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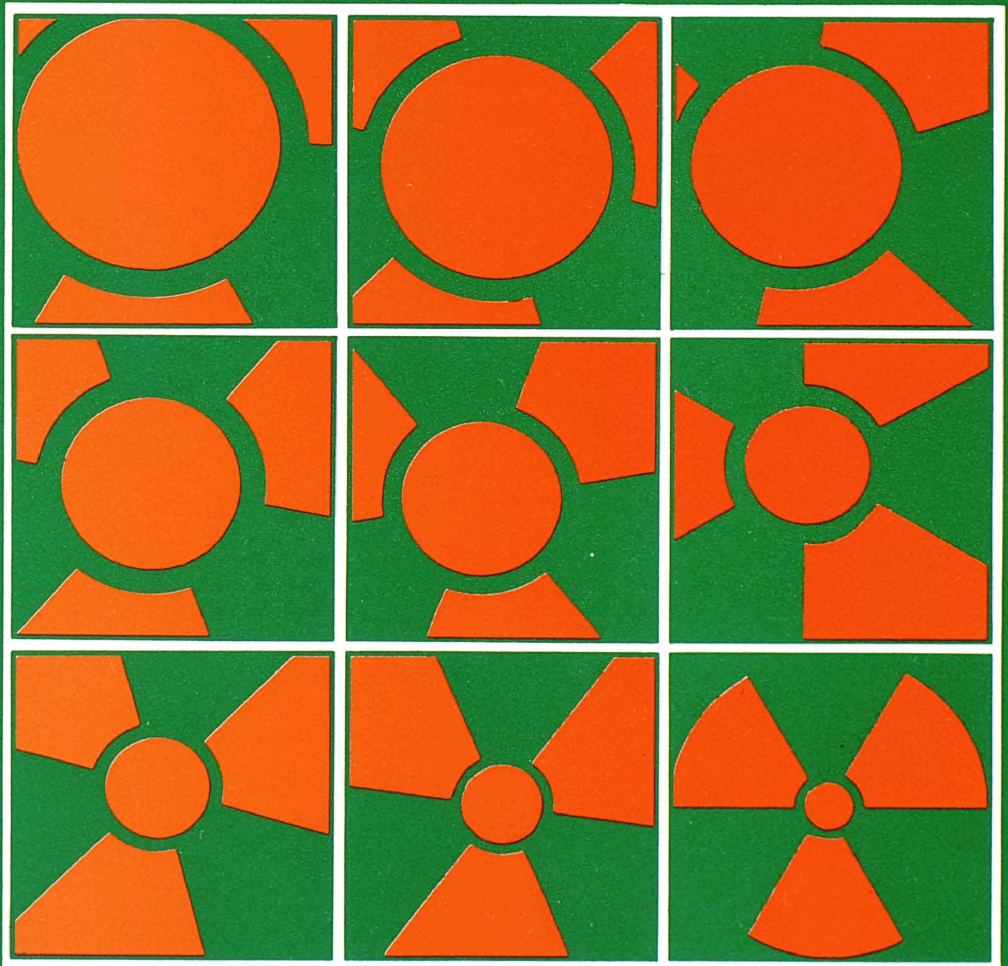

Report

EUR 12891 EN

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Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle's Eye and Broubster

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Topical report

Work carried out under cost-sharing contract No FI1W/0073
with the European Atomic Energy Community in the framework
of its third R&D programme on 'Management and storage of
radioactive waste', Part 1, Task 4 'Geological disposal studies'

Directorate-General
Science, Research and Development

1990

EUR 12891 EN

Published by the
COMMISSION OF THE EUROPEAN COMMUNITIES

Directorate-General
Telecommunications, Information Industries and Innovation

L-2920 Luxembourg

Cataloguing data can be found at the end of this publication

Luxembourg: Office for Official Publications of the European Communities, 1990

ISBN 92-826-1593-6 Catalogue number: CD-NA-12891-EN-C

Printed in Belgium

PREFACE

The British Geological Survey (BGS) has been conducting a co-ordinated research programme studying natural analogue sites at Broubster, Caithness, N Scotland and at Needle's Eye at Southwick on the Solway coast in Scotland. This work on natural radioactive geochemical systems has been carried out with the aim of improving our confidence in using predictive models of radionuclide migration in the geosphere. It has involved collaboration with the Harwell Laboratory and SURRC, East Kilbride for U/Th series analytical work, and with WS Atkins Engineering Sciences and the Ecole des Mines de Paris for modelling. The natural analogue work jointly carried out has been supported by the Department of the Environment from July 1986 to March 1989 and by the Commission of the European Communities from July 1988 to September 1989 under the CEC shared-cost action MIRAGE II Project.

This report is one of a series being produced from this effort and it discusses the sorption behaviour of uranium in the sediment groundwater systems at these two sites. Other reports, listed below, give detailed accounts of specific features of the sites, including their geological, topographical, hydrogeological and geochemical characteristics.

Broubster reports

1. 'The geological, geochemical, topographical and hydrogeological characteristics of the Broubster natural analogue site, Caithness' by TK Ball and AE Milodowski. British Geological Survey (BGS) Technical Report WE/89/37 and DOE Report DOE/RW/89.069.

2. 'Geochemical modelling of the Broubster natural analogue site, Caithness, Scotland' by D. Read of WS Atkins Engineering Sciences. BGS Technical Report WE/88/43 and DOE Report DOE/RW/89.005.

3. 'The development of portable equipment to study physical and chemical phases in natural water' by N. Breward and D. Peachey. BGS Technical Report WE/88/25 and DOE Report DOE/RW/88.102.

4. 'The uranium source-term mineralogy and geochemistry at the Broubster natural analogue site, Caithness' by A.E. Milodowski, I.R. Basham , E.K. Hyslop and J.M. Pearce. BGS Technical Report WE/89/50 and DOE Report DOE/RW/89.073.

5. 'The characterisation of organics from the natural analogue site at Broubster, Caithness, Scotland' by B. Smith, M. Stuart, B. Vickers and D. Peachey. BGS Technical Report WE/89/33.

