

The influence of humic acid on the migration of +1 and +2 cations through quartz sand

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ABSTRACT

The behaviour of anthropogenically produced cations in the geosphere is an important and ever growing area of study. Of particular importance is the movement of cations with respect to silicate minerals as these minerals and rocks constitute a large proportion of the geosphere. We have examined radiometrically, using column and batch sorption studies, the migration and/or sorption of varying concentrations of caesium and nickel with respect to sand. Further, we have monitored the impact of humic acid on sand and the ternary system. Herein we report the behaviour of how both these cations behave with humic acid concentrations as high as 100 ppm at fixed ionic strength and pH.

INTRODUCTION

In the UK, deep burial in crystalline rock repositories is one option for long-term radioactive waste containment and disposal. A large proportion of the overburden rock in the UK is sandstone, which is a sedimentary material rich in α -quartz and/or another silicate minerals. Hence, an understanding of the sorption processes and transport behaviour of radionuclides in silicate systems is essential to establish the long-term effects of deep burial of radioactive wastes.

Silicates sorb radionuclides poorly by comparison with clays, and the degree of crystallinity of the silicate mineral may influence the degree of sorption. Radionuclide complexation by humic acid (HA), a naturally occurring colloidal substance of ill-defined chemical structure ubiquitous in soils and groundwaters, may also influence sorption and transport behaviour. HA can bind cations in 'exchangeable' and non-exchangeable' binding modes through its oxygen donor atoms.^{1,2} When the aqueous phase contains HA, the sorption and transport behaviour of cations may change. Sorption of HA-radionuclide species to the silicate surface could immobilise it, or HA complexation may enhance radionuclide transport, or leave the transport properties unaffected. Indeed, Yoshida *et al.* found that breakthrough curves for Sr through a quartz sand column were identical in the presence or absence of HA.³

UV-vis spectrophotometric studies into HA sorption kinetics onto simple quartz sand in the absence of

metal ions reveals that initial rapid HA uptake is followed by a much slower sorption.⁴ Low molecular weight (MW) aromatic components (MW < 4800 Da, weight-average molecular weight 1450 Da) preferentially sorbed in the fast kinetic step, whereas higher MW components (MW 1400-9200 Da, weight-average molecular weight 3700 Da) sorbed in the slow kinetic step.

Ionic strength and pH may also affect radionuclide migration through sands when HA is present. Whereas HA enhances Eu migration in quartz sand at low ionic strength, at high ionic strength, HA hindered migration compared to that in the absence of HA.³ As ionic strength increases, adsorption of Eu on quartz sand in the absence of HA decreases. The kinetics and mechanism of Eu sorption on sandy sediment from Gorleben (Germany) containing humic substances, at $[Eu] = 3 \times 10^{-8} \text{ mol dm}^{-3}$, were strongly pH-dependent.⁵ At pH 4.8, Eu sorbed mainly as a humate complex from the HA solution, and sorption was accelerated by HA addition. The presence of humic substances in slightly alkaline solutions suppressed the sorption rate due to the slow dissociation of Eu-humate complexes. Desorption experiments to determine ⁶⁰Co, ⁸⁵Sr and ¹³⁴Cs retention mechanisms in natural silica sand columns were performed by changes of pH and ionic strength and by injection of natural organic matter (NOM).⁶ Injection of KCl (0.1 mol dm^{-3}) released greater amounts of radionuclides compared with injection of NOM, with ¹³⁴Cs retention the strongest in each

case, this behaviour was attributed to the strong retention by clay coatings on the sand surfaces. We have previously modelled the HA and fulvic acid promoted migration of Co and Eu through silicate minerals by applying the k1-D chemical transport model.^{1,2} The k1-D model is a flexible research code which allows the inclusion of kinetic data alongside transport and chemical equilibria.⁷ For aqueous geochemical calculations, the code uses three different sets of equations: mass balance, equilibrium and kinetic.

In this paper we describe results of batch sorption studies and column studies which investigate the behaviour of Ni²⁺, Cs⁺ and humic acid with sand.

