquatic environments
95 and will be present in groundwaters with concentrations dependent upon the host rock
96 environment and recharge source and pathway. Furthermore, organic wastes and cellulose
97 degradation products in emplaced wastes may also contribute to production of substances
98 with natural organic matter type properties within the GDZ (Baston et al., 1994). DOM exerts
99 a powerful control on chemical conditions in waters and soils, influencing the transport and
100 retention of metals (Tipping et al., 2011). Binding of cationic metals to DOM can result in
101 increased solubility of metal salts and transport of DOM may result in simultaneous transport
102 of bound metals. The influence of organic matter on radionuclide migration has been
103 recognised as a significant source of uncertainty in radioactive waste management (Glaus et
104 al., 1997).

105
106 *1.1. Rationale for DOM studies at high pH*

107 *1.1.1. Organic matter concentrations and sources to and within the GDF*

108 Geological environments have a varied range of DOM concentrations. Typical groundwater
109 concentrations vary depending upon host rock and location. Measurements in granitic
110 waters are in the range 0.02 – 0.04 mg L⁻¹ in Switzerland and 2 – 10 mg L⁻¹ in France and

111 Sweden, salt dome groundwaters in the Gorleben region of Germany have concentrations in
112 the range 0.9 – 127 mg L⁻¹, and sedimentary deposits in France, Belgium and the UK have
113 concentrations in the range 2 – 120 mg L⁻¹ (Gooddy and Hinsby, 2008; and compilation in
114 Reiller et al., 2002). Thus, host geology will strongly influence the concentrations of DOM
115 that may come into contact with radionuclides in the GDF. Alkali conditions also have the
116 potential to convert clay immobilised hydrophobic organic matter to dissolved forms (Claret
117 et al., 2003; Courdouan et al., 2007a, 2007b). Degradation of emplaced organic wastes may
118 lead to the genesis of dissolved organic materials with binding properties similar to natural
119 organic matter. The placement of waste containers containing cellulose is identified as an
120 aspect of geodisposal that requires additional consideration, due to potential for enhanced
121 radionuclide transport in the vicinity of such wastes (Crossland and Vines, 2001). A review of
122 cellulose degradation under alkaline conditions, including resulting products and their
123 functional groups, is presented in Knill and Kennedy (2003). If regional surface waters are
124 used in the preparation of cement materials the DOM content of these waters may add to the
125 DOM pool during cement leaching.

126
127 *1.1.2. Evolution of cement induced pH conditions*

128 Chemical degradation reactions that can occur in hydrated cement include dissolution,
129 leaching and associated processes, such as carbonation (dissolution of portlandite as a
130 result of calcite precipitation and resultant reduction in Ca solution concentrations) and
131 decalcification (ionic leaching from dissolution of portlandite and calcium-silicate hydrates
132 (C–S–H) in hydrated cement; Glasser et al., 2008). These reactions induce gradual changes
133 to the composition of the interstitial water, from typical “young” concrete leachate with a pH
134 above 13, to more evolved leachate with a pH lower than 10 (Jacques et al., 2010). Figure 1
135 is a generalised schematic of the stages of pH evolution during cement degradation. Four
136 stages of cement degradation can be identified depending on the pH and cement pore water
137 controlling cement phases. Stage 1 has a pH greater than 12.5 with high concentrations of
138 Na and K ions. The pH of this stage will depend upon the cement composition, and this

139 varies between several countries' disposal concepts. Stage 2 has a pH controlled by the
140 dissolution of portlandite ($\text{Ca}(\text{OH})_2$). Stage 3 starts when all portlandite has been leached out
141 of the cement, and the pH drops to 10.0, when the pore water composition is buffered by
142 different cement phases including C–S–H amongst others. Stage 4 has a pH lower than 10
143 with calcite and aggregate minerals present. Finally, the interstitial water composition will be
144 influenced principally by the chemistry of the groundwater. The duration of the different
145 stages will be dependent upon flow rates and groundwater composition (Jacques et al.,
146 2010). Changes are not restricted to chemical evolution as physical properties such as
147 porosity will also be affected (Hoch et al., 2012).

148

149 *1.1.3. Radionuclides present within intermediate level waste*

150 Emplaced wastes are likely to contain complex radionuclide mixtures in varying matrixes.
151 National reporting of waste inventories is generally in the form of waste volumes within given
152 categories (e.g. ILW). For example, as reported by International Atomic Energy Agency
153 member states in the Net-Enabled Radioactive Waste Management Database (IAEA-
154 NEWMDB; <http://newmdb.iaea.org>). Differences in the categorisation of wastes between
155 countries can make inter-comparison and full evaluation difficult, and reporting requirements
156 do not oblige quantification of the different radionuclides within the wastes. The UK and USA
157 both publish inventories of radionuclides and their activities within different waste classes.
158 The US Department of Energy publish an Annual Transuranic Waste Inventory Report (USA-
159 DOE, 2009), which excludes defence related wastes and spent fuel. The UK Nuclear
160 Decommissioning Authority and Department for Energy and Climate Change produce a joint
161 triennial report on the UK radioactive waste inventory, and this includes high, intermediate
162 and low level wastes produced from uranium enrichment, nuclear fuel manufacture, nuclear
163 power production, spent fuel reprocessing, research and development, medical and
164 industrial sources and defence activities. Spent fuel currently in storage is not included
165 (NDA/DECC, 2011). Table 1 details all of the ILW classified radionuclides within the UK
166 inventory that have half-lives of 100000 years or greater. These isotopes will be present in

167 any nuclear power related radioactive waste, with the relative quantities dependent upon
168 exact life cycle processes. Those in bold are present at activities higher than 0.1 TBq. It is
169 instructive to consider these wastes in terms of their chemical concentrations and the molar
170 amount per TBq is shown. Radionuclides present in the ILW inventory at quantities greater
171 than 10^3 moles include ^{93}Zr , ^{99}Tc , ^{135}Cs , ^{232}Th , ^{235}U , ^{236}U , ^{238}U and ^{237}Np .

172
173 *1.1.4. Interactions between radionuclides, DOM and mineral surfaces*

174 Figure 2 shows the performance assessment steps that are required when considering the
175 importance of DOM on radionuclide transport in a GDF. Assuming DOM is present the
176 following interactions require consideration. Does the radionuclide have an affinity for DOM
177 binding (in either oxidised or reduced forms)? Is the binding reversible, particularly across
178 the strong geochemical gradients of the GDZ? Does the presence of DOM affect the redox
179 state of the radionuclide and therefore the solubility? What influence do ternary systems
180 (radionuclide-DOM-mineral surface) have on radionuclide mobility? This review seeks to
181 address these questions whilst considering the chemical conditions within the disposal
182 facility and cementitious GDZ.

183
184 *1.2. Scope of this review*

185 This review considers literature where measurements have been made on DOM-
186 radionuclide interactions at pH values relevant to a cementitious GDF. Estimations for the
187 purpose of performance assessment can only be bound within reasonably defined limits
188 based on the quality and availability of direct data. This review only includes experimental
189 data, or models that have been formulated from such data. The selection criteria included a
190 requirement that data should cover a significant pH range above 8. Whilst this considerably
191 restricts both the range of study types and the number of manuscripts, it enables an
192 assessment of the current knowledge of DOM-radionuclide interactions at high pH without
193 resorting to extrapolation or assumptions that behaviour is analogous to lower pH systems. It
194 is worth noting that the brevity of aspects such as kinetics and redox processes compared
195 to, for example, ternary systems, reflects data availability, rather than their comparative

196 importance. The literature search was performed for all nuclides from ^{93}Zr and heavier and
197 present in UK ILW above 0.1 TBq (Table 1). However, the majority of the available data are
198 for actinides and thus, the review is largely focussed on these elements. The vast majority of
199 the work reviewed here was not specifically targeted at radionuclide behaviour in and around
200 GDFs or high pH environments. We have focussed only on the parts of these studies that
201 are relevant to our aims and scope. For a more general overview of the last decade of
202 progress in understanding of DOM related mobility and reactivity of radionuclides and not
203 specifically related to high pH systems, readers are referred to the review of Bryan et al.
204 (2012). A wide ranging journal special issue focussing on geodisposal, covering mineral
205 transformations, near and far field evolution, microbial science, and other relevant topics
206 has recently been published (Evans, 2012).

207
208 This review makes extensive use of the electronic Supporting Information facility to show
209 relationships between pH and DOM binding in binary systems as well as plotting together all
210 existing experimental evidence for high pH ternary systems. We refer to specific figures in
211 the Supporting Information in the relevant sections of the text.

212 213 *1.3. A note on terminology*

214 We use the term dissolved organic matter (DOM) to refer generally to the entirety of the
215 natural organic carbon constituents of aqueous systems. The term dissolved only infers that
216 the DOM is the amount present after solutions have been passed through a 0.45 μm filter.
217 Most experiments are performed on isolated fractions of DOM and thus these (humic acid,
218 HA; fulvic acid, FA; and humin) are referred to specifically when used. The term organic
219 acids is used when referring to both HA and FA. In order to avoid confusion when referring
220 to the interactions of radionuclides with DOM and mineral surfaces, we use the term binding
221 when referring to DOM and sorption to refer to interactions with minerals. No difference in
222 interaction mechanisms should be inferred from the use of these different terminologies.
223 Where we refer to all actinides with a given oxidation state, M, is used (e.g. MO_2^{2+} , refers to
224 the hexavalent oxidation states of U, Pu and Np).

225
226

2. The binary radionuclide-DOM system

227 The binary relationships between radionuclide cations and DOM are typically analysed using
228 isolated humic (HA) or fulvic acids (FA), which are constituents of DOM that are
229 operationally defined based on the separation method. They are separated from non-ionic
230 humin by retention on an anion exchange column, then HA is separated from FA by
231 precipitation at pH 1, conditions under which fulvic acid remains dissolved. Studies of these
232 equilibrium interactions are typically designed to obtain complexation constants (β ; Kim and
233 Czerwinski, 1996) that are conditional for the exact experimental conditions under which
234 they are obtained (this is referred to as a formation or reaction constant in some literature).
235 For examples of pH trends for these constants see Reiller, 2005 and Reiller et al., 2008.
236 These constants are typically defined as $\beta = [\text{RN-HA}]/([\text{RN}]_f \cdot [\text{HA}]_f)$; where concentrations are
237 represented by; $[\text{RN-HA}]$, the radionuclide-humic acid species; $[\text{RN}]_f$, the free ion of the
238 radionuclide (e.g., the UO_2^{2+} ion); and $[\text{HA}]_f$, the free ion concentration of HA. As HA is
239 generally added to experiments in terms of mass per unit volume, conversion to molar (or
240 equivalents) concentration is achieved by applying experimental knowledge of the proton
241 dissociation properties at a given pH, obtained from potentiometric titration (Kim et al.,
242 1990).

243
244

245 Variables such as ionic strength and the chosen electrolyte tend to have only a small effect
246 on the values obtained (Glaus et al., 1997). Variation of the type of HA tends to yield
247 complexation constant values that are within one order of magnitude of each other (Lubal et
248 al., 2000) and FA typically exhibits lower binding strengths than HA (Glaus et al., 1997).
249 Several cationic forms of radionuclides can exist depending upon the exact redox conditions.
250 The following sections review the effects of redox conditions and the importance of
251 hydrolysed species over the pH range under consideration, then the literature for
252 experimental binary systems and the application of data in the formulation of comprehensive
thermodynamic models are reviewed.