6. 'Uranium series disequilibrium studies at the Broubster analogue site' by G. Longworth, M. Ivanovich and M.A. Wilkins. Harwell Report AERE-R 13609, 20pp. (1989).

Needle's Eye Reports

1. 'The geology, hydrogeology and geochemistry of the Needle's Eye natural analogue site' by PJ Hooker. BGS Technical Report in preparation.

2. 'Hydrogeochemistry of the Needle's Eye site: first interpretation' by R Doublet, Ph Jamet and R Soubeyran. Ecole des Mines de Paris, Fontainebleau, CIG Report LHM/RD/88/59 (in French) and in English as BGS Technical Report WE/89/55 and DOE Report DOE/RW/89.078.

3. 'Modelling of the Needle's Eye natural analogue' by Ph Jamet, P Lachassagne, R Doublet and E Ledoux. Ecole des Mines de Paris, Fontainebleau, CIG Report LHM/RD/89/81 (in English).

4. 'The location of uranium in source rocks and sites of secondary deposition at the Needle's Eye natural analogue site, Dumfries and Galloway' by IR Basham, AE Milodowski, EK Hyslop, and J M Pearce. BGS Technical Report WE/89/56 and DOE Report DOE/RW/89.091.

5. 'Natural decay series radionuclide studies at the Needle's Eye natural analogue site, 1986-1989' by AB MacKenzie, RD Scott, CM Houston and PJ Hooker. SURRC Report and DOE Report DOE/RW/89.104.

6. 'A uranium geochemical study at the natural analogue site of Needle's Eye, SW Scotland. by PD Roberts, TK Ball, PJ Hooker, and AE Milodowski. 1989. Proc. XII Int Symp. on the Scientific Basis for Nuclear Waste Management, Berlin, October 1988. Materials Res. Soc. Symp. Proc. Vol 127, 933-940.

EXECUTIVE SUMMARY

Studying a natural geochemical system characterised by movements of radioactivity can yield data which can be used to test applications of mass transport codes. Codes such as CHEMTARD are employed to predict the fate of radionuclides migrating from proposed radioactive waste repositories. Equally, it is important to test applications of the CHEMVAL thermodynamic database and equilibrium speciation codes with data acquired from real geological materials in order to create confidence in their use as predictors of the chemical forms of radionuclides. To this end the British Geological Survey has been conducting a number of investigations of locations where natural analogues of radionuclide migration can be recognised, with the purpose of describing the processes of movement of uranium, thorium and rare earth elements in sediments. In this way, data can be compiled to be used in testing the modelling and inherent ideas of the processes underpinning the codes. The sites of uranium mineralisation at Needle's Eye in Dumfries and Galloway, Scotland and Broubster in Caithness, N Scotland, present easily accessible locations suitable for such studies with the emphasis on the role of organics in the distributions of the natural radioactive elements of uranium and thorium.

This report describes the results of sorption experiments designed to provide essential data for migration modelling. Sorption of ^{233}U from natural groundwater onto peat from Broubster and silt from Needles Eye was studied under atmospheric conditions and different pH regimes. The temperature was maintained at 10°C and, in the case of Needle's Eye silt, the kinetics of sorption were followed. The results were analysed in conjunction with speciation modelling in an attempt to understand the sorption mechanisms and to extrapolate the findings to cover the range of conditions likely to be met in the field.

Two different sets of experiments were carried out with Needle's Eye silt. In the first the pH was maintained at 6.0 by the addition of HCl. In the second the pH was allowed to drift from its initial value of 6.7 to 7.9. Distribution ratios at pH 6.0 were higher than at pH 6.7-7.9. At both pH values an initial rapid sorption was followed by slow sorption but only at pH 6.7-7.9 did the slow sorption follow first-order kinetics during the first week.

In order to explain these observations speciation modelling was carried out. This showed that under the experimental conditions used the uranium should be present as a mixture of negatively charged and neutral carbonate complexes with the proportions of each species differing markedy at pH 6.0 and 7.0. It is postulated that $UO_2(CO_3)_2^{2-}$ and UO_2CO_3 are

more readily sorbed than $UO_2(CO_3)_3^{4-}$ and that sorption of uranium carbonate complexes is by displacement of carbonate ligands in a series of surface-complexation reactions with oxide surfaces.

The Needle's Eye groundwater used in the sorption experiments was very different in composition to that in the field because it had been stored in air and iron and manganese oxyhydroxides had precipitated out. Uranium speciation in a groundwater, taken from the same horizon but analysed immediately after collection was , therefore, modelled under both reducing (Eh=0 mV) and oxidising (Eh=400 mV) conditions. It seems probable that in the field, even under oxic conditions, sorption and organic complexation will be higher than in the laboratory experiments. At zero Eh most of the uranium should be reduced to the IV state and strongly sorbed. If organic material is available complexation is likely to be complete.

Distribution ratios for Broubster peat were greater than 10^4 ml/g at pH values of both 6.5 and 7.0. Speciation modelling indicated that carbonate complexation should dominate in the groundwater but it is suggested that given sufficiently strong interaction with the solid substrate then, as a result of mass action, complexation/sorption will be nearly complete.

Finally an attempt was made to estimate likely distribution coefficients for use in migration modelling. It is suggested that , until ranges are narrowed by further work , the

<u>silt layers</u> at Needle's Eye be divided into three Eh and pH regimes *viz*

(i) oxidising with pH 6.5 to 8.0 Best estimate 10^2 ml/g . Range 10^1 to 10^3 ml/g
(ii) oxidising with pH 6.5 to 4.0 Best estimate 10^3 ml/g . Range 10^2 to 10^4 ml/g
(iii) reducing (Eh ≤ OmV): pH 4 to 8 Best estimate >10^4ml/g. Range 10^3 to 10^6ml/g

For <u>peat layers</u> at both sites, suggested values for modelling purposes are:

Best estimate >10^4ml/g. Range 10^3 to 10^6ml/g .