EXPERIMENTAL

Materials

All chemicals were reagent grade or higher. Deionised water was used in preparation of all solutions. Sand (BDH), Humic acid (Sigma-Aldrich), NaClO₄ (Acros), MES buffer (Fisher), Nickel nitrate (Sigma), caesium nitrate (Sigma). All studies were carried out in distilled water. The sand used had a measured surface⁸ area of 0.0502 ± 0.0014 m²/g.

Methods

Sorption experiments were carried out in plastic sample vials with ca. 5 g of sand and 5 cm³ (liquid to solid ratio: 1 g cm⁻³) of metal nitrate solution (either CsNO₃ or Ni(NO₃)₂) 10⁻² - 1 × 10⁻¹² mol dm⁻³ or humic acid solution 5 – 200 ppm) at a fixed pH of 6. In the case where humic acid has been studied in the presence of metal, then 100 µl of the appropriate concentration of metal nitrate solution was added to the equilibrated sand – humic acid mixture. The solution was then spiked with either ¹³⁷Cs or ⁶³Ni (~3 KBq). All sorption experiments were carried out by shaking these solutions in 20 cm³ plastic vials on a flat bed shaker for the duration of the experiment at room temperature (typically 1 week to allow humic acid equilibration and then a further week to allow the ternary system to equilibrate, unless otherwise stated). After this, 2 cm³ of the supernatant was removed and analysed by gamma spectroscopy on a Cobra II Auto-gamma spectrometer for Cs-137, a gamma emitter or by liquid scintillation counting on a Tri-Carb Liquid Scintillation Analyzer for Ni-63 a beta emitter. Humic acid concentrations were monitored using a Carey Instruments UV-vis spectrometer. The amount of metal adsorbed was calculated by comparing activities of the solution before and after adsorption, as described in section 2.3. All sorption experiments were carried out in triplicate under ambient conditions.

Column experiments were carried out using column with dimensions of 5cm diameter and 8 cm

length and packed with 190 g of sand. Metal salt solutions were run at a rate of 0.1 cm³ min⁻¹.

Analysis

In order to determine the appropriate parameters to compare the sorption of various ions in this study, the following equations were used to calculate the metal concentration under consideration:

$$\text{Cation } Z^{x+} \text{ in solution:} \\ Z^{x+} = \frac{A(RN)}{A_0(RN)} \cdot [Z^{x+}]_0 \quad (1)$$

$$\text{Sorbed concentration:} \\ [Z^{x+}]_0 - Z^{x+} = [Z^{x+}]_{\text{sorb}} \quad (2)$$

$$\text{Partition coefficient:} \\ R_d = \frac{A_0(RN) - A(RN)}{A(RN)} \quad (3)$$

Where, A₀(RN) = initial concentration of activity in solution (cpm); A(RN) = activity in solution measured after solid solution contact (cpm); [Z^{x+}]₀ = Initial concentration of metal in solution (mol dm⁻³); [Z^{x+}]_{sorb} = cation concentration sorbed onto clay surface.

RESULTS AND DISCUSSION

Sorption studies

Humic acid and sand

Sand was exposed to various concentrations (5, 10, 20, 50, 100 and 200 ppm) of humic acid in 0.1 mol dm⁻³ NaClO₄ over a period of 1 week; after this period the amount of humic acid sorbed was measured. In these systems the pH of the humic acid solution was not fixed, allowing the sand to buffer the suspensions. The data for the sorption process are summarised in Table 1.

Table 1 Extent of sorption of humic acid on sand after 7 days

[Humic Acid] ₀ (ppm)	pH	% sorbed
5	5.14	97.50
10	5.14	91.69
20	5.04	84.97
50	5.00	52.54
100	5.39	30.38
200	5.79	17.49

Overall, it can be seen that with increasing HA concentration the degree of sorption increases until the system is almost saturated. This is summarised in Figure 1. It can be clearly seen from that sorption isotherm that the sand is virtually saturated.