253
254 *2.1. Radionuclide forms under varying redox conditions*

255 Radionuclides, particularly actinides (but also Sn), can exist in a number of different cationic
256 forms. These oxidation states vary depending principally on the redox potential (Eh) of the
257 system and the pH. Figure 3 shows Pourbaix plots for four actinides that are present in
258 intermediate-level radioactive wastes. These figures illustrate that at high pH, a lower redox
259 potential is required to reduce these radionuclides. The oxidised and reduced forms will have
260 different binding strengths to organic acids and thus, understanding of the electrochemical
261 potential within and around a GDF is an important aspect of performance assessment. To
262 limit mobility, reducing conditions are considered to be preferable, due to much lower
263 solubility of tetravalent actinides compared to the pentavalent and hexavalent forms (NDA,
264 2010). A discussion of the potential for organic acids to influence changes to redox states is
265 included in section 4.4.

266
267 *2.2. Changes to concentrations of hydrolysed species with increasing pH*

268 Changes in pH tend to give the largest variations in complexation constants due to the
269 combined factors of, competition of radionuclide cations with protons, variation in the
270 concentrations of free ion due to changes in hydrolysis of the radionuclide cation, and
271 changes to the deprotonation of the free organic acid. Figure 3 shows the pH at which
272 different hydrolysis species become dominant for several actinide cations. Under both
273 cementitious repository and circumneutral groundwater pH conditions, inorganic tetravalent
274 actinides (M^{4+}) will be largely present as $M(OH)_4^0$ species throughout the pH range.
275 Depending upon concentration, tetravalent actinides may form colloids and polymeric
276 species, which may affect interactions with DOM. Pentavalent ions ($M(V)O_2^+$) will be present
277 as the anionic $M(V)O_2(OH)_2^-$ ion, only under the highest pH conditions expected within a
278 cementitious repository. As conditions evolve, the $M(V)O_2OH^0$ hydrolysis product will
279 dominate the inorganic speciation over several of the cement degradation phases (Figure 1).
280 The free ion will dominate at circumneutral groundwater pH values. For the hexavalent ions

281 $(M(VI)O_2^{2+})$ the anionic species $M(VI)O_2(OH)_3^-$ and $M(VI)O_2(OH)_4^{2-}$ are predicted to
282 dominate over the entire evolving pH range.

283
284 As the concentration of OH^- increases, it will compete with DOM binding sites and may also
285 result in the formation of hydrolysed species that themselves are capable of binding. The
286 following sections consider experimental studies and thermodynamic modelling relevant to
287 such conditions.

288 289 *2.3. Laboratory data*

290 Laboratory studies of DOM interactions with metal cations are typically performed under pH
291 conditions where hydrolysis products are not a major fraction of the inorganic metal (a large
292 compilation of such work is cited within the supplementary information of Tipping et al.,
293 2011). This enables consideration of only simple, binary metal - DOM complexes but not
294 more complex interactions, such as potential binding of hydrolysed cations. Whilst not
295 widespread, several studies do include measurements at high pH and these studies are
296 reviewed here.

297
298 Experimental methods for the determination of radionuclide binding to organic acids often
299 use an additional ligand with known stability constants that competes with humic or fulvic
300 acid for binding (e.g. oxalate, iminodiacetate, carbonate; Glaus et al., 1997). This is required
301 for many elements at lower pH values to ensure that there are measurable fractions of
302 radionuclides in both the DOM bound and non-DOM bound fractions (this latter fraction
303 tending to be in the smaller molecular size range than the DOM bound metal).

304 305 *2.3.1. Tetravalent thorium and uranium*

306 The dominant inorganic hydrolysis complex for tetravalent actinides is likely to be $M(OH)_4$
307 above pH values of ~ 5 (Figure 3). A further hydrolysed species ($M(OH)_5^-$) has been
308 suggested (Grenthe et al., 1992), based on increased solubility of tetravalent metal oxides
309 (MO_2) at high pH values. However, recent literature compilations of stability constants

310 (Hummel et al., 2002; Duro et al., 2006) attribute these phenomena to the fact that oxidation
311 of M(IV) to M(VI) occurs at a lower redox potential as the pH increases (as shown in Figure
312 3). Thus, the apparent solubility increase can be due to the oxidation of tetravalent to
313 hexavalent actinides with the subsequent formation of MO_2^{2+} hydrolysis complexes in
314 solution (Hummel et al., 2002; Duro et al., 2006). The $\text{M}(\text{OH})_4$ complex is predicted to be the
315 dominant hydrolysis product across a large pH range, and this has implications for the
316 binding of tetravalent actinides to DOM. Once the pH is sufficiently high that $\text{M}(\text{OH})_4$ forms,
317 as further hydrolysis is not considered to occur, the pH may have a reduced effect on the
318 amount of metal bound to DOM (although, effects due to increasing deprotonation of organic
319 acids will also operate). Thus, we review studies that cover a wider pH range, but still where
320 the $\text{M}(\text{OH})_4$ species dominates.

321
322 Beneš (2009) used free-liquid electrophoresis techniques to examine the complexation of
323 thorium with purified Aldrich HA over the pH range 2 to 11. In the absence of other strongly
324 complexing ligands, it was found that Th(IV)-HA complexes represent close to 100% of the
325 total solution concentration. This behaviour was observed up to the maximum pH studied of
326 11. The study concluded that at $\text{pH} \geq 8$ only the mixed complex $\text{Th}(\text{OH})_4\text{HA}^{y-}$ is formed. In the
327 presence of carbonates ($10^{-3} \text{ mol L}^{-1}$) and over the pH range 8.25 – 11, HA binding is
328 suppressed to 25-40% in the presence of 0.1 mg L^{-1} HA and to 60-83% in the presence of 1
329 mg L^{-1} HA. In an environmental context Th(IV) has been demonstrated to be strongly
330 associated with natural organic matter derived from marine origin (Quigley et al., 2001).
331 Whilst the terms "sorption" and "complexation" are used to describe the interaction with
332 organic matter the exact mechanisms are not explicitly known (Quigley et al., 2001).
333 Interactions could be typical ligand complexation reaction but alternate mechanisms could
334 also be involved given the uncharged nature of the hydrolysed Th(IV) complex at high pH.
335 See section 2.3.1.1. for a discussion of possible alternate interaction mechanisms proposed
336 for tetravalent technetium.

337

338 Warwick et al. (2005) studied U^{4+} binding to boom clay and Aldrich HAs over the pH range 6-
339 9. The method employed controlled the total dissolved U by allowing equilibrium with a
340 controlling solid phase (UO_2). HA concentrations in the study were 0.02–1 g L⁻¹. For Aldrich
341 HA, the median value of the U – HA complex was >95% of the total dissolved metal, with a
342 range of 46.4-99.8%. For boom clay HA, organic complexes represented >99.7% for all
343 measurements.

344 345 2.3.1.1. Alternate interaction mechanisms proposed for tetravalent Tc

346 It has been hypothesised that the interaction mechanism of tetravalent technetium (which
347 exists under reducing conditions) with organic acids does not proceed as a typical functional
348 group complexation reaction. Maes et al. (2003), concluded that sorption must proceed via a
349 “hydrophobic sorption” mechanism based on results that showed that the interaction
350 constant with organic acids remained constant over a very large range of metal loadings
351 (see also Gu et al., 2011). This concept was further examined by Maes et al. (2004), who
352 termed an alternate mechanism “colloidal interaction with humic substances”. Evidence for
353 this mechanism was provided by observations of shorter bond lengths for interactions of
354 Tc(IV) with carboxylic acid ligands than in HA containing samples. They concluded that with
355 increasing Tc(IV) concentrations associated with HA, larger polymers ($TcO_2 \cdot xH_2O$) are
356 involved.

357 358 2.3.2. Neptunyl (NpO_2^+)

359 As neptunyl(V) does not exhibit strong binding, it is generally investigated experimentally in
360 simple binary mixtures. Hydrolysis species do not dominate the inorganic speciation until pH
361 ~11, thus, these experiments tend to cover a larger pH range than other radionuclides.
362 Several studies report results of experiments that range up to pH 9.8 and where results are
363 presented (or can be calculated from the presented data) in terms of the fraction of the total
364 neptunyl(V) that is complexed with organic acids (Kim and Sekine, 1991; Marquardt et al.,
365 1996; Glaus et al., 1997; Marquardt and Kim, 1998a, 1998b). Using data from these studies,
366 we have investigated the relationship between pH and the fraction of neptunyl(V) bound to

367 HA, as well as the effect of ionic strength and HA concentration on these relationships
368 (Figures of binding trends with pH and regression slopes for all reviewed data are shown in
369 Supporting Information Figures S1a and b, and Table S1). Across all of the conditions
370 studied, there is a universal trend of increasing binding with pH. Typically, linear regression
371 of these data show increases in binding of >5% per pH unit (range 2.3 – 17.3%). Only the
372 Glaus et al. (1997) data, at an ionic strength of 0.02 mol L⁻¹, have slopes less than 5%.

373
374 Some general trends can be identified from the data; an increased gradient is observed with
375 increasing ionic strength; binding increases as the HA concentrations is increased; and there
376 are generally greater gradients for the Gorleben isolated HA (GoHA) than the purified Aldrich
377 HA (PAHA), although, GoHA has been studied in experiments with higher HA concentrations
378 (186-1000 mg L⁻¹ compared to 3.3-33.3 for PAHA).

379 380 2.3.3. Uranyl (UO₂²⁺)

381 As shown in Figure 3, the dominant inorganic uranyl(VI) species in the absence of carbonate
382 are the anionic third and fourth hydrolysis products. For HA or FA to form complexes with
383 uranyl(VI) at high pH, the binding sites must effectively compete with the OH⁻ ligand. Thus, it
384 is expected that the fraction of hexavalent actinides present as organic acid complexes will
385 fall as the pH increases. Stockdale and Bryan (2012) reported results consistent with this
386 expectation. Sorption to Suwannee River HA was found to be ~80% at pH 9.9, which then
387 fell approximately linearly to ≤20% at pH value of ~ 11.5 or greater.

388
389 Zeh et al (1997) performed experiments on pH adjusted natural Gorleben groundwaters to
390 which additional uranyl(VI) was added. They observed low levels of binding to DOM in the
391 absence of carbonate of 5.9% at pH 8.8 and 1% at pH 10.1. Glaus et al., (1997) measured
392 HA and FA uranyl(VI) complexation up to pH 10.1. As competing ligands had to be used in
393 their experiments, it is difficult to review these data in terms of the fraction bound, due to
394 changing complexation properties of the additional ligand as the pH changes. Carbonate is
395 used as the ligand in some experiments. As this is mostly in the CO₃²⁻ form above pH 8.3,

396 changes to data with increasing pH will reflect the competition with OH⁻ ligand as
397 competition with the carbonate competing ligand will be largely unchanged over the pH
398 range. Experiments using purified Aldrich humic acid (PAHA) were performed at pH 9 and
399 10 for a range of ionic strength and HA concentration, where the carbonate concentrations
400 were fixed at 2×10^{-4} mol L⁻¹ (figures of these data are included in the Supporting
401 Information, Figures S2a and b). Results show a large fall in binding to HA when the pH is
402 increased from 9 to 10. Increased ionic strength yields lower levels of binding and this is
403 particularly manifest at pH 9 (e.g., in experiments containing 6.66 mg L⁻¹ HA, binding is
404 >50% at I = 0.02, but only 25% at I = 0.2). Li et al. (1980), observed high levels of organic
405 complexation (>90%) for a soil HA across the pH range 6 to 9.