CONTENTS

1. INTRODUCTION

The short-term aim of this programme has been to achieve a better understanding of the migration behaviour of uranium, thorium, rare earth elements and iodine in a variety of shallow sedimentary and weathering environments. The long-term aim is to validate research model predictions of radionuclide migration over long time-scales, and to provide confidence in the application of such codes in the performance assessments of proposed radioactive-waste repositories.

Two sites showing uranium anomalies have been investigated in detail . These are the Needle's Eye site at Southwick on the Solway coast, Scotland and Broubster, Caithness, N. Scotland. Here extensive sampling and analysis of groundwater, rocks and sediments together with sorption studies and speciation modelling have been carried out.

At Needle's Eye interest centres on a number of pitchblende veins trending north beneath coastal sediments and then outcropping in the cliff. The anoxic peaty soil layers near the cliff base are particularly enriched in uranium with values as high as 880 ppm correlating positively with the amount of organic matter present. (Hooker *et al.,* 1987).

The Broubster site is characterised by surficial sedimentary deposits of brown earths and peat which still play host to the transport and retardation of U/Th series isotopes and rare earth elements (REE) involving processes that have probably been going on for at least about 5000 years over a distance of the order of 100 m. The source of the natural radioactivity is a thin mineralised limestone layer exposed to weathering and leaching. Radioactive hydrocarbons are intimately associated with the uraniferous mineralisation (Ball and Milodowski, 1989).

Migration of radionuclides such as uranium and thorium in water-rock systems is largely controlled by precipitation/dissolution and adsorption/desorption reactions. The relative importance of these will depend on the concentration and speciation of the radionuclide and on the tendency of the radionuclide-containing minerals to precipitate. Thus in the vicinity of the uraniferous veins, where uranium concentrations are relatively high, precipitation/dissolution reactions involving uranium oxide, phosphate and silicate minerals might control solubility and hence migration. However, within a short distance of the veins, and away from a source of uranium, sorption will be the dominant process controlling partitioning between solid and liquid phases.

Clearly, therefore, it is essential that sorption be accounted for in the development of a model that will adequately describe the migration of uranium through a natural site. The two materials selected for these preliminary sorption experiments were:

(i) the silty material from Needle's Eye through which uranium appears to have migrated. This material contains quartz, clays and a variable amount of organic material. Field measurements indicated that the pH of the associated groundwater ranges from 5.3 to 7.5 and the Eh from -5mV to 400mV.

(ii) the peaty material from Broubster. This material appears to be a sink for uranium and contains up to 1000ppm uranium. Field measurements showed that the associated groundwaters tended to be oxidising (Eh 175 to 419 mV) and slightly acidic (pH 5.3 to 6.9).

Uranium speciation in groundwaters, even in the absence of organic ligands, is extremely complex. Four well-defined oxidation states (III, IV, V & VI) of uranium exist (although only three of these [IV, V and VI] exist in natural systems) and speciation depends on pH, Eh, carbonate, phosphate and organic-ligand concentrations. Inorganic complexes may be negatively charged(e.g. $UO_2(CO_3)_3^{4-}$) , neutral (e.g. $UO_2CO_3^0$) or positively charged (e.g. UO_2^+). Similarly, organic complexes may be neutral or charged depending on conditions and the organic ligand. Generally sorption of the oxidised species (V & VI) is lower than that of the reduced (IV) species and reduction to U-IV normally results in immobilisation. (Allard, *et al.*, 1984; Skytte Jensen, 1982; Hsi and Langmuir, 1985).

The bulk mineralogy is often deceptive because the surfaces of minerals tend to be coated with oxides and/or organic material. Thus, although quartz is relatively inert and clays have a net charge deficiency which is negative and permanent, surface impurities such as hydrated iron oxides and hydrated alumina may dominate the sorption characteristics. The charge on oxide and hydroxide surfaces is pH dependent being negative at high pH values and positive at low pH values. The point at which they reverse their charge (ZPC) is not known accurately and will vary from sample to sample and within samples as a function of ageing etc. Wayman (1977) reports estimated values for hydrated iron oxides in the range 8.5 to 8.7 and for hydrated alumina from 2.2 to 5.6. Greenland and Hayes (1978) report values of 2, 2.5, 6.7 and 8.2, respectively, for kaolinite, silica (>SiOH surface), goethite (FeOOH surface) and gibbsite (>AlOH surface). Kinniburgh *et al.* (1975) reported that the ZPC for freshly prepared iron and aluminium hydroxide gels and the amorphous product of heating gibbsite

$Al(OH)_3$ fell at pH 8.1, 9.4 and 8.3, respectively.

The mechanism of uranium fixation on organic matter is not well understood but probably involves sorption, complexation, cation-exchange, reduction or a combination of these. Under oxidising conditions it is generally assumed trace concentrations of uranium are taken up by rapid ion exchange and complexation of UO_2^{2+} with acidic functional groups (L^-), (Zielinski and Meier, 1988; Van Der Weijden and Van Leeuwen, 1985; Shanbhag and Choppin, 1981; Li *et al*, 1980; Borovec *et al.*, 1979) e.g

$L_2UO_2 \iff L\,UO_2^+ + L^- \qquad \beta_1$

$L\,UO_2^+ \iff UO_2^{2+} + L^- \qquad \beta_2$

i.e.

$$\frac{[UO_2^{2+}][L^-]^2}{[L_2UO_2]} = \beta_1\beta_2$$

In the situation where trace quantities of uranium are sorbed onto solid organic material (e.g. peat) then $[L^-]$ is large and$[UO_2^{2+}]/[L_2UO_2]$ is small and very little uranium remains in solution.

Because the sediment-groundwater system is so complex the problem of obtaining values for use in migration modelling was tackled from two angles. Firstly , the sorption of uranium onto fresh samples of silt and peat from the associated groundwater was measured in standard distribution-ratio determinations. Secondly, the speciation in the groundwater was modelled using the PHREEQE code in conjunction with a thermodynamic database compiled by Cross *et al.* (1987). An attempt was then made to understand the sorption mechanisms and to extrapolate the findings to cover the range of conditions likely to be encountered in the field. Speciation was modelled using the composition of the groundwater used in the sorption experiments. For the Broubster site this was similar to the field composition but in the case of Needle's Eye the field composition, pH and Eh were very different from those of the water used in the laboratory experiments. Speciation modelling was, therefore, carried out using both field and laboratory compositions and the likely effect that such differences would have on sorption is discussed.