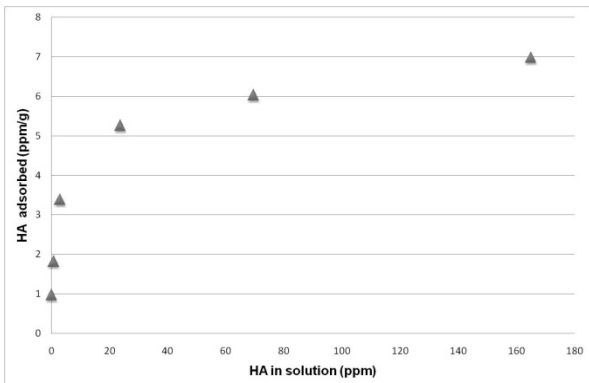


Figure 1 Plot of adsorption of humic acid on sand in a $1 \text{ cm}^3 \text{ g}^{-1}$ system after 7 days where pH was maintained at 6 at ambient temperature

Caesium, Humic acid and Sand

The isotherm of Cs^+ on sand is shown in figure 2.

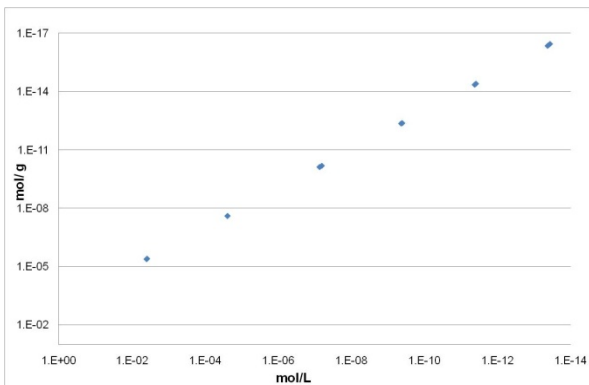


Figure 2 Sorption isotherm of Cs^+ on sand in a $1 \text{ cm}^3 \text{ g}^{-1}$ system after 7 days where pH was maintained at 6 at ambient temperature

The data was collected was for a system with a solid to liquid ratio of 1:1, $\text{cm}^3 \text{ g}^{-1}$ a fixed pH of 6 using 0.01 mol dm^{-3} MES buffer, and 0.1 mol dm^{-3} NaClO_4 . R_d values under these conditions were very low, ranging from $25 \text{ cm}^3 \text{ g}^{-1}$ for $1 \times 10^{-12} \text{ mol dm}^{-3}$ Cs^+ to $2 \text{ cm}^3 \text{ g}^{-1}$ for $1 \times 10^{-2} \text{ mol dm}^{-3}$ Cs^+ .

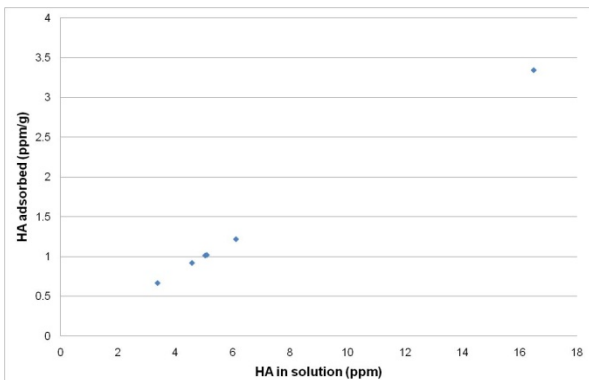


Figure 3 Isotherm for HA on sand in the presence of Cs^+ in a $1 \text{ cm}^3 \text{ g}^{-1}$ system after 7 days where pH was maintained at 6 at ambient temperature

A typical isotherm is shown in Figure 3 for humic acid in the presence of Cs , $1 \times 10^{-2} \text{ mol dm}^{-3}$. Comparison of Figures 2 and 3 shows the Cs^+ does slightly decrease the amount of humic acid bound to the sand surface, even after a week of

pre-equilibration of the sand and the HA. However, no appreciable change in the amount of sorption of HA was caused by changing the concentration of Cs^+ ($10^{-2} - 10^{-12} \text{ mol dm}^{-3}$).

Nickel, Humic acid and Sand

The isotherm for Ni on sand is shown in Figure 4. The isotherm is very similar to that of Cs (Figure 2). However, the R_d values are lower across the concentration range and were determined to be $2 \text{ cm}^3 \text{ g}^{-1}$. Ni is, in this case, clearly less sorbing than Cs.