406
407 Typically, the data of Zeh et al (1997) and Glaus et al. (1997) exhibit lower levels of binding
408 for data at pH 10 than those of Li et al., (1980) and Stockdale and Bryan (2012). This may in
409 part be related to different binding strengths of the different HAs and the presence/absence
410 of competing ligands, but may additionally be as a result of contrasting metal to HA ratios
411 ($\sim 10^{-8}$ mol mg⁻¹ in Li et al., 1980; $\sim 5 \times 10^{-10}$ mol mg⁻¹ in Stockdale and Bryan, 2012; and 30
412 to 6×10^{-9} mol mg⁻¹ in Glaus et al., 1997). Higher metal loadings can result in lower
413 sorption, and this is evident for Np(V) FA and HA interactions as shown in Fig. S1b of the
414 Supporting Information.

415 416 2.3.4. Iodide

417 Huang and Lu (1991) studied the interaction between HA and iodide in the presence of
418 buffer solutions. Increased humic acid concentrations result in increased binding and at pH
419 7.2 to 10.5 bound iodide represented $\sim 70\%$ of the total, this fell to $<60\%$ at pH 11.5. These
420 experiments were performed under ambient atmospheric conditions. Additional experiments
421 under nitrogen found that binding was only $\sim 20\%$, suggesting that binding is coupled to
422 redox reactions. Analysis of these systems in the presence of free radical scavengers

423 showed that free radicals are involved in the reaction and that these are present in the HA
424 (see section 4.4. for further discussion of DOM mediated redox processes).

425 426 *2.3.5. Caesium sorption to humin*

427 Studies that focus specifically on the non-ionic fraction of DOM are scarce and seldom do
428 these works cover high pH systems. One such study is that of Helal et al. (1998), who
429 observed binding of Cs⁺ to humin of 13% at pH 8, rising to 23% at pH 10. However, this
430 study was performed at high metal to DOM loadings. Lofts et al. (2002), observed poor
431 sorption of Cs⁺ to HA in soils and binding over the pH range 2 to 8 was attributed solely to
432 electrostatic effects, rather than binding at specific cation binding sites.

433 434 *2.4. Speciation modelling*

435 *2.4.1. Thermodynamic data for inorganic complexes*

436 The accuracy of any model that performs calculations of chemical speciation will be directly
437 dependent upon the quality and availability of stability constant data for simple inorganic
438 complexes (e.g., hydrolysis products or carbonate species). Major efforts were made in the
439 1960s and 1970s to compile these data into user friendly volumes (Sillen and Martell, 1964
440 and 1971; Martell and Smith, 1974 and subsequent volumes). The speciation community
441 has benefitted greatly from the critical NIST electronic database of stability constant data
442 that was periodically updated until 2004 (Smith and Martell, 2004). International projects
443 such as CHEMVAL (Read and Broyd, 1991) and the Nuclear Energy Agency's
444 Thermodynamic Data Base Project (now in its third decade; <http://www.oecd-nea.org/dbtdb/>
445 [accessed 19/03/12]) have sought to evaluate critically the data for radionuclide species.
446 These efforts have been built upon by national compilations that have presented data in a
447 more pragmatic, complete format and have also evaluated error ranges for these variables
448 (Hummel et al., 2002; Duro et al., 2006).

449 450 *2.4.2. Comprehensive speciation modelling*

451 While knowledge of conditional stability constants for FA or HA complexes, or an
452 understanding of the levels of organic binding, give us information for the conditions under

453 which they were determined, it is difficult to extrapolate these data to conditions found in the
454 field. Differences affecting aqueous speciation may include factors such as ionic strength,
455 electrolyte composition, concentrations of other dissolved cations, temperature, pH and
456 DOM concentration and composition. In order to utilise the knowledge obtained from
457 laboratory binding studies and enable their application to real systems, models have been
458 developed. Comprehensive speciation models of FA and HA binding are those that deal with
459 competitive interactions involving all cations (including H⁺), and take account of ionic
460 strength effects and metal–proton exchange ratios (Tipping et al., 2011). Examples of such
461 models are the Humic Ion Binding Models V-VII (Tipping and Hurley, 1992; Tipping, 1998;
462 Tipping et al., 2011) incorporated into the inorganic speciation code WHAM (Tipping, 1994;
463 <http://www.ceh.ac.uk/products/software/wham/>) and NICA-Donnan (Kinniburgh et al., 1999;
464 Milne et al., 2003). These models permit calculation of chemical speciation in the presence
465 of organic acids for systems more complex than those of laboratory HA or FA binding
466 experiments. Nevertheless, extensive use of these experimental data is involved in the
467 parameterisation of the models. A model that can be used to make predictions of
468 radionuclide speciation is clearly more desirable for performance assessment purposes than
469 fixed upper limits. However, exhaustive testing and validation is required and uncertainty
470 should be included in any calculations.

471
472 The main difference between the two modelling approaches is that NICA-Donnan utilises a
473 continuous distribution approach to the definition of the cation binding sites, whereas the
474 Humic Ion Binding Models utilise a discrete site approach. The above models have been
475 previously applied to the study of radionuclide speciation. Actinide binding to HA and FA was
476 examined using Model V by Tipping (1993); Simulation of retention and transport of several
477 radionuclides in the soils of a catchment was performed using Model V coupled to a
478 transport model (Tipping, 1996); Model VII (Tipping et al., 2011) included several
479 radionuclide cations and, using established methods based on linear free energy
480 relationships, Stockdale et al. (2011) estimated constants for several additional cationic

481 radionuclide species for this model (Pd^{2+} , Sn^{2+} , U^{4+} , NpO_2^{2+} , Pu^{4+} and PuO_2^{2+}); NICA-Donnan
482 parameters for Th^{4+} (estimated) and UO_2^{2+} (calculated) were determined by Milne et al.,
483 (2003) and UO_2^{2+} binding, as assessed by the model, was examined further by Saito et al.
484 (2004); Marang et al. (2008) used NICA-Donnan to compare predictions and data for
485 europium competitive binding experiments.

486
487 The studies highlighted above have improved the models and allowed inclusion of many
488 radionuclide cations in the default models and in some cases have provided testing against
489 experimental data. However, few have sought to validate or improve the models specifically
490 for the high pH conditions that will be experienced in a GDF. Recent work by Stockdale and
491 Bryan (2012) compared experimental data with predictions using WHAM/Model VII for
492 simple systems containing UO_2^{2+} and Suwanee river humic acid (SRHA) over the pH range
493 ~10-13. Figure 4 shows comparison of modelled and measured organic complexes from the
494 experiments of Stockdale and Bryan (2012; SRHA in absence of competing metals or
495 ligands) and Glaus et al. (1997; data for purified Aldrich HA and Laurentian soil FA at pH 9
496 and 10 only and in the presence of carbonate as detailed in the figure caption). There is a
497 clear divergence between modelled values and measurements as the pH increases.
498 Stockdale and Bryan (2012) found that, using the default model parameters, representative
499 predictions were only obtained up to ~pH 10.5. Predictions were poorer in the presence of
500 competing cations. These discrepancies were attributed to; unavailability of specific binding
501 constant for the organic acid used or possible binding of more hydrolysed species than
502 allowed by the model. The model default is to consider that the free ion and first hydrolysis
503 species can bind and evidence for the existence of uranyl(VI) hydroxide organic acid species
504 have been reported in the literature (Pashalidis and Buckau, 2007; Sachs et al., 2005).
505 Additional experimental data are clearly required in order to test fully such models for
506 uranyl(VI) in high pH systems. Whilst not yet utilised in modelling, experimental data do exist
507 to enable addition of the neptunyl(V) cation to such models. These datasets (see references

508 in Section 2.3.2.) also allow evaluation at a higher pH than for most other cations due to
509 hydrolysis occurring at a higher pH than for many other actinide cations.

510

511 **3. The ternary radionuclide-DOM-mineral surface system**

512 Ternary systems are those that include a solid mineral, dissolved radionuclide and DOM
513 (typically as HA or FA), as well as an electrolyte to control the ionic strength. Results of
514 ternary system experiments have been found to be a complex function of the system
515 components, the molar ratio of the components, and in some instances, the sequence in
516 which components are added (Lenhart and Honeyman, 1999). Table 2 shows the minerals
517 that have been investigated in ternary systems over our pH of interest, together with the
518 radionuclide and the atmospheric conditions under which the experiments were performed.

519

520 The extent of radionuclide binding to both DOM and mineral surfaces, and the DOM binding
521 to the mineral surface all affect the mobility of radionuclides in different ways. Figure 5
522 shows how differences in these three types of sorption can affect the transport of
523 radionuclide cations. In addition to these scenarios, it should also be recognised that simple
524 additive models that combine understanding of binary humic-radionuclide, humic-mineral
525 surface and radionuclide-mineral surfaces may not be effective in describing the ternary
526 system (Takahashi et al., 1999). This is consistent with the observations of Tipping et al.
527 (1983), who observed that enhanced sorption of copper to goethite (at pH 5.5) could not
528 simply be attributed to sorption to bound HA. Enhanced adsorption was attributed to the
529 creation of extra uptake sites of relatively high affinity when goethite and HA interact.

530

531 Before reviewing the three-component studies, we summarise the available data for DOM
532 binding to the minerals included in this review.

533

534 *3.1. DOM binding to mineral surfaces*

535 Several of the studies of ternary systems reviewed here also measured the retention of HA
536 or FA onto mineral surfaces in the absence of radionuclides (italicised references included in
537 Table 3 identify these studies). For the majority of minerals, HA and FA sorption generally

538 follows one of the two trends shown in Figure 6, both of which show sorption decreasing with
539 increasing pH. One trend is a general linear fall in binding over the entire pH range.
540 Alternatively, sorption can exhibit a generally linear decrease in the mid pH region with
541 zones of high and unchanging sorption at low pH and low or no sorption at high pH. Several
542 exceptions to this trend are observed for some minerals in some studies. FA sorbed to
543 goethite, studied by Guo et al. (2009), remained above 70% up to pH ~10.5 (FA = 20 mg L⁻¹,
544 goethite = 5 g L⁻¹). A separate study found lower sorption levels of >20% at pH 8.3 for a HA,
545 but at a lower HA to mineral ratio (Kalmykov et al., 2008; HA = 53 mg L⁻¹, goethite = 0.22 g
546 L⁻¹). Quartz has been observed to exhibit poor or no sorption of HA (Schmeide et al., 2000;
547 Sachs et al., 2004), although sorption to commercial fumed silica following the patterns
548 identified in Figure 6 has been reported (Kumar et al., 2006). Sachs et al. (2004), observed
549 no sorption of HA to biotite at pH ~9, but above this (pH 10-11) some limited sorption (~15%)
550 was exhibited. For a discussion of possible mechanisms for DOM binding to mineral
551 surfaces see Murphy et al. (1999).

552
553 In addition to mineral type and pH, some studies have also investigated the effect on humic
554 binding of ionic strength and the concentration of the radionuclide ion. Lenhart and
555 Honeyman (1999) found HA sorption to hematite was ~20% lower at an ionic strength of 0.1
556 compared to 0.01 at a HA concentration of 53 mg L⁻¹ and 0.9 g L⁻¹ of hematite. This
557 contrasts to the observation of Reiller et al. (2002), who showed that sorption was greater at
558 higher ionic strength (0.1 vs. 0.01) and the difference between sorption at the two ionic
559 strength diverges as the pH increases. At pH ~10 and at I = 0.01 the sorption to goethite
560 (500 mg L⁻¹; HA = 11.1 mg L⁻¹) is < 10%, at I = 0.1 sorption is ~40%. Differences are much
561 less evident for FA (Reiller et al., 2002). The effect of radionuclides on humic binding to
562 kaolinite (4 mg L⁻¹ solid-liquid ratios) has been investigated. Krepova et al. (2006) observed
563 increased HA binding in the presence of uranyl(VI) and this increase is correlated with the
564 concentration of the radionuclide (HA = 10 mg L⁻¹). Schmeide and Bernhard (2010)

565 performed similar experiments with neptunyl(V) however no effect of radionuclide presence
566 was observed (HA = 10 mg L⁻¹).