2. MATERIALS

2.1 Needle's Eye

Sampling points and sample codes are described with reference to the grid described by Roberts *et al.* (1989)

Silt: A 50cm core was collected at position NE19,-20. The core was sealed and stored at 4°C in the dark. Two months later the seal was removed from the base of the core, 2 cm of silt was discarded and a sample then removed for experimental work. The core was in good condition and no oxidation (as judged by the condition of the metal cutting ring) had occurred.

Preliminary experiments were carried out with material which had been collected ten months previously (NE 18, -10 profile :140-160cm depth : 4/2/88). This material had been stored in a sealed bag at 4°C in the dark.

Groundwater: Groundwater (NE/42) was collected from a pit 1 meter west of the core (position NE, 18,-20) at a depth of 50cm. It was stored in contact with silt in the dark at 4°C. Two weeks after collection it was filtered through 0.2μm filters. A quantity of iron hydroxides was retained by the filters. Apparently this had precipitated out after collection. During filtration the pH rose from 6.7 to 8.5 because CO_2 was lost from solution when a vacuum was applied. The pH was, therefore, readjusted to 6.7 with 0.5N HCl . A sample of this water was analysed by ICP-OES and DIONEX ion chromatography for major cations and anions. Both water samples contained high sodium and chloride concentrations indicating a seawater component in their compositions.

The composition is given in Table 1 together with that of water NE/33. This water sample was collected from the same horizon as NE/42 but about 10m away (at location NE 18,-10) and analysed immediately after collection. The most striking difference between the two groundwaters is the high iron and manganese content of NE/33. The measured field Eh of NE/33 was +397mV but this is unlikely to be correct in view of the high iron and manganese content.

Table 1 Needle's Eye Groundwater Compositions

Element	mM/Kg		mg/l	
	NE/42 (Lab)	NE/33 (Field)	NE/42 (Lab)	NE/33 (Field)
Ca	1.30	2.55	51.2	102
Mg	3.48	3.05	83.1	74
Na	40.3	15.2	927	349
K	0.91	0.059	34.9	2.3
Fe	0.013	0.11	0.72	6.16
Mn	0.0117	0.21	0.65	11.5
Sr	0.0062	0.0158	0.54	1.38
Ba	0.000104	0.00027	0.014	0.038
Al	0.00332	0.0048	0.088	0.13
Si	0.077	0.22	2.16	6.18
HCO3	2.37	0.61	140	37
Cl	487	25.3	1650	898
SO4	2.31	0.102	222	99.8
F	0.0295	0.009	0.55	0.17
TOC			55.0	5.9

pH: NE/42 = 6.7 pH: NE/33 = 5.34

Eh: NE/42 ≈ 400 mV Eh: field = 397mV ?

Spiked Groundwater: 5ml ^{233}U solution (15.7KBq in 1 M HNO_3, obtained from Harwell) was evaporated slowly to dryness under a lamp. The residue taken up in 250 ml filtered groundwater and the pH was adjusted to 6.7 with 0.5N HCl. The ^{233}U concentration in this water was 9.45×10^{-7}M i.e. slightly higher than the maximum ^{238}U concentration (47dpm or 2.64×10^{-7}M) measured in Needle's Eye water samples (Hooker *et al.* 1986). This concentration was chosen in an attempt to ensure that the equilibrium concentrations in the aqueous phase, after equilibration with the silt, would be of the same order as concentrations in the field. This spiked groundwater was then placed in an incubator at 10°C and allowed to equilibrate for several weeks.

2.2 Broubster

The Broubster site is described in detail in a BGS Report (Ball and Milodowski, 1989). Sampling points and sample codes are described in detail in this report.

Peat: Peat was cut from the base of the peat layer and immediately transferred to a plastic box (15cm x 17 cm x 22cm) leaving no air space. The box was tightly sealed and transferred to a cool room where it was stored at 4°C. The sub-sample used for the distribution ratio determinations was taken from the centre of the block using a coring device. The water content was determined by drying to constant weight at 35°C and found to be 77%.

Groundwater: Water was obtained from the surface of Pit 4 by digging a 25 cm deep hole and collecting the water as it drained into the hole. It was stored in contact with solid peat (about 10g/l) in plastic bottles at 4°C. At the time of collection the pH was 6.8. Before use this water was filtered through 0.2µm filters whereupon the pH rose to 7.7, presumably because of degassing and loss of CO_2 and other gases.

Spiked Groundwater: 5ml ^{233}U solution (15.7KBq in 1 M HNO_3, obtained from Harwell) was evaporated slowly to dryness under a lamp. The residue was dissolved in 0.5 ml 0.5 M $NaHCO_3$ and diluted to 250 ml with filtered groundwater. The pH was then readjusted to 7.7 by the addition of one drop of 9M HCl. The uranium concentration in the final solution was 7.55×10^{-7}M and the ^{233}U activity was 3600 dpm/ml. This spiked groundwater was then placed in an incubator at 10°C and allowed to equilibrate for six weeks.

A sample of blank groundwater was prepared by adding 0.5 ml 0.5M $NaHCO_3$ and one drop of 9M HCl to 250 ml filtered groundwater. This was analysed by ICP-OES and anion chromatography. The results of this analysis are given in Table 2.