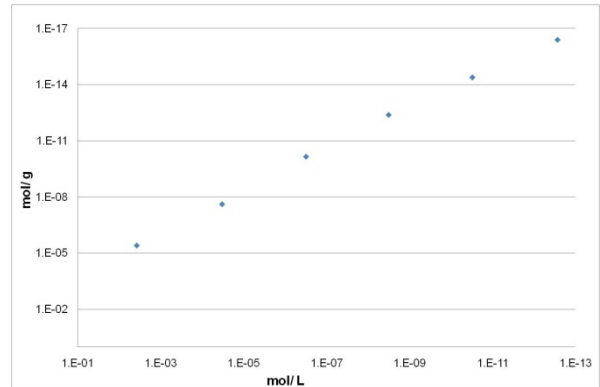


Figure 4 Isotherm of sorption of Ni^{2+} on sand in a $1 \text{ cm}^3 \text{ g}^{-1}$ system after 7 days where pH was maintained at 6 at ambient temperature

Humic acid solutions (5, 10, 20, 50, 70 and 100 ppm) in 0.1 mol dm^{-3} NaClO_4 , fixed at pH 6 with 0.01 mol dm^{-3} MES were allowed to equilibrate with sand samples for one week prior to adding nickel nitrate ($1 \times 10^{-12} - 1 \times 10^{-2} \text{ mol dm}^{-3}$) to the equilibrated solutions. After an additional week, the effect of the nickel on the mobility of the humic acid was measured by UV-vis spectroscopy.

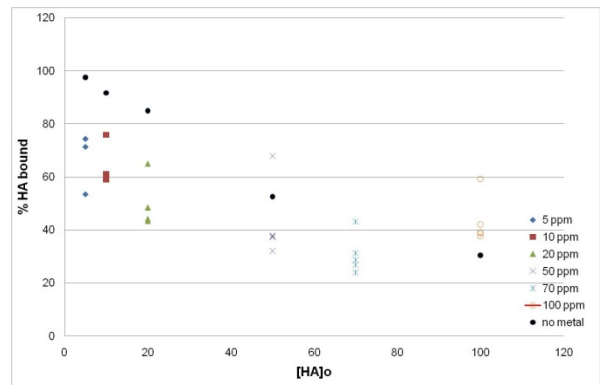


Figure 5 Plot showing the amount of HA bound to the sand as a function of initial HA concentration in a $1 \text{ cm}^3 \text{ g}^{-1}$ system after 14 days, where pH was maintained at 6 at ambient temperature

It was seen that increasing concentration of Ni^{2+} increased the amount of HA bound to the sand surface. The extent of this can be seen in Figure 5.

At lower HA concentrations (5 – 50 ppm), Figure 5 shows that in the presence of Ni^{2+} ions, the overall amount of HA bound to the sand is reduced, thus suggesting that the Ni^{2+} ions are competing for sites on the sand with HA. At higher concentrations

(70 – 100 ppm) of HA the opposite behaviour is evident; where increasing metal concentration enhances the amount of humic acid bound to the sand. Although in both cases it is assumed that an equilibrium must exist between Ni-sand and Ni-HA, ternary complexes must also be formed. The greater sorption at the higher HA concentrations may be a result of more of these ternary species being formed.

Column Studies

Column studies were carried out in a up/down-flooding fashion, where metal of interest is loaded onto column and then washed off as described by Bryan *et al*². The sand was fully equilibrated for 4 days this was monitored by pH and UV-vis. The column was packed with the electrolyte, either deionised water, $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ or $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ and 100 ppm HA used for the study. All columns used 190 g of sand, and the porosity varied between 40 - 45%.