567
568 *3.1.1. Effect of concentration on the extent of HA sorption*

569 One critical aspect of DOM sorption to minerals is the ratio of organic matter to the mineral
570 surface. Two studies have investigated how the fraction sorbed is altered by the HA
571 concentration. Figure 7 shows data for HA sorption to kaolinite over a range of HA
572 concentrations (data from Niitsu et al., 1997). There is a general trend of decreasing sorption
573 as the HA concentration increases, coupled with lower sorption as the pH increases.
574 Consistent with these data, Schmeide et al. (2000), studied HA sorption to phyllite in the
575 presence of 1 μmol L⁻¹ uranyl(VI) and at HA concentrations of 5 and 60 mg L⁻¹. At the higher
576 concentration, sorption is 10-20% across the pH range 7 to 9.5. At the lower concentration
577 sorption is greater than 75% across the same pH range.

578
579 *3.2. Ternary systems*

580 Ternary system experiments are typically performed on crushed minerals of varying mass to
581 volume ratios and with various concentrations of radionuclide and organic acids. Thus, direct
582 comparison of data from different studies is difficult. Here we examine the general trend that
583 the presence of HA/FA has on the system. For several systems there is sufficient data to
584 compare results for experiments performed under conditions where CO₂ is absent, and
585 present in equilibrium with the system. We also review data from experiments that
586 investigate the effect of component addition order and those experiments that compare
587 results using mixed minerals with those from individual minerals. Results are reviewed here
588 in order of mineral classification as followed in Table 2 (largely ordered according to the
589 Dana Classification; Gaines et al., 1997). A full compilation of figures showing radionuclide
590 sorption to minerals in both the presence and absence of HA or FA for all studies cited in
591 Table 2 is included in the Supporting Information, together with annotations of the
592 concentrations of each component and the ionic strength, specific figures are referred to in

593 the relevant sections. Sections 3.2.1. to 3.3.3. include studies that either do not report the
594 atmospheric conditions under which the experiments were performed or that are performed
595 within a CO₂ free nitrogen atmosphere. Where ambient atmospheric condition were used
596 these are reviewed in section 3.2.4. Table 2 includes the CO₂ conditions for each study.

597
598 Several studies cited within this section use very high Th(IV) concentrations that are likely to
599 result in a solution concentration that far exceeds the solubility product for solid Th(IV)
600 phases. Results of such experiments cannot be interpreted solely in terms of mineral surface
601 or organic acid sorption, as other processes such as surface precipitation or the formation of
602 inorganic colloids may occur. Aggregation of DOM may result from the presence of these
603 levels of Th(IV) (Quigley et al., 2001), further complicating the interpretation of results.
604 Whilst, we have included these studies in the reviewed work, we advise caution in the
605 interpretation of these systems.

606 607 3.2.1. Simple oxides

608 3.2.1.1. γ -Al₂O₃

609 High levels of sorption (~95-100%) were observed for Th(IV) and U(VI) across the pH range
610 7-11.8 in the absence of HA or FA. For Th(IV), the presence of HA or FA lowered the
611 fraction sorbed by ~6-17% and both organic acids had identical effects (Chen and Wang,
612 2007a). For U(VI), no influence from FA was evinced from the available data (Zuyi et al.,
613 2000). Np(V) also exhibited high levels of sorption in the absence of HA (rising from ~75% at
614 pH 7.8 to ≥95% over the pH range 10.4-11). Sorption is not suppressed significantly in the
615 presence of 1 mg L⁻¹ HA, but increasingly lower sorption was seen when the HA
616 concentrations were increased to 5, 25 and 50 mg L⁻¹, where sorption fell by as much as
617 15% (Righetto et al., 1991). Iodide sorption was observed to be low (<20%) across the pH
618 range 7-10 and no clear variation could be distinguished from results where HA was present
619 (Zuyi et al., 2000). These data are illustrated in Figure S3a in the Supporting Information.

620
621

622 3.2.1.2. Iron oxides

623 Sorption of neptunyl(V) to goethite was observed to be >90% above pH 7.7, but in the
624 presence of HA this was lowered by up to 12% (Kalmykov et al., 2008). Th(IV; Yan et al.,
625 2011) and U(VI; Guo et al., 2009) sorption to goethite and Np(IV; Jain et al., 2007) sorption
626 to haematite was ~100% in the presence or absence of HA from pH ~7 up to pH 9, 10.4 and
627 9.8, for Th(IV), U(VI) and Np(IV), respectively. Th(IV) sorption to haematite, which was
628 ~100% in the absence of HA, was found to be significantly suppressed when HA was
629 present (Reiller et al., 2005). Sorption was lowered by ~70% at pH 7 and ~35% at pH 10.4. It
630 may be expected that Np(IV) and Th(IV) may exhibit similar behaviours due to the dominant
631 hydrolysis product of both metals being the $M(OH)_4$ species. However, the Th(IV) study of
632 Reiller et al. (2005) used a HA to mineral ratio of 222 mg g⁻¹, in contrast to the Np(IV) study
633 of Jain et al. (2007), where a ratio of 0.66 mg g⁻¹ was used (metal concentrations only vary
634 by a factor of 10). This may account for the large difference between results. These data are
635 illustrated in Figure S3b in the Supporting Information.

636 3.2.1.2. Silica (laboratory and natural)

638 The results of sorption experiments for Np(V) reveal marked differences between laboratory
639 prepared or commercially produced silica and naturally sourced material. The studies of
640 Righetto et al. (1991; laboratory synthesised) and Pathak and Choppin (2007; commercial
641 material) show a trend, in the absence of HA, of increasing sorption as pH increases, from
642 close to no sorption at pH 7 to >70% at pH 10 (with a peak apparent at pH 10 in the Righetto
643 et al., 1991 work). At low concentrations of HA, sorption is enhanced across the pH range (1
644 and 2 mg L⁻¹; Righetto et al., 1991). At higher concentrations (5 and 10 mg L⁻¹, Righetto et
645 al., 1991; 100 mg L⁻¹, Pathak and Choppin, 2007) sorption is enhanced until pH 9.3±0.5,
646 above which sorption is suppressed. Sachs et al. (2004), studied sorption to natural silica
647 and also observed increasing sorption as pH increased, with a maximum of 32% at pH
648 ~10.6. Sorption is suppressed by <14% in the presence of HA (100 mg L⁻¹). Lower sorption
649 in this study may be as a result of the availability of surface sites rather than site affinity, as

650 there is a very large difference in particle sizes coupled with similar mass to volume ratios.
651 Differences in the presence of HA will in large part be due to the contrasting sorption of HA
652 to the different silica samples as discussed in section 3.1. Whilst maxima are demonstrated
653 by several of the Np(V) datasets, further work is needed to elucidate fully the apparent
654 reduction in sorption at higher pH.

655
656 Th(IV) sorption to commercial silica was >90% in the absence of HA at pH 7-11.6. In the
657 presence of HA or FA and above pH 9, sorption is suppressed. Constant falling sorption is
658 observed up to pH 10-10.5, after which it remains at approximately 45% up to pH 11.7 (Chen
659 and Wang, 2007b). Zirconium sorption to commercial silica decreased with pH and was
660 unaffected by the presence of HA. Sorption fell from >90% at pH 7.3 to 55-62% at pH 12.5
661 (Takahashi et al., 1999). These data are illustrated in Figure S3c in the Supporting
662 Information.

663 664 3.2.2. *Phyllosilicates*

665 3.2.2.1. *Kaolinite*

666 Two studies have examined Np(V) sorption to kaolinite. In both, in the absence of HA
667 sorption increases as the pH increases and levels rise from <20% at pH 7 to >90% at pH 11.
668 In the presence of high concentrations of HA ($\geq 20 \text{ mg L}^{-1}$; Schmeide and Bernhard, 2010;
669 Niitsu et al., 1997) sorption is enhanced in the presence of HA by up to 24% up to pH 7.5-9.
670 At higher pH, sorption is suppressed in the presence of HA by as much as 21%. At lower HA
671 concentrations (5 and 10 mg L^{-1} ; Niitsu et al., 1997), no influence from the presence of HA is
672 observed. Křepelová et al. (2006), measured sorption of uranyl(VI) to kaolinite and observed
673 high levels (>90%) across the pH range 7 to 10. The presence of HA suppresses sorption by
674 $4 \pm 3\%$ and $24 \pm 7\%$ when 10 and 50 mg L^{-1} are present, respectively. Zr(IV) sorbs strongly to
675 kaolinite over the pH range 7-13. HA suppresses sorption by as much as 65% at pH 8, but
676 this effect becomes smaller as the pH increases, falling to ~10% by pH 11 (Takahashi et al.,
677 1999; component addition order was also investigated and this is reviewed in section 3.2.6.).

678 Buda et al. (2008) observed that the presence of HA lowered the fraction of Pu³⁺ that sorbed
679 to kaolinite, from >95% sorption over the pH range 7 to 10. The extent of the suppression
680 was strongly dependent upon the order in which the experimental components were added
681 (these aspects are discussed further in section 3.2.6). These data are illustrated in Figure
682 S3d in the Supporting Information.

683
684 *3.2.2.2. Muscovite and biotite*

685 Sachs et al. (2004) measured sorption of neptunyl(V) to biotite and muscovite. For biotite,
686 sorption increased from 14% at pH 7.7 to 77% at pH 11. In the presence of HA, sorption was
687 suppressed by 10±6% across the pH range. For muscovite, sorption increased from
688 undetectable levels at pH 7.8 to a peak of 41% at pH 10.5. In the presence of HA, sorption
689 was elevated by <10% up to pH 9.6, above which sorption was suppressed to below 21% up
690 to the maximum studied pH of 10.7. These data are illustrated in Figure S3e in the
691 Supporting Information.

692
693 *3.2.2.3. Rectorite and palygorskite*

694 Data in this section are illustrated in Figure S3f and S3g in the Supporting Information. Two
695 studies, on different forms of rectorite, demonstrated that Th(IV) binding was high (>93%) in
696 the absence of HA or FA and across the pH range 7 to 11 (Chang et al., 2007; Na-rectorite;
697 Yu et al., 2008; Al-pillared rectorite). In the presence of FA, sorption was increasingly
698 suppressed as the pH increased. Sorption decreased to no less than 79% at pH 7.6, and at
699 pH 10.8 one study observed sorption as low as 35%. Results for HA revealed stark
700 differences between the studies. Chang et al. (2007), found no decrease in the fraction
701 sorbed in the presence of HA. Whereas, Yu et al. (2008), observed a similar trend to that of
702 FA but with less suppression of sorption. This difference may be attributable to the difference
703 in the mineral forms as most of the other experimental conditions are similar, with the
704 exception of ionic strength, which differs by an order of magnitude between the two studies.

705

706 Binding of uranyl(VI) to rectorite was examined by Korichi and Bensmaili (2009) and Zhao et
707 al. (2011). In the absence of HA, sorption decreased as the pH increased. Korichi and
708 Bensmaili (2009) observed a decrease from ~100% at pH 7 to 40±4% at pH 10. Zhao et al.
709 (2011) observed a decrease from ~60% at pH 7 to 34% at pH 9. These two mineral samples
710 have different origins and also differ in the measured surface areas. Zhao et al. (2011),
711 observed suppression of sorption of up to ~20% in the presence of FA and up to ~10% in the
712 presence of HA. Korichi and Bensmaili (2009) observed enhancement of sorption of up to
713 25% in the presence of 10 mg L⁻¹ HA. In the presence of 100 mg L⁻¹ HA, sorption was
714 suppressed by up to 35% up to pH 8.5, above which sorption is enhanced by as much as
715 25%. Even where sorption was enhanced in the presence of HA, there is a universal trend of
716 decreased sorption as pH increases.