Table 2 Composition of Broubster Groundwater

Element (Species)	mg/l	M	Element (Species)	mg/l	M
Ca	49.5	1.2×10^{-3}	HCO_3^-	190	3.1×10^{-3}
Mg	10.79	4.4×10^{-4}	Cl^-	45.9	1.3×10^{-3}
Na	43.4	1.9×10^{-3}	SO_4^{2-}	16.2	1.7×10^{-4}
K	3.57	9.1×10^{-5}	NO_3^-	0.93	1.5×10^{-5}
Si	1.24	4.4×10^{-5}	Br^-	1.85	2.3×10^{-5}
Ba	0.097	7.1×10^{-7}	NO_2^-	0.73	1.6×10^{-5}
Sr	0.199	2.3×10^{-6}	HPO_4^{2-}	0.0	0.0
Mn	0.017	3.1×10^{-7}	S	37.57	1.17×10^{-3}
Fe	0.0	0.0	TOC	15.4	
Al	0.08	3.0×10^{-6}	TIC	34.2	

pH=7.7

TOC=Total organic carbon. TIC= Total inorganic carbon

3. EXPERIMENTAL

The experimental basis involved the measurement of the distribution ratio (R_d) to determine the extent to which uranium had sorbed onto the sediment. The distribution ratio for a species is defined as :-

$$R_d = \frac{\text{concentration of the species on the solid phase}}{\text{concentration of the species in the liquid phase}}$$

Any convenient units may be used and R_d has dimensions volume/weight, usually ml/g or m^3/kg. Frequently, several different species of an element are present but only the total concentration of the element is determined. In these cases the measured distribution ratios are overall or average R_d values.

3.1 Needle's Eye Silt

3.1.1 Preliminary distribution ratios using old silt
(NE, 18-10 : Collected 4/2/88)

Approximately 0.5g (dry wt.) was weighed into polypropylene centrifuge tubes. 20 ml of unspiked groundwater were added and the tubes were placed in a water bath and shaken gently for 18 hours. The tubes were then centrifuged at 4000 rpm for 15 minutes and the wash carefully removed. The pH of the wash was 7.6.

Spiked groundwater (pH=6.7) was then added and the solid-solution ratio and initial uranium concentration calculated. The tubes were returned to the water bath and shaking continued for 16 days. They were then centrifuged for five minutes at 4000rpm and the supernate filtered through 0.1 µm filters. 1.0g portions were placed in liquid scintillation vials with 10ml Optiphase Hisafe III and counted in a LKB 1219SM low-level liquid scintillation counter .

3.1.2 Sorption kinetics at different pH values using fresh silt
(NE 18,-20 ; Collected on 15/12/88)

Experiments were carried out under two different pH conditions.

(a) The prepared groundwaters were used without any further pH adjustment (exactly as in the preliminary experiment (Section 3.1.1).

(b) The pH was maintained at 6.0. Thus the pH of the spiked and unspiked groundwater was adjusted to 6.0 before addition to the silt. During the sorption experiment the pH was periodically checked and, if necessary, adjusted to 6.0 with one or two drops of 0.1M or 0.01M HCl.

The kinetics of sorption were studied as follows:-
Duplicate samples (0.5g dry weight) were weighed into 50ml polypropylene tubes. 20 ml of unspiked groundwater were added and the tubes were placed in a water bath at 10°C and shaken gently for 18 hours. They were then centrifuged at 4000 rpm for 15 min and the wash carefully removed. The pH of the wash was measured.

Sufficient spiked groundwater was then added to give a solid-solution ratio of 0.5g/20ml and the tubes were returned to the shaking water bath at 10°C. At intervals (the first after 15 min), one of each pair was removed and centrifuged for 5 min. Exactly 1.0 ml was removed and the tube returned to the water bath. The samples were filtered through 0.1μm filters. 0.5g portions of the filtered supernate were placed in mini-vials with 5 ml of Optiphase Hisafe III and counted on an LKB 1219SM liquid scintillation counter.

The second tube of each pair was sampled in the same way but at intervals of seven to fourteen days.

3.2 Broubster Peat

Samples (either 1 g wet weight or 3g of a slurry containing 0.043 g/ml) of peat were weighed into plastic centrifuge tubes. Sufficient spiked groundwater (filtered through 0.1μm Nucleopore filters immediately before use) was added to each tube to make the total volume of the aqueous phase 17 ml. The tubes were sealed and placed at a 45° angle in a shaking water bath at 10°C and shaken at about 10 strokes/min. After 28 days they were removed from the water bath and centrifuged for 10 min. 1g portions were transferred to liquid-scintillation vials. The effect of phase-separation technique and the possibility of sorption onto Amicon cones was investigated as follows:-

(i) 2 ml were passed through a 0.2 μm Nucleopore and discarded. A further 1.5 ml were passed through the same filter. 1.0 g was transferred to a scintillation vial.

(ii) 4 ml were passed through a 25 000 nominal molecular weight cut-off Amicon CF25 cone and discarded. A further 1.5ml were passed through the cone and 1.0 g was transferred to a scintillation vial.

(iii) A further 1.5 ml were passed through the cone and 1.0 g was transferred to a scintillation vial.

(iv) A further 1.5 ml were passed through the cone and 1.0 g was transferred to a scintillation vial.
The pH of the remaining liquid, still in contact with the peat, was then measured.

10 g of Optiphase Hisafe-3 were added to each vial and the samples were counted on the liquid scintillation counter.

4. RESULTS

4.1 Needle's Eye Silt

4.1.1 Preliminary Distribution Ratios

The results of these preliminary experiments are given in Table 3. The difference between the two results is probably a reflection of the accuracy of the determination and not caused by the factor of two difference in solid/solution ratio. The errors quoted are based on counting statistics only and do not reflect the accuracy of the method. The error of the weighted mean (external consistency) is a better reflection of precision.

Table 3 Preliminary Distribution Ratios
Silt NE 18, 10 Profile 140-160. Collected 4/2/88

No	Final pH	m/v (kg/l)	Rd (ml/g)	Weighted Mean
NE-1	7.1	0.0307	141±6	161±27
NE-2	7.2	0.0609	196±8	

Initial pH = 6.7. Temperature 10°C. Shaking time 16 days. Phase separation 0.1μm filters

4.2 Kinetic Experiments

The results of these experiments are given in Table 4 and illustrated in Figures 1a and 1b. A study of these shows the following:

(i) Effect of pH : Sorption at pH=6 was significantly greater than at pH=7.