Sand Columns ran with nickel solutions

Three columns were run using Ni-63 as a radiometric tracer. The first of these used $\text{Ni}(\text{NO}_3)_2$ in deionised water ($1 \times 10^{-6} \text{ mol dm}^{-3}$, 1000 cm^3). It was observed that the column completely retained the nickel as none of it came off the column either while loading or washing off with a further 1000 cm^3 of deionised water. This behaviour could be explained by the fact that the buffering of water with sand only results in pH 8. At this pH a large proportion of the Ni species is thought to be present as hydroxide which may have precipitated through the column onto the sand surface.⁹

The second column in this series was conditioned in $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ using $0.01 \text{ mol dm}^{-3} \text{ MES}$ buffer to fix the pH at 6 prior to addition of Ni. Figure 6 shows the behaviour of Ni in the column under these conditions.

Figure 6 clearly indicates that a certain amount of interaction must occur with HA which is bound to the sand and the Ni^{2+} species as a longer time period is required before any meaningful value for C/C_0 can be seen. Further, the volume of elution is larger than that of the tritium shown in the same plot. Tritium is ran through each column prior to the metal species as a non-retarded tracer to assess the elution volume of an unreacting species and to determine the porosity and packing characteristics of the column.

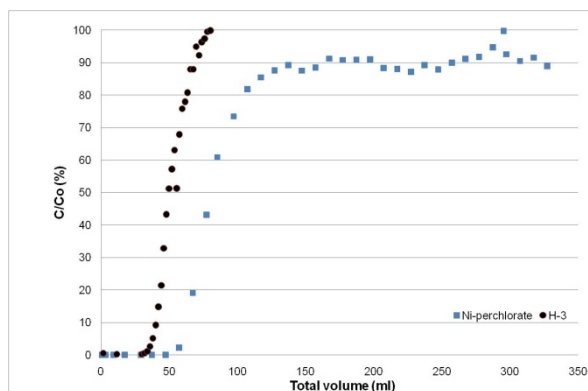


Figure 6 Plots of (a) tritium and (b) $\text{Ni}(\text{NO}_3)_2$ $1 \times 10^{-6} \text{ mol dm}^{-3}$ both present in a $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ solution through sand. The pH was fixed at 6 at ambient temperature and the flow rate was $0.1 \text{ cm}^3 \text{ min}^{-1}$

The third column in this study was run after being conditioned in 100 ppm HA, $0.1 \text{ mol dm}^{-3} \text{ NaClO}_4$ using $0.01 \text{ mol dm}^{-3} \text{ MES}$ buffer to fix at pH 6 prior to use. The conditioning solution was changed until HA concentration remained steady; this was determined by UV-vis spectroscopy. The Ni^{2+} solution was at a concentration of $1 \times 10^{-6} \text{ mol dm}^{-3}$ and was made in 100 ppm HA similar to the conditioning solution.

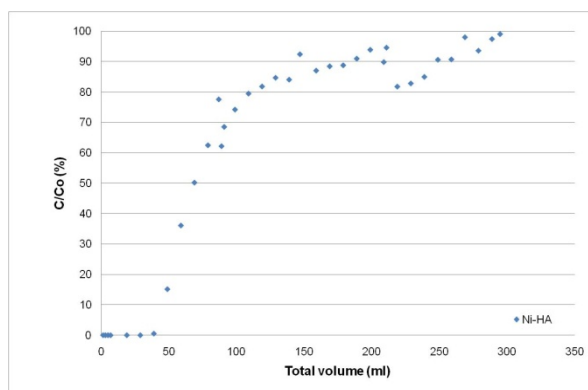


Figure 7 The movement of Ni^{2+} and humic acid through a sand column, with pH maintained at 6 at ambient temperature and the flow rate was $0.1 \text{ cm}^3 \text{ min}^{-1}$

Figure 7 shows that although the ^{63}Ni was detected at lower volumes than the corresponding column with no HA, overall it took longer for the Ni^{2+} to reach $C/C_0 = 100\%$. This can be attributed to the fact that the Ni^{2+} which is loaded on to the column interacts with the humic acid which is bound to the sand as it goes through the column forming weak, exchangeable associations, as it goes through the sand column. However this can be further confirmed by running columns with varying HA concentration.