717
718 Sorption of uranyl(VI) to palygorskite was observed to exhibit similar behaviour to sorption
719 onto rectorite. In the absence of HA, sorption at pH 7 of >90% fell to 21% at pH 9.3 (Niu et
720 al., 2009) and 25% at pH 10.1 (Zhu et al., 2011). In the presence of HA, sorption is
721 enhanced and the magnitude of the enhancement was related to the concentration of HA. In
722 the presence of 10 mg L⁻¹ HA (Niu et al., 2009) sorption is ~100% up to pH 9.8, and this falls
723 to 76% at pH 12. Lower concentrations of HA (5 mg L⁻¹, Niu et al., 2009; 7 mg L⁻¹, Zhu et al.,
724 2011) result in approximately linear profiles where sorption is enhanced. This ranges from no
725 enhancement at the sorption maximum at pH 7 to sorption enhanced by 63% at pH 9.3 (Niu
726 et al., 2009) and 32% at pH 9.6 (Zhu et al., 2011).

727 728 3.2.3. *Tektosilicates (orthoclase and albite)*

729 Neptunyl(V) sorption to albite was observed to increase from below detectable levels at pH 8
730 to ~9% at pH 9.6. Above this pH, sorption increased more rapidly, to reach a peak of 37% at
731 pH 11.2. No effect of HA was evident up to pH 10, but above this pH, sorption was
732 suppressed to a maximum of 16% over the experimental pH range that extended up to 11.2
733 (Sachs et al., 2004).

734
735 Neptunyl(V) sorption to orthoclase in the absence of HA climbs from below detection at pH
736 7.5 to reach a peak of 33.5% at pH 10.5. In the presence of HA, sorption was slightly
737 enhanced up to pH 8.5, above which sorption was suppressed to a maximum of 13% over
738 the experimental pH range that extended up to 10.3 (Sachs et al., 2004). These data are
739 illustrated in Figure S3h in the Supporting Information.

740
741 *3.2.4. Ternary experiments in equilibrium with atmospheric CO₂*

742 Data in this section are illustrated in Figure S4 in the Supporting Information. A large
743 proportion of the studies reviewed here either do not report the atmospheric conditions under
744 which the experiments were performed or report that ambient atmospheric condition were
745 used (detailed in Table 2). A smaller number of studies are performed within a CO₂ free
746 nitrogen atmosphere. A potential issue with not controlling the atmosphere, is that at high
747 pH, dissolution of carbon dioxide can result in high carbonate concentrations. The
748 concentration of CO₃²⁻ will increase with pH and can reach very high levels. For example
749 dissolved CO₃²⁻ will reach molar concentrations at equilibrium at approximately pH 11
750 (Stumm and Morgan, 1996). The carbonate ligand will compete with both mineral surface
751 and organic matter binding sites and all cationic forms of actinides can form carbonate
752 species. As equilibrium concentrations of carbonate are very high at high pH, carbonate
753 species may dominate the speciation within these ternary systems.

754
755 The extent to which carbonates influence experimental results when CO₂ is not controlled
756 will depend upon how much control is exerted over the experimental procedures. Controls of
757 significant influence may include, for example, the storage conditions and handling of NaOH
758 stock and exposure time of pH adjusted solutions to the atmosphere. Stockdale and Bryan
759 (2012), performed high pH binary experiments for uranyl(VI) and HA under ambient
760 conditions but where experimental procedures attempted to minimise carbonate in the
761 solutions. Additional experiments where 10⁻⁴ mol L⁻¹ CO₃²⁻ were added, resulted in no
762 observable difference to the amount bound in the absence of the addition. These

763 experiments were also performed at a pH where the CO_3^{2-} addition was predicted by
764 speciation modelling to yield the largest difference to the experimental results. These results
765 gave some indication that the procedures used to minimise CO_2 dissolution (using freshly
766 drawn MQ water, freshly preparing the NaOH solutions and minimising atmospheric
767 exposure time) were successful in avoiding speciation changes influenced by carbonates
768 (although it is recognised that formation of ternary HA- UO_2 - CO_3 complexes may also
769 produce these results). Thus, for those ternary experiments where the atmosphere was not
770 controlled, any influence from carbonate may be minimal, however, as handling conditions
771 are not widely reported, effects due to the presence of carbonate cannot be ruled out.

772
773 Several studies performed ternary experiments under conditions where dissolved carbonate
774 was at equilibrium with atmospheric CO_2 . For experiments at high pH, this generally involves
775 addition of CO_3^{2-} prepared from soluble salts, as otherwise dissolution of atmospheric CO_2
776 to reach equilibrium is very slow (e.g., Schmeide et al., 2000). Uranyl(VI) sorption to
777 haematite, in a solution in equilibrium with atmospheric CO_2 , shows a steep fall from ~100%
778 bound at pH 8-8.5 to no detectable binding at pH 9.5-10. The presence of HA has the effect
779 of shifting the curve backwards by up to 0.2 of a pH unit, depending upon the ratio of HA to
780 mineral (Lenhart and Honeyman, 1999; Murphy et al., 1999). U(VI) sorption to quartz,
781 muscovite and albite has been investigated up to pH 9.6. Sorption is 39% (quartz), 65%
782 (muscovite) and 30% (albite) at pH 7.2, and this falls rapidly to undetectable levels by pH 8-
783 8.5. No clear influence from HA is evident from these data, except for quartz, where the
784 presence of HA suppresses mineral sorption across the pH range 7-8 (Schmeide et al.,
785 2000).

786
787 Ternary system sorption to kaolinite in the presence and absence of carbonate (CO_2
788 equilibrium) has been investigated for both uranyl(VI) (Křepelová et al., 2006; Sachs and
789 Bernhard, 2008) and neptunyl(V) (Schmeide and Bernhard, 2010). For uranyl(VI), sorption in
790 the absence of HA was >90% up to pH ~8.2, then a rapid decline was observed up to pH 9-

791 10 and this was observed by both Křepelová et al. (2006) and Sachs and Bernhard (2008).
792 However, in the presence of HA there was a large discrepancy between the studies despite
793 very similar experimental conditions. Sachs and Bernhard (2008), observed 40-50% sorption
794 up to pH 8.5, subsequently falling to undetectable levels by pH 10. Křepelová et al. (2006),
795 also observed lower sorption up to pH 8.5. However, above this pH only a small fall in
796 sorption was observed until pH 9, then sorption is constant and above 50% until the
797 maximum pH measured of pH 10. Data for sorption of neptunyl(V) to kaolinite in the
798 presence of carbonate tend to exhibit a bell-shaped curve. An example of these data,
799 alongside data from experiments where CO₂ is absent, is shown in Figure 8. In the absence
800 of HA, the rising part of the curve closely follows that obtained in the absence of carbonates,
801 deviation from this is then exhibited when the curve peaks at pH ~9 and then sorption falls to
802 ~20% at pH 10.5. The presence of HA tends to suppress sorption across the pH range
803 (Schmeide and Bernhard, 2010).

804
805 These studies have used concentrations of carbonate that would be present if a solution was
806 in equilibrium with CO₂ in the open atmosphere. Within a GDF such conditions will not exist
807 and carbonate concentrations will be a function of the groundwater concentration, microbial
808 activity and will also be buffered by precipitation/dissolution reactions with the Ca that is
809 present within the cement system (Jacques et al., 2010). Concentrations within a high pH
810 GDF will not reach those seen in the experiments and therefore the effect on sorption and
811 HA speciation will be significantly less than that observed in these systems.

812 813 *3.2.5. Ternary experiments where no influence from HA/FA is observed*

814 In addition to those detailed in the previous section, several further experiments reveal no
815 observable influence on the sorption of radionuclides to minerals in the presence of organic
816 acids. Several studies of Th sorption to bentonite and montmorillonite found >90% sorption
817 in the presence and absence of HA and sorption was independent of pH across the range 7-
818 12 (Xu et al., 2006; Lu et al., 2011; Chen et al., 2006). U(VI) sorption to ZrP₂O₇ (pH 7.2-9.0)
819 and TiO₂ (pH 9.9-11.1) was >90% in absence or presence of FA (Qian et al., 2010; Zhijun et

820 al., 2004). Studies of pertechnetate sorption to haematite and kaolinite found no observable
821 sorption, nor variation to this in the presence of HA (Kumar et al., 2007; Takahashi et al.,
822 1999). Cs was found to sorb 48-67% to synthetic Na-aluminosilicate over the pH range 6.9
823 to 9.9 (with a positive gradient), but no influence of HA was observed (Singh et al., 2010).
824 These data are illustrated in Figure S5a and S5b in the Supporting Information.

825 826 3.2.6. Order of component addition and relevance to the GDF system

827 Some studies have sought to address the question of whether or not the order in which the
828 components are added to a ternary system experiment can affect the experimental results.
829 Sorption of Pu^{3+} to kaolinite in the presence of HA was investigated by Buda et al. (2008) for
830 several component addition order scenarios (Supporting Information, Figure S3d). In the
831 absence of HA, sorption was >95% across the pH range studied (up to pH 10). Addition of
832 HA 48 hours after the combination of the metal and mineral components resulted in sorption
833 that was suppressed by ~5%. Where the components were added all together or where the
834 mineral and HA were pre-equilibrated for 48 hours prior to metal addition, sorption was
835 suppressed to a greater extent, falling to ~80% across the pH range. The only addition
836 scenario that resulted in a pH dependency was where the HA and metal were pre-
837 equilibrated for 48 hours prior to addition of the mineral. In this case sorption was
838 suppressed to ~80% at pH 7 falling to ~35% at pH 10. This suggests that kinetics are
839 important (i.e. slow reversibility of the HA bound metal), and that the effect of pH may be
840 related to the sorption of HA onto the kaolinite as the sorption trend follows that of HA
841 sorption (Figure 6).

842
843 Interactions between thorium, haematite and HA have been studied in relation to addition
844 order (Reiller et al., 2005). Where thorium is pre-equilibrated with haematite before addition
845 of HA, no effect on sorption is observed over the pH range 7-10.5. Where HA is pre-
846 equilibrated with haematite before addition of the metal, sorption is suppressed, and this
847 effect diminishes as the pH increases. Under this scenario, sorption is ~10% at pH 7 and
848 rises to ~60% at pH 10.3. The tendency for more metal to stay in solution when HA is pre-

849 equilibrated with the mineral was also observed for Zr sorption to kaolinite (Takehashi et al.,
850 1999). Reiller et al. (2005) attributed this behaviour to disequilibrium between different size
851 fractions of the HA, thus resulting in metal interacting with HA in solution. The possibility of
852 irreversibility of sorption of strongly hydrolysed metal to haematite (where they are allowed to
853 pre-equilibrate before addition of HA) was also suggested as a reason for the difference
854 between the two addition order scenarios. However, further investigation was suggested.
855 The same study also observed effects related to the ratio of HA sorption sites to mineral
856 surface sorption sites. These effects diminished to some extent at higher pH values, but
857 remained significant for most ratios above ~3.