(ii) Reproducibility : Agreement between the duplicate samples after one week was good. There there was no significant difference between distribution ratios after one week for the two samples maintained at pH 6. The difference between the two samples in which the pH was not controlled was probably due to the fact that the final pH in the undisturbed system was 7.3 as compared with 8.0 for the system that was sampled. Thus the change in solid-solution ratio and the removal of a small amount of fines during sampling seem to have had little effect.

Agreement with results of the preliminary experiment using old silt and a similar pH range (Table 3) was good considering the longer shaking time and difference in sample pre-treatment.

(iii) Kinetics: At both pH=6 and pH=7 an initial rapid sorption was followed by a gradual decrease in solution concentration. At pH=7 the concentration after 5 hours was not significantly different from the concentration after 15 minutes whereas at pH 6.0 the concentration dropped further by a factor of two during the interval between 15 minutes and 5 hours.

Table 4 Kinetics of uranium sorption in silt groundwater system

Initial pH=6.7. pH not adjusted					Initial pH=6.0 pH adjusted to 6.0 after each reading				
Expt	time hr	pH	^{233}U in soln cpm/g	Rd ml/g	Expt	time hr	pH	^{233}U in soln cpm/g	Rd ml/g
A2	0	6.8	4584		B1	0	6.0	4618	
	0.37		2631	31.5		0.4	7.0	1517	83
	0.72		3042	23.4		2.6	7.0	980	148
	1.63		2904	24.7		5.1	6.0	916	161
	4.87		2804	27.0		24.0	6.0	660	237
	69.03		1964	51.3		51.0	6.0	531	301
	98.0	7.9	1503	75.4		99.0	6.0	197	861
	122.2	8.0	1661	66.1					
	122.5	8.0	1566	71.5					
	170.3	8.0	1727	62.9		170	6.0	375	440
A1	0	7.2	4480		B2	0	6.0		
	170.5	7.3	1096	125.6			6.0	445	373

Note (1) Counting errors were insignificant compared with other experimental errors and are, therefore, not given.

(2) The pH values listed are the values measured immediately after sampling and before adjustment.
Expts A1 and A2 pH was never adjusted.
Expt B1 pH adjusted to 6.0 after each reading
Expt B2 pH adjusted to 6.0 daily

Figure 2a is a graph of $\ln C/C_0$ against time for Expt A2 (uncontrolled pH). If the first point is excluded the remaining points can be fitted to straight line with gradient 0.0051 (r=0.96). It appears, therefore, that the slow sorption that follows the initial rapid loss from solution is first order with rate constant 0.005 h^{-1}.

Figure 2b is a similar graph for Expt B1 (pH=6.0). Once again an initial rapid sorption is followed by a slow increase in the amount sorbed. A straight line cannot be fitted to these points which might indicate that different mechanisms are involved.

Several possible mechanismss for this type of behaviour can be postulated. Thus more than one species may have been involved in sorption, each having different sorption rates. The rate-determining step could be either the sorption rate of the species with the slowest rate or inter-conversion rates between the species. Alternatively, rapid surface surface sorption followed by slower diffusion-controlled processes or initial sorption followed by gradual isotope exchange with natural uranium in the samples could explain this behaviour.