Sand Columns run with caesium solutions

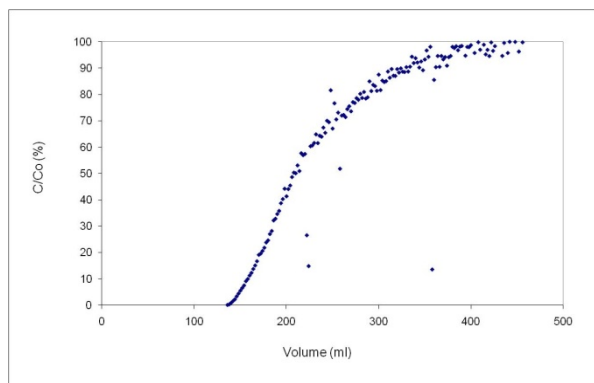


Figure 8 The movement of Cs through sand column ran at ambient temperature with flow rate $0.1 \text{ cm}^3 \text{ min}^{-1}$

^{137}Cs was used as a radiotracer to determine the movement of Cs^+ through a column of sand as shown in Figure 8.

It was found that in the case of $\text{Cs}(\text{NO}_3)$ ($1 \times 10^{-6} \text{ mol dm}^{-3}$) dissolved in deionised water, the flow interaction of Cs^+ with the sand is quite extensive with the initial volume at which the ^{137}Cs starts to appear in the outlet is almost 100 cm^3 greater than the corresponding Ni^{2+} column. However it must be noted that no other competing cations are present in this column and so all the sorption sites available will be occupied by Cs^+ , so, a direct comparison with Ni^{2+} cannot be made at this stage.

CONCLUSIONS

Sand has been shown to have a very low surface area and consequently will have few sorption sites and accounts for the low sorption, a maximum value of $25 \text{ cm}^{-3} \text{ g}^{-1}$ has been observed with $\text{Cs}(\text{NO}_3)_2$. It has been established that using a 1:1 solid to liquid ratio for sorption studies, it is possible to determine very low R_d values. On introduction of HA into the system we have seen that Cs^+ decreases the amount of humic acid bound to the sand surface and in the case of Ni^{2+} we see that the behaviour is a function of both the HA and metal cation concentration.

Where column experiments have been performed, clear evidence exists that both Cs and Ni interact with the sand surfaces. In the case where a Ni solution is run the Ni has thought to have precipitated on the sand. Fixing the pH to pH 6 allows the Ni^{2+} to travel through the column and introducing a high concentration of HA slows the travel of the Ni^{2+} ions through column. The movement of Cs^+ in a solution with no competing cations is not affected to the same extent as the Ni^{2+} , however further column studies are required to confirm this.

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REFERENCES

1. N. D. Bryan, D. L. M. Jones, R. E. Keepax, D. H. Farrelly, L. G. Abrahamsen, A. Pitois, P. Ivanov, P. Warwick and N. Evans, *J. Environ. Monit.*, 2007, **9**, 329-347.
2. N. D. Bryan, J. Barlow, P. Warwick, S. Stephens, J. J. W. Higgs and D. Griffin, *J. Environ. Monit.*, 2005, **7**, 196-202.
3. T. Yoshida and M. Suzuki, *J. Radioanal. Nucl. Chem.*, 2006, **270**, 363-368.
4. A. Pitois, L. G. Abrahamsen, P. I. Ivanov, N. D. Bryan, *J. Colloid. Interface Sci.*, 2008, **325**, 93-100.
5. P. Benes, K. Stamberg, D. Vopalka, L. Siroky and S. Prochazkova, *J. Radioanal. Nucl. Chem.*, 2003, **256**, 465-472.
6. N. Solovitch-Vella, J. M. Garnier, *Environmental Pollution*, 2006, **141**, 98-106.
7. W. Schüßler, R. Artinger, J. I. Kim, N. D. Bryan and D. Griffin, *J. Contam. Hydrol.*, 2001, **47**, 311-322.
8. S. J. Kemp, G. Turner and D. Wagner, Initial testing and laboratory manual for the Micromeritics Gemini VI physisorption system. *British Geological Survey Internal Report*, IR/08/086. 41pp. 2009.
9. J van der Lee, JChess 3.0 École des Mines de Paris, Centre de Géosciences, 35, rue Saint Honoré à Fontainebleau, France, 2003.