858
859 In relation to host rock associated with geological disposal it is, perhaps, more constructive
860 to consider experiments where the HA and mineral are pre-equilibrated, and the radionuclide
861 is pre-equilibrated with HA under the conditions expected within the cement leachate. This
862 scenario approximately mirrors containment failure, resulting in availability of radionuclides
863 within an environment where the groundwater HA and host rock or concrete have been in
864 contact for an extended period. The difficulty is in relating these experiments on very short
865 timescales (laboratory experiments typically <1 month) to those of the GDF system where
866 the times for processes (e.g. HA - mineral interactions) will be on the scale of thousands of
867 years or more.

868 869 *3.2.7. Comparing mixed phase sorption to that observed for separate phases*

870 Two studies have investigated the sorption behaviour of crushed whole rock together with
871 separate studies of some constituent phases identified in those rocks. Schmeide et al.
872 (2000), analysed uranyl(VI) sorption to phyllite (composed of, by volume, 48% quartz, 25%
873 chlorite, 20% muscovite and 5% albite). Sachs et al. (2004), analysed neptunyl(V) sorption
874 to granite (composed of, by volume, 45% quartz, 35% orthoclase, 7.5% albite, 7.5% biotite,
875 4% muscovite).

876

877 Schmeide et al. (2000) observed that HA sorption to phyllite was much higher than that
878 predicted by the constituent mineral phases, particularly over the alkali pH range (7-9.6),
879 where sorption was >75% in the presence of 5 mg L⁻¹ HA (see Figure 4 in the Supporting
880 Information). Higher concentrations of HA (60 mg L⁻¹) resulted in a much lower fraction
881 being bound, as low as 10-15% across the pH range 7.5-9.5. The increased HA sorption on
882 the natural phyllite sample was explained by the existence of ferrihydrite sorption sites,
883 created by leaching of iron from chlorite and subsequent precipitation of a secondary mineral
884 phase. This process was observed visually as a reddish-brownish thin film deposited on the
885 phyllite. This did not occur within the chlorite experiments, due to the mineral being sourced
886 from a location where natural leaching had occurred. Carbonate dominates the speciation of
887 uranyl(VI) in these experiments at high pH as there were performed in equilibrium with
888 atmospheric CO₂, thus, above ~pH 9 it is not possible to infer any further relationship
889 between the mineral and its constituent phases.

890
891 Sachs et al. (2004) analysed the sorption of HA (27 mg L⁻¹) onto granite and five constituent
892 mineral phases (see the relevant sections of Figure 3 in the Supporting Information). Of the
893 constituent phases, only biotite exhibited HA sorption at pH 9 to 11 (~10-15%). Granite
894 shows low, but detectable, sorption across the pH range 8 to 10 (<10% with a ±5% error
895 margin). Granite did not exhibit the sorption peak for neptunyl(V) binding that was observed
896 in some of the separate phases (muscovite, orthoclase and quartz). A roughly linear trend is
897 observed across the pH range 8-11, with sorption increasing with pH. The presence of HA
898 suppresses sorption by ≤25% across this pH range, and this is consistent with low HA
899 sorption and increasing binding of neptunyl(V) to HA as the pH increases, as reviewed in
900 section 2.3.2. Sorption of neptunyl(V) to granite follows the same pattern as sorption to
901 biotite, but with ~20% lower sorption levels across the high pH range, Sachs et al. (2004)
902 conclude that this is the dominating phase for neptunyl(V) sorption within the granite rock.
903 Sakamoto et al. (2000), investigated neptunyl(V) uptake onto crushed granite in column
904 studies in the presence and absence of HA or FA (20 mg L⁻¹) at pH ~9.5. Breakthrough

905 curves of the column experiments showed enhanced breakthrough of neptunyl(V) in the
906 presence of HA and this effect was further enhanced for FA. However, whilst steady state
907 concentrations of neptunyl(V) appear after ~12 pore volumes in the absence of HA/FA, in
908 their presence a steady state is not reached over the experimental period (15 pore volumes).
909 This hysteresis may be attributed to some limited sorption of the organic acids to mineral
910 surfaces and/or (as suggested by Sakamoto et al., 2000) size fractionation filtration effects
911 through the column and the difference in sorption properties of the different size fractions.

912
913 A study of the effect of natural cellulose degradation products (wood leachate) was
914 performed on two UK natural minerals (London clay and Caithness flagstones) by Berry et
915 al. (1991). Results of the batch sorption experiments on uranyl(VI) and plutonium (oxidation
916 state not reported) showed that generally sorption decreased in the presence of cellulose
917 degradation products at a pH value of ~11. These experiments were performed at very high
918 dissolved organic carbon concentrations (~3 g L⁻¹). Baston et al. (1994) examined the effect
919 of the presence of cellulose degradation products on uranium binding to a crushed natural
920 tuff. Results suggested only the presence of high concentrations of organic materials could
921 lower the amounts sorbed to the minerals. Sorption to cement backfill material in the
922 presence and absence of cellulose degradation products (CDPs) was investigated by Felipe-
923 Sotelo et al. (2012) at pH 12.8. Cs was not affected by the presence of the CDPs, a notable
924 reduction in the sorption of Th was observed and in the case of uranium, the presence of
925 CDP increased the sorption to cement by almost one order of magnitude.

926
927 **4. Assessment of natural organic matter related mobility and reactivity of**
928 **radionuclides**

929 The previous two sections contain the vast majority of the data that have been gathered on
930 the influence of dissolved organic carbon on radionuclide speciation in high pH systems.
931 However, there are several other areas, where fewer data exist, that may be equally
932 important when considering the influence of DOM on radionuclide reactions and transport,
933 such as binding reversibility kinetics and DOM mediated redox reactions. This section

934 summarises our current understanding of binary and ternary systems, before reviewing
935 these additional areas of potential importance. Gaps in our knowledge and future data needs
936 are discussed within each section.

937
938 *4.1. Summary of the current status of understanding of binary HA - radionuclide systems*

939 Despite studies of radionuclide binding to DOM (principally humic and fulvic acids) being
940 limited for high pH systems, there is a reasonable breadth of data that cover most of the
941 main actinide redox states (IV-VI). Data show strong binding of both tetra-hydrolysed Th^{4+}
942 and U^{4+} , suggesting similar behaviour may be exhibited by Np^{4+} and Pu^{4+} , for which data do
943 not currently exist. Neptunyl(V) has been shown to have an increasing affinity for binding to
944 organic acids as pH increases. Interactions of organic acids with uranyl(VI) show some
945 limited binding at pH 13 and increasing binding as the pH decreases. A strong interaction
946 (i.e., ~100% binding) in the absence of competing ligands is observed at around pH 10.
947 Modelling can predict uranyl(VI) binding behaviour reasonably well up to pH 10.5, and in the
948 presence of carbonate is also predicted to bind at high pH (see section 2.4.2. and the
949 Supporting Information for plots of relevant experimental data from Glaus et al., 1997).
950 However, more testing against appropriate experimental data is required to assess fully the
951 potential utility of comprehensive speciation models for high pH systems. Furthermore, it
952 may be required for future models to include additional ternary complexes (e.g.,
953 $\text{UO}_2(\text{CO}_3)_2\text{HA}(\text{II})^{4-}$; Steudtner et al., 2011a, b). However, further work is required to
954 determine fully if such complexes are significant at environmental concentrations for metal
955 and HA and in the presence of other solution components that will be present in both natural
956 and geodisposal environments.

957
958 Although release of trace elements from concrete will be limited by interaction with the
959 cement hydrate phases, they can be subject to leaching (Moudilou et al., 2002; Engelsen et
960 al., 2010) and trace metals will also be present in groundwater. Calcium will be present in
961 significant concentration within the GDF. Thus, further research into the effects of competing
962 ions (including systems with multiple radionuclides) would yield information more relevant to

963 the real system and could also provide data to validate further comprehensive speciation
964 models.

965
966 *4.2. Summary of HA influences on radionuclide sorption to minerals*

967 There is a universal trend of decreasing HA sorption as pH increases. However, levels of
968 sorption to minerals that are significant at natural DOM concentrations (see section 1.1.1.)
969 may be obscured by performing experiments at high HA loadings. This is shown in the data
970 of Schmeide et al. (2000) and Niitsu et al. (1997) (Figure 7) where the fraction of sorption is
971 related to the HA concentration. These data suggest the maximum loading capacity is
972 increasingly limited as pH increases, but is potentially still significant at high pH for low HA
973 concentrations. Investigations that use high levels of HA may result in prediction of higher
974 solution concentrations (and thus overestimation of the transportable pool) than otherwise
975 may be expected. For example, neptunyl(V) with a strong sorption efficiency to mineral
976 surfaces at high pH (e.g., kaolinite; Schmeide and Bernhard, 2010) may be held in solution
977 by high concentrations of HA. However, if HA concentrations were lower, the speciation in
978 the system is more likely to be dominated by mineral sorption, as well as neptunyl(V) bound
979 to HA that is itself preferentially sorbed to the mineral surface. More investigation is required
980 to determine sorption at both, more natural HA concentrations, and for pH values up to 13 or
981 more that will be reached within a cementitious GDF.

982
983 Whilst different minerals can exhibit diverse sorption trends, some general patterns can be
984 elucidated from the ternary system data (in the absence of atmospheric CO₂). The majority
985 of the minerals exhibit strong sorption of uranyl(VI) and thorium at high pH. This sorption can
986 to some extent be suppressed by the presence of organic acids and the degree of the
987 suppression can vary as the pH changes. Neptunyl(V) generally exhibits increased sorption
988 as the pH increases. More complex behaviour is shown for this ion, where sorption is often
989 enhanced by the presence of organic acids across part of the pH range, and this switches to
990 suppression of binding across the higher part of the pH range. Some evidence of a sorption
991 maximum is apparent for neptunyl(V), but data at higher pH are required to elucidate this

992 fully across the full range of minerals. Pertchnetate does not exhibit measureable sorption
993 in either the presence or absence of organic acids. All high pH data from the ternary system
994 studies reviewed in section 3.2.2. are illustrated in the Supporting Information.

995
996 Carbonate has been shown to reduce sorption to mineral surfaces. However, several of
997 these experiments have been undertaken at very high carbonate concentrations (particularly
998 at high pH) and thus, cannot be related to the carbonate conditions that will exist within a
999 GDF. Further work is required to elucidate the potential impact of carbonate under GDF
1000 relevant conditions.

1001
1002 *4.2.1. Applicability of crushed single mineral studies to intact rock systems*

1003 Ternary system experiments have resulted in intriguing findings related to other aspects of
1004 radionuclide interactions, including; formation of more surface active secondary mineral
1005 phases (Schmeide et al., 2000); insights into the kinetics of sorption to both mineral surfaces
1006 and HA (Buda et al., 2008; Reiller et al., 2005); and oxidation processes that can occur at
1007 high pH (Schmeide and Bernhard, 2010; discussed in section 4.4.). A significant advantage
1008 of single mineral studies is that they allow constrained data to be obtained for each mineral
1009 phase, which can then be used to interpret more complex systems, for example, the study of
1010 Sachs et al. (2004) who used these data to determine the significant controlling phase for
1011 sorption to crushed whole rock.