Fig. 1a U-233 sorption on Needles Eye Silt

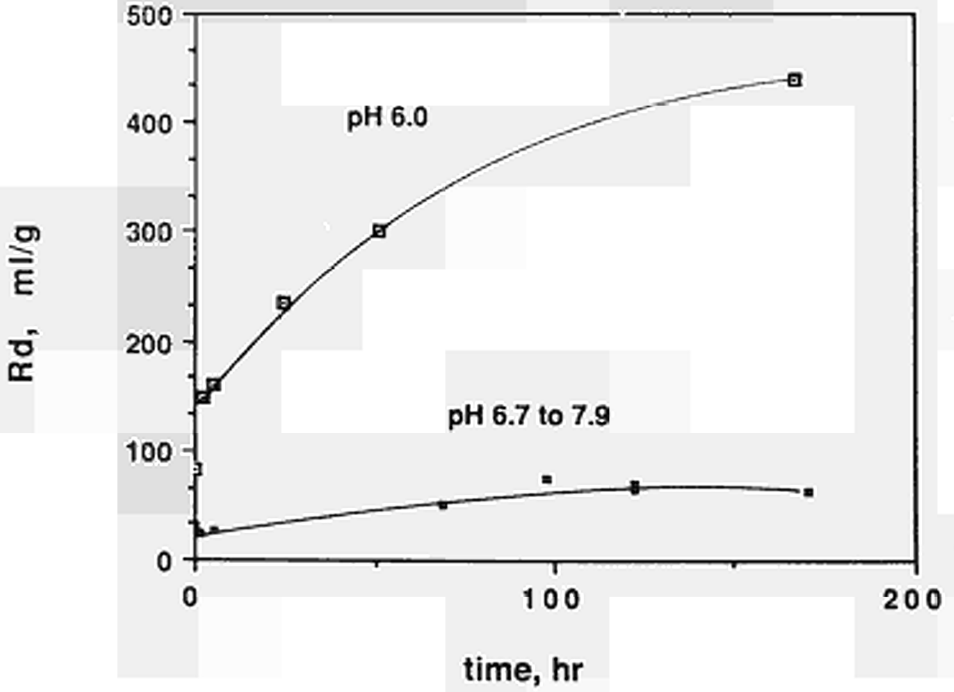


Fig 1b. U-233 sorption on Needles Eye silt

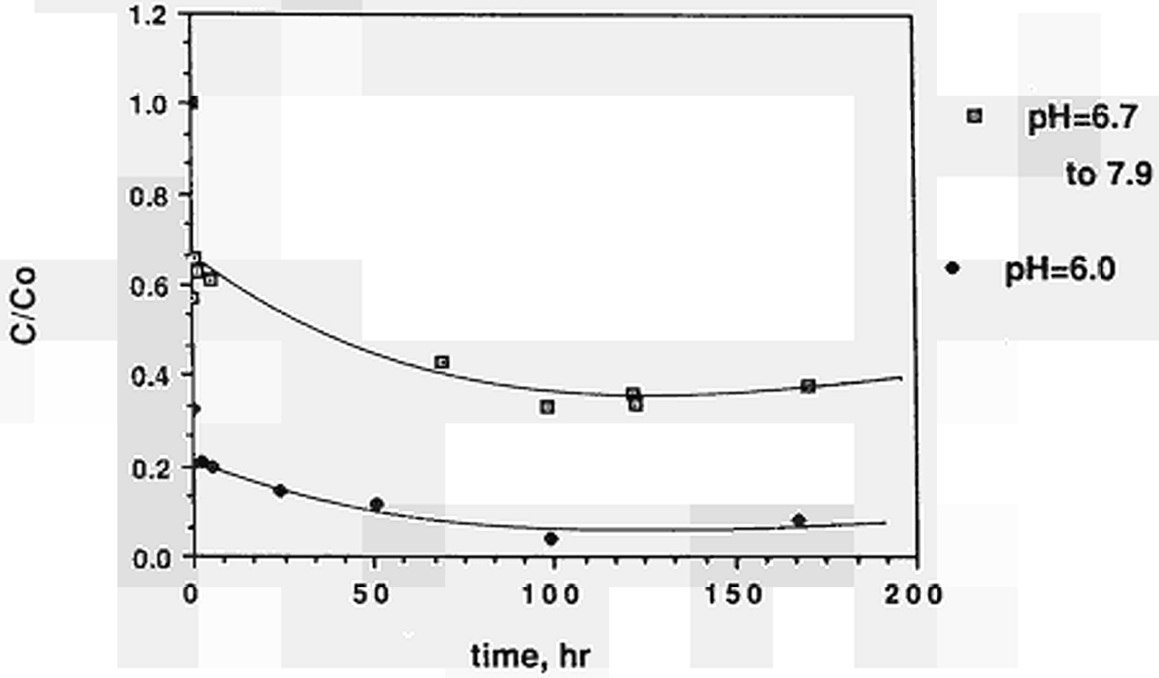


Fig 2a. U-233 Sorption kinetics: uncontrolled pH

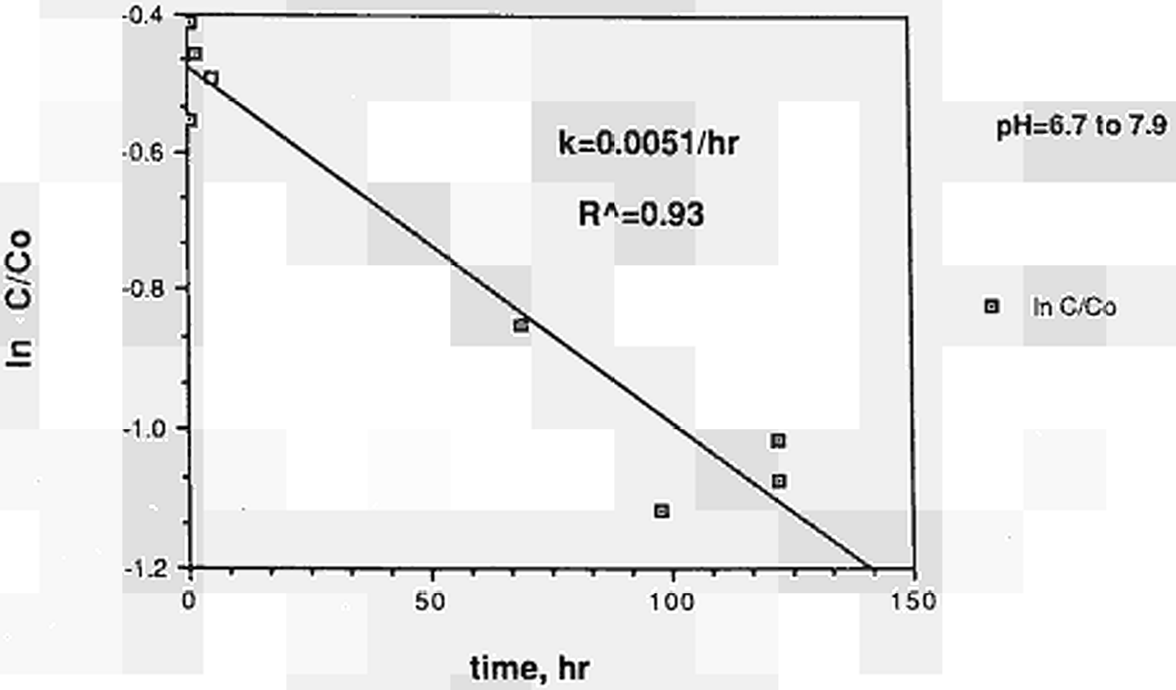
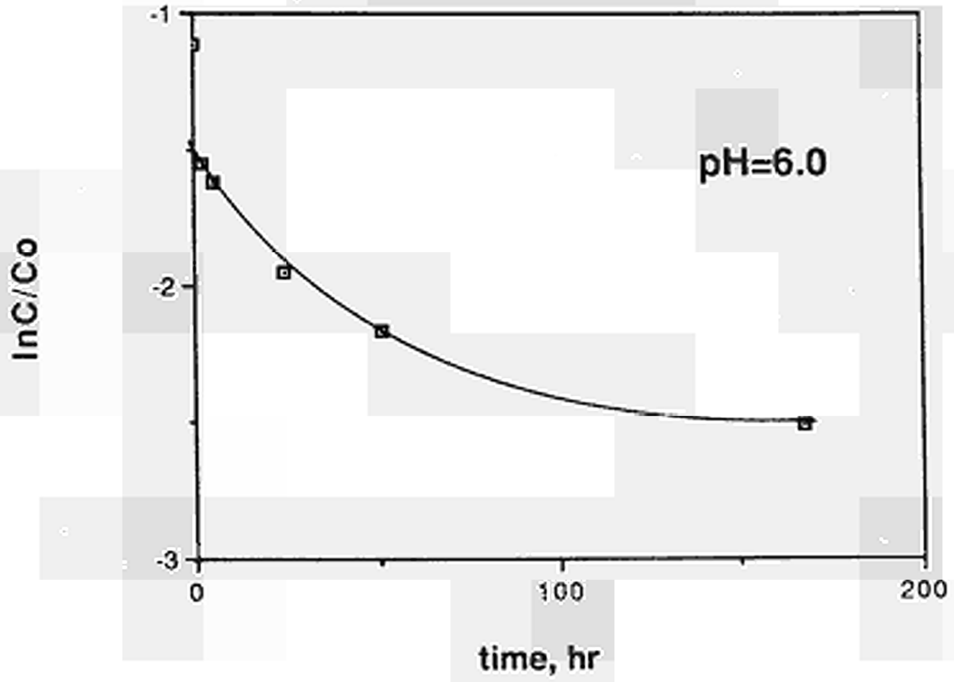