1012
1013 A significant disadvantage of these type of experiments is that they give only basic
1014 information about the system as they do not mimic the conditions that will occur in flow
1015 through natural systems in terms of available sorption sites, and metal and DOM
1016 concentrations (not to mention the host of other effects caused by the mineralogy of the
1017 rocks in question and subsequent interactions with the high pH concrete leachates).
1018 Furthermore, flow pathways could exhibit a vastly different mineralogy (and therefore
1019 sorption properties) than crushed whole rock. Extensive examination of fracture mineralogy
1020 has been made in the case of the proposed geodisposal site in Forsmark, Sweden

1021 (Sandström et al., 2008). Whilst experiments relating data from both packed columns and
1022 batch methods has been performed for a natural groundwater systems (e.g. Artinger et al.,
1023 2002), there has been no attempt to link batch measurement (on whole rock or constituent
1024 phases) to whole rock experiments and clearly this is an urgent requirement. Batch ternary
1025 system experiments vary widely in the concentrations and ratios of all three components.
1026 Until these measurements can be put into the context of the whole rock and the effect of
1027 these ratios can be predicted, there is limited utility for the data being produced to contribute
1028 to radiological performance assessments.

1029 1030 *4.3. DOM and reversibility kinetics*

1031 Section 2. reviewed the data for equilibrium DOM – radionuclide systems. An additional
1032 consideration for these interaction is the kinetics of the binding reversibility. Two binding
1033 modes are generally invoked to explain metal – DOM kinetics. These are, a rapidly
1034 exchangeable fraction (on the laboratory timescale), and a kinetically limited fraction (often
1035 referred to as a non-exchangeable fraction; e.g. Bryan et al., 2012) In reality, there is a
1036 continuum of first order dissociation rates (King et al., 2001) that operate within this fraction.
1037 A number of techniques have been developed to study the kinetically limited fraction,
1038 including ligand competition (e.g., Rate et al., 1993), although the most common is the cation
1039 exchange resin competition method (King et al., 2001; Monsallier et al., 2003). A method
1040 using resin competition combined with well defined gel diffusion for measurement of multiple
1041 rate constants of HA and FA metal complexes has recently been developed (Levy et al.,
1042 2012; these data are termed kinetic signatures by the authors). These studies have typically
1043 been performed at acidic to neutral pH values. Such techniques cannot be universally
1044 applied at high pH values as resin binding is limited by competition with the hydroxide ligand,
1045 and for some resins such as Cellphos, chemical instability at high pH.

1046
1047 Slow kinetics have been shown to operate for DOM at high pH, as observed in several
1048 ternary system experiments (Reiller et al., 2005; Buda et al., 2008; Schmeide and Bernhard,
1049 2010). As there is likely to be strong competition between some mineral surfaces and DOM

1050 binding, these components could potentially be used to examine kinetics in high pH systems
1051 in place of cation exchange resins.

1052
1053 *4.4. DOM influenced changes to redox speciation*

1054 Isolated HAs have been shown to be involved in the reduction of oxidised forms of metals.
1055 Examples of data from abiotic laboratory experiments include, Np(VI) reduction to Np(V)
1056 (Yaozhong et al., 1993), Np(V) reduction to Np(IV) (Schmeide and Bernhard, 2009) for
1057 natural and synthetic humic acids (SHA; an oxidation product of hydroquinone synthesized
1058 in the presence of glutamic acid; Sachs et al., 2004), and Pu(VI) and Pu(V) reduction to
1059 Pu(IV) (Marquardt et al., 2004). Typically, reduction rates are inversely proportional to proton
1060 concentrations (e.g., Yaozhong et al., 1993; Marquardt et al., 2004). This is attributed to the
1061 rate being proportional to the amount of metal bound to the HA. As the HA is deprotonated
1062 with increasing pH, the fraction of metal bound increases. Clearly, this will vary, depending
1063 upon the binding strength of the specific metal ions and the behaviour of the hydrolysis
1064 products that form as pH increases (as discussed in section 2).

1065
1066 Schmeide and Bernhard (2010) investigated the interaction of Np⁴⁺, pre-equilibrated with
1067 SHA, with kaolinite. This was used in place of an alternative widely used synthetic HA (type
1068 M42) because preliminary tests had shown that this could not stabilize electrochemically
1069 prepared Np(IV) during the sorption experiment (between pH 5 and 11, 40-50% of the total
1070 Np was re-oxidized to Np(V) during the experiment under oxygen and carbon dioxide free
1071 conditions; Schmeide and Bernhard, 2010). These synthetic HA were developed to probe
1072 the redox stability of humic-radionuclide complexes and were designed to be highly redox
1073 reactive, containing a much greater number of active phenolic and carboxylic sites than the
1074 widely used Aldrich HA (Sachs et al., 2004). Schmeide and Bernhard (2010), reported strong
1075 sorption of Np(IV) to kaolinite in the absence of SHA. Sorption is low in the presence of SHA,
1076 which was attributed to the addition order of the components and consistent with other
1077 studies for tetravalent actinides (e.g. Reiller et al., 2005). In the presence of the SHA, the
1078 results show that above pH 8.8, sorption is enhanced as pH increases. However, this

1079 increase in sorption is directly proportional to the fraction of the Np(IV) that is oxidised to
1080 Np(V). Given this observation and those of the preliminary experiments on the M42 HA,
1081 these results suggest that there is abiotic oxidation of the Np(IV). The role of SHA in this
1082 oxidation is not discussed. However, given that no similar behaviour in the Np – kaolinite
1083 only system is stated, these results indicate SHA may be involved in the oxidation
1084 mechanism, due to the strong association of Np(IV) as a result of the pre-equilibration, and
1085 the need for an electron transfer conduit for the reaction to proceed. These results are
1086 somewhat contrary to those of Schmeide and Bernhard (2009), who showed for some SHAs,
1087 that the reduction of Np(V) to Np(IV) proceeded faster at pH 9 than at lower pH values. Bulk
1088 natural organic matter (isolated by reverse osmosis) has been shown to have a much higher
1089 concentration of organic radicals than isolated HA and FA (Paul et al., 2006), demonstrating
1090 that DOM in nature may have greater redox properties than in those substances generally
1091 used in laboratory analysis.

1092
1093 It has been shown that bacteria can donate electrons to DOM, which in turn donate electrons
1094 to oxidised metals, thus causing reduction (Lovely et al., 1996; who discovered Fe(III)
1095 reduction to Fe(II) mediated by DOM in the presence of *Geobacter metallireducens*). These
1096 reactions have also been demonstrated for U(VI) reduction to U(IV), which is not a significant
1097 reaction in the presence of DOM and the absence of microbial populations (Gu and Chen,
1098 2003; Lee et al., 2012). Work is currently underway to examine the potential for such
1099 mechanisms to reduce oxidised forms of radionuclides at high pH. (K. Morris, Pers. Comm.).
1100 Diverse aerobic microbial populations have been reported for natural hyperalkaline
1101 environments (e.g., Tiago et al., 2004).

1102
1103 Clearly, there is potential for DOM to perform a function in the reduction, and potentially in
1104 the oxidation (see also section 2.3.4.), of radionuclides. Given the large difference in
1105 solubility (and thus transport potential) between the different oxidation states, this is clearly a
1106 fertile field for further investigations.

1107

1108 *4.5. Natural analogues*

1109 It has been recognised since the early 1980s that natural analogues can inform the science
1110 relating to deep disposal of radioactive waste (see Chapman et al., 1984, for an early
1111 summary of natural analogue applications, including earlier references; available freely from
1112 <http://www.skb.se>). Data from natural analogue environments can help to bridge the gap
1113 between the spatial scales of laboratory and in situ experiments, and the requirements for
1114 safety assessments on much longer time-scales (Savage, 2011). These aspects have been
1115 subject to periodic review (Smellie et al., 1997; Savage, 2011). Field scale testing is also
1116 being used towards the same aim (e.g., Geckeis et al., 2004). Whilst DOM is often referred
1117 to in relation to natural analogues, no studies have specifically investigated hyperalkaline
1118 environments with respect to the effects on the speciation and transport of radionuclides.

1119
1120 An example of such a study that investigated DOM-metal complexation in hyperalkaline
1121 environments is that of Hartland et al. (2010; 2011). This work investigated the association of
1122 a range of metals (Ba, Sr, V, Cu, Ni, Co) with DOM in cave dripwater of pH 11.7 ± 0.4
1123 (Poole's Cavern, UK). Evidence from this study suggests strong association of several metal
1124 ions with DOM in high pH systems. Sites such as this, represent an opportunity to assess
1125 the binding of naturally occurring radionuclides (Th, U) to DOM present in the environment,
1126 providing that detectable concentrations are present. Furthermore, investigations on more
1127 abundant transition metals may inform our understanding of divalent metals with radiological
1128 relevance, such as Pd and Sn.

1129
1130 *4.6. Future data requirements*

1131 In the geodisposal environment, any binding or sorption of radionuclides has to be
1132 considered in the context of a lowering of the solution concentration and thus shifting the
1133 equilibrium of excess solid phases towards dissolution. For this reason binding or sorption
1134 values above ~90% are more informative for performance assessment purposes if
1135 presented either in terms of distribution coefficients or log values for the concentrations
1136 remaining in solution. For example let us consider a scenario where kinetic factors are

1137 absent and a hypothetical solid-solution equilibrium concentration in the absence of binding
1138 is 10^{-9} mol L⁻¹. If the presence of organic acids resulted in 90% of the dissolved radionuclide
1139 being bound then the total solution concentration would increase to 10^{-8} mol L⁻¹, 99.99%
1140 binding would result in an solution concentration of 10^{-5} mol L⁻¹. The majority of binary
1141 system studies present data for exact concentrations of bound and inorganic forms (or
1142 variants from which these can be calculated). Distribution of species within the inorganic
1143 fraction can then be modelled using stability constants derived from experimental data.
1144 Whilst many of the ternary system experiments reviewed here include distribution coefficient
1145 data for experiments performed at a single pH with other conditions varied. Generally,
1146 results from pH variation experiments are presented in terms of percentage binding
1147 (exceptions where distribution coefficients are used are; Niitsu et al., 1997; Buda et al.,
1148 2008; Chen and Wang, 2007; Wang et al., 2003). As can be seen in the ternary system data
1149 presented in the Supporting Information, there are large numbers of mineral and pH
1150 combinations that result in >90% sorption. For such work to have full applications in
1151 performance assessment there is a need for data to be presented in a way where the effect
1152 on solid phase dissolution can be interpreted fully.

1153 1154 *4.7. Summary*

1155 From the limited data available, it is clearly evident that if geosphere transport considerations
1156 are a required part of GDF performance and safety assessment (i.e., where containment
1157 failure cannot be ruled out), then dissolved organic matter related transport requires careful
1158 consideration within the assessment. This review highlights the many aspects of
1159 radionuclide interactions with DOM and those areas that are poorly understood and require
1160 further work.

1161 1162 **Supporting Information**

1163 Figures showing linear regressions of the reviewed neptunyl(V) and uranyl(VI) organic acid
1164 binding data, and of the high pH ternary system data, are included in the electronic
1165 Supporting Information for this manuscript.

1166
1167

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1170

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1491

1492 **Tables**

1493 Table 1. Radionuclides with half-lives greater than 10^5 years and total activity in
 1494 quantified UK intermediate level waste (ILW). Data in bold indicate those
 1495 radionuclides with more than 0.1 TBq of activity in ILW. (see text for details of how
 1496 these inventories are calculated).

Nuclide	Half life (My)	TBq in UK ILW ¹	kg per TBq	Moles per TBq
¹⁰ Be	1.60×10^0	3.7×10^{-1}	1.21×10^{-5}	1.21×10^2
³⁶ Cl	3.02×10^{-1}	1.0×10^1	8.25×10^{-1}	2.29×10^1
⁴⁰ K	1.28×10^3	1.0×10^{-2}	3.89×10^3	9.71×10^4
⁴¹ Ca	1.03×10^{-1}	3.6×10^0	3.20×10^{-1}	7.82×10^0
⁵³ Mn	3.70×10^0	1.8×10^{-6}	1.49×10^1	2.81×10^2
⁸¹ Kr	2.10×10^{-1}	1.0×10^{-5}	1.29×10^0	1.59×10^1
⁸⁷ Rb	4.80×10^4	1.8×10^{-5}	3.17×10^5	3.64×10^6
⁹³ Zr	1.53×10^0	1.5×10^2	1.08×10^1	1.16×10^2
⁹² Nb	3.50×10^1	1.8×10^{-5}	2.44×10^2	2.66×10^3
⁹⁷ Tc	2.60×10^0	4.3×10^{-9}	1.91×10^1	1.97×10^2
⁹⁹ Tc	2.13×10^{-1}	4.8×10^2	1.60×10^0	1.62×10^1
¹⁰⁷ Pd	6.50×10^0	6.0×10^{-1}	5.23×10^1	4.93×10^2
¹²⁶ Sn	1.00×10^{-1}	5.2×10^0	9.56×10^{-1}	7.59×10^0
¹²⁹ I	1.57×10^1	5.9×10^{-1}	1.54×10^2	1.19×10^3
¹³⁵ Cs	2.30×10^0	6.8×10^0	2.36×10^1	1.75×10^2
¹³⁸ La	1.05×10^5	1.3×10^{-11}	1.10×10^6	7.97×10^6
¹⁴⁷ Sm	1.06×10^5	1.4×10^{-5}	1.18×10^6	8.04×10^6
¹⁷⁶ Lu	3.61×10^4	1.3×10^{-8}	4.82×10^5	2.74×10^6
¹⁸² Hf	8.99×10^0	3.6×10^{-9}	1.24×10^2	6.82×10^2
²⁰⁵ Pb	1.52×10^1	1.0×10^{-4}	2.36×10^2	1.15×10^3
²⁰⁸ Bi	3.68×10^{-1}	1.8×10^{-7}	5.81×10^0	2.79×10^1
^{210m} Bi	3.00×10^0	1.8×10^{-7}	4.78×10^1	2.28×10^2
²³² Th	1.41×10^4	2.3×10^{-1}	2.48×10^5	1.07×10^6
²³³ U	1.59×10^{-1}	1.6×10^0	2.81×10^0	1.21×10^1
²³⁴ U	2.46×10^{-1}	1.7×10^1	4.37×10^0	1.87×10^1
²³⁵ U	7.04×10^2	5.5×10^{-1}	1.26×10^4	5.34×10^4
²³⁶ U	2.34×10^1	1.5×10^0	4.19×10^2	1.78×10^3
²³⁸ U	4.47×10^3	1.7×10^1	8.07×10^4	3.39×10^5
²³⁷ Np	2.14×10^0	6.9×10^1	3.85×10^1	1.62×10^2
²⁴² Pu	3.74×10^{-1}	5.6×10^0	6.87×10^0	2.84×10^1
²⁴⁸ Cm	3.40×10^{-1}	7.8×10^{-3}	6.40×10^0	2.58×10^1

1497 ¹NDA/DECC, (2011)

1498

1499 Table 2. Minerals and radionuclides investigated in ternary system experiments at high pH. Italicised
 1500 references are those studies that included experiments of the binary DOM-mineral system.

Mineral (Dana classification number)	Radionuclide ion	Maximum pH	CO ₂ conditions ¹	Reference	
Simple oxides					
<i>γ</i> -Al ₂ O ₃	UO ₂ ²⁺	11	n/r	Zuyi et al., 2000	
	NpO ₂ ⁺	11.5	n/r	<i>Righetto et al., 1991</i>	
	Th ⁴⁺	12	Ambient	Chen and Wang, 2007a	
Goethite (06.01.01.02)	I ⁻	10	n/r	Zuyi et al., 2000	
	UO ₂ ²⁺	10.5	n/r	<i>Guo et al., 2009</i>	
	NpO ₂ ⁺	9	N ₂	<i>Kalmykov et al., 2008</i>	
Haematite (04.03.01.02)	Th ⁴⁺	9	n/r	Yan et al., 2011	
	UO ₂ ²⁺	9.5	pCO ₂	<i>Lenhart and Honeyman, 1999</i>	
	Np ⁴⁺	10	pCO ₂	<i>Murphy et al., 1999</i>	
Silica (Quartz) (75.01.03.01)	Np ⁴⁺	10	n/r	<i>Jain et al., 2007</i>	
	Th ⁴⁺	10.5	n/r	<i>Reiller et al., 2002; Cromières et al., 1998</i>	
	TcO ₄ ⁻	9.5	n/r	Kumar et al., 2007	
	UO ₂ ²⁺	9.5	pCO ₂	<i>Schmeide et al., 2000</i>	
	NpO ₂ ⁺	10	n/r	Righetto et al., 1991	
			11	N ₂	<i>Sachs et al., 2004</i>
			10	n/r	Pathak and Choppin, 2007
TiO ₂	Th ⁴⁺	12	Ambient	Chen and Wang, 2007b	
	Zr ⁴⁺	12.5	n/r	<i>Takahashi et al., 1996; 1999</i>	
	Cs ⁺	9.5	n/r	<i>Kumar et al., 2006</i>	
	UO ₂ ²⁺	11	n/r	Zhijun et al., 2004	
	Phosphates				
ZrP ₂ O ₇	UO ₂ ²⁺	9	Ambient	Qian et al., 2010	
Phyllosilicates					
Kaolinite (71.01.01.02)	UO ₂ ²⁺	10	N ₂ and pCO ₂	<i>Křepelová et al., 2006</i>	
		10	pCO ₂	<i>Sachs and Bernhard, 2008</i>	
	NpO ₂ ⁺	11	N ₂ and pCO ₂	<i>Schmeide and Bernhard, 2010</i>	
		11	N ₂	<i>Niitsu et al., 1997</i>	
	Zr ⁴⁺	13	n/r	<i>Takahashi et al., 1999</i>	
Muscovite (71.02.02a.01)	Pu ³⁺	10	n/r	Buda et al., 2008	
	TcO ₄ ⁻	12	n/r	<i>Takahashi et al., 1996; 1999</i>	
	UO ₂ ²⁺	10	pCO ₂	<i>Schmeide et al., 2000</i>	
	NpO ₂ ⁺	11	N ₂	<i>Sachs et al., 2004</i>	
	Biotite (71.02.02b.02)	NpO ₂ ⁺	11	N ₂	<i>Sachs et al., 2004</i>
Bentonite (71.03.01a.01)	Th ⁴⁺	12	Ambient	Xu et al., 2006	
Montmorillonite (71.03.01a.02)		12	Ambient	Lu et al., 2011	
	Th ⁴⁺	11	Ambient	Chen et al., 2006	
Rectorite (71.04.02.07)	UO ₂ ²⁺	9	Ambient	Zhao et al., 2011	
		10	n/r	Korichi and Bensmaili, 2009	
	Th ⁴⁺	11	Ambient	Yu et al., 2008	
Palygorskite (74.03.01a.01)		11.5	Ambient	Chang et al., 2007	
	UO ₂ ²⁺	12	n/r	<i>Niu et al., 2009</i>	
		9.5	Ambient	Zhu et al., 2011	
Tektosilicates					
Orthoclase (76.01.01.01)	NpO ₂ ⁺	10	N ₂	<i>Sachs et al., 2004</i>	
	UO ₂ ²⁺	10	pCO ₂	<i>Schmeide et al., 2000</i>	
Albite (76.01.03.01)	NpO ₂ ⁺	11	N ₂	<i>Sachs et al., 2004</i>	
Mixed / others					
Phyllite	UO ₂ ²⁺	9.5	pCO ₂	<i>Schmeide et al., 2000</i>	
Granite	NpO ₂ ⁺	11	N ₂	<i>Sachs et al., 2004</i>	
Synthetic Na-aluminosilicate	Cs ⁺	10	Ambient	Singh et al., 2010	

1501 ¹N₂, pCO₂ and ambient, denote absence of CO₂, equilibrium with atmospheric CO₂ and no specific
 1502 controls on CO₂, respectively. n/r is where gas controls are not reported in the experimental methods.

1503

1504 **Figure captions**

1505

1506 Figure 1. Schematic of the evolution of pH during various phases of cement degradation.
1507 Based on the modelling of Jacques et al. (2010). See text for discussion.

1508

1509 Figure 2. Key elements in considering the effects of DOM on reaction and transport
1510 dynamics within a geological disposal facility (Modified from Miller et al., 2000).

1511

1512 Figure 3. Pourbaix plots of dissolved actinide species under varying redox conditions and
1513 pH. Plots were obtained using the freely available Hydra and Medusa programs of
1514 Puigdomenech (<http://www.kemi.kth.se/medusa/>; accessed Jan 19th 2012), which
1515 incorporates aspects of the SOLGASWATER program of Eriksson (1979). To show the main
1516 dissolved components, the model was used in the mode where crystalline solids are
1517 excluded (precipitation is permitted), actinide concentrations were set at 10^{-9} mol L⁻¹ and
1518 ionic strength was zero. M(OH)₅⁻ species were excluded from the database due to reasons
1519 discussed in Section 2.3.1. The valence of the species are coded red, white, yellow and grey
1520 for trivalent, tetravalent (and septavalent Np), pentavalent and hexavalent actinides,
1521 respectively. Legends for some Np and Pu species are given shorthand for clarity, they are;
1522 a = NpO₂(OH), b = NpO₂(OH)₂⁻, c = Np(OH)₂²⁺, d = PuO₂²⁺, e = PuO₂(OH)⁺, f = Pu(OH)₂²⁺, g =
1523 PuO₂(OH), h = Pu(OH)₂⁺.

1524

1525 Figure 4. Comparison of measured and modelled concentrations for uranyl(VI) complexation
1526 with organic acids. Modelling was performed using WHAM/Model VII with the default binding
1527 parameters, error ranges were obtained by varying these default values by ± 0.3 log units
1528 (Lofts and Tipping, 2011). Measured values from Glaus et al. (1997) are those data for
1529 experiments at pH values greater than 9 and in the presence of carbonates ($\sum \text{CO}_3^{2-} = 2 \times$
1530 10^{-4} mol L⁻¹ for humic acid; $\sum \text{CO}_3^{2-} = 1-1.5 \times 10^{-3}$ mol L⁻¹ for FAs). For clarity only one of
1531 every three error bars for this dataset are shown. Data from Stockdale and Bryan (2012) are
1532 for Suwannee River HA, reproduced by permission of Mineralogical Magazine.

1533

1534 Figure 5. Unique effects in ternary systems under different scenarios of radionuclide (RN)
1535 sorption/binding. Three types of coupling are considered; sorption of RN to mineral surfaces
1536 (MS), binding of RN to dissolved organic matter (DOM), and sorption of DOM onto MS.

1537

1538 Figure 6. Typical sorption behaviours of organic acids to mineral surfaces. See text for
1539 discussion.

1540

1541 Figure 7. The effect of HA concentration and pH on sorption onto kaolinite. Data re-plotted
1542 from Niitsu et al. (1997; Fig. 1). The pH is the mean for all data and the range represents two
1543 sigma from the mean.

1544

1545 Figure 8. Neptunyl(V) sorption to kaolinite in the absence (closed symbols) and presence
1546 (open symbols) of HA. Circles represent experiments performed in the absence of CO₂ and
1547 triangles represent experiments where CO₂ is in equilibrium with the atmosphere. Data from
1548 Schmeide and Bernhard (2010), experimental conditions were; NpO₂⁺ = 10⁻⁶ mol L⁻¹; I =
1549 0.01 mol L⁻¹ NaClO₄; HA = 50 mg L⁻¹; m/v = 4 g L⁻¹.

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