Fig 2b. U-233 Sorption Kinetics. pH maintained at 6.0



4.2 Broubster Peat

The results are given in Table 5. The errors are based on counting statistics only and all values are the weighted mean of two determinations. The initial U-233 activity was about 3000 cpm/ml and the final activity was between 12 and 30 cpm/ml i.e. close to the limit of detection (the blank count was 34 cpm/ml) and errors are, therefore, large. The activity of the spiked groundwater in the tube containing no solid phase remained unchanged indicating that sorption to the plastic had not occurred.

Table 5 Uranium distribution ratios on peat

No	Solid-Soln	Final	Rd , ml/g x 10^{-4}				
	ratio, g/l	pH	centrifuged	0.2µm	1st CF25	2nd CF25	3rd CF25
1	6.97	7.0	1.20±0.18	2.81±0.85	2.29±0.58	2.61±0.74	1.70±0.34
2	7.26	7.0	1.59±0.31	1.58±0.30	1.73±0.36	2.10±0.52	1.55±0.29
Mean			1.3±0.2	1.7±0.4	1.9±0.3	2.3±0.4	1.6±0.2
3	13.67	6.5	1.07±0.26	1.15±0.29	1.29±0.37	1.53±0.5	1.35±0.40
4	14.26	6.5	1.02±0.24	0.91±0.0.2	1.41±0.45	1.31±0.39	1.43±0.46
Mean			1.0±0.2	1.0±0.2	1.3±0.3	1.4±0.3	1.4±.0.3

Initial Uranium concentration 7.55×10^{-7}M. Initial pH=7.4. Temperature 10°C. Time 28 days.
CF25 : Amicon CF25 cones- nominal cut-off 30 000Dalton

The effect of improved phase separation was small indicating that the traces of uranium in solution were not sorbed onto particles in the 25 000 Dalton to 0.2 µm range. Changing the solid/solution ratio had a small but significant effect. This may have been due to the presence of some pseudo-colloidal uranium or it may be the result of a systematic error in allowing for the water content of the two different samples of peat.

The pH of all samples decreased during the equilibration period. This was probably caused by an increase in the concentration of organic acids during the shaking period. The fact the decrease in pH was greater for the higher concentration of peat indicates that a significant proportion of the acidity came from the peat rather than from CO_2 in the air.

5. SPECIATION MODELLING

In order to aid the interpretation of the results speciation modelling was carried out using the PHREEQE code (Parkhurst, *et al.* 1980) and the Harwell/Nirex database (Hatches, 1988). The speciation was calculated for different groundwater compositions at several different pH and Eh values. The total organic carbon in the groundwaters was relatively high. The effect that this might have on speciation was estimated by calculating the effect that an equivalent concentration of ethylene diamine tetraacetic acid (EDTA) would have on speciation (assuming that the ratio of carbon to carboxylic groups was the same as in EDTA). EDTA is a strong complexant and should exhibit binding intensities at least as strong as the strongest metal-natural organic matter interactions that will be observed (Quinn *et al.*, 1989). The assumption is, therefore, made that if EDTA does not bind with uranium then neither will humic or fulvic material. This may not be valid over the complete pH range but, in the absence of accurate data for U-fulvic and -humic complexes, it is considered to be a reasonable first approach.

The systems modelled were:-

(1) Needle's Eye groundwater used in the laboratory experiments (NE/42 : Table 1) containing 9.45×10^{-7}M uranium at pH values of 6.0 and 7.0.

2) Needle's Eye groundwater NE/33 containing 9.45×10^{-7}M uranium. Because iron had clearly precipitated out of the groundwater before it was used in the sorption experiments it was feared that the laboratory conditions were not representative of field conditions. The effect of using the composition of water analysed immediately after collection was, therefore, determined. Uranium speciation (9.45×10^{-7}M uranium) in groundwater with the composition of NE/33 was calculated. (Table 1). The most striking difference between the two groundwaters is the high iron and manganese content of NE/33. The measured field Eh of NE/33 was +397mV but this is unlikely to be correct in view of the high iron (Fe^{2+}) and manganese (Mn^{2+}) content. Modelling was, therefore carried out at both +397mV and the more realistic value of 0mV. The pH was kept at the measured value of 5.7.

(3) Broubster groundwater of the actual composition (Table 2) and pH values used in the sorption experiments. Only oxidising conditions (Eh 400mV) were considered.

Tables 6 & 7 show the major species predicted by this modelling. Speciation in the water used in the laboratory experiments (NE/42) remained unchanged when the Eh was reduced from 400mV to 112mV and the results for these two Eh values are, therefore, not given separately.

Table 6 Calculated Uranium Speciation in Water from Needle's Eye

Species	LAB COMPOSITION (NE/42)				FIELD COMPOSITION (NE/33)			
	No Organics		EDTA*		No Organics		EDTA *	
	pH=6	pH=7	pH=6	pH=7	pH = 5.3			
	(400mV & 112mV)				0mV	397mV	0mV	397mV
U in Oxidation State VI								
UO_2^{2+}	0.28	0.00	0.00	0.00	0.02	**8.40**	0.02	**4.91**
UO_2OH^+	0.28	0.02	0.35	0.03	0.02	**5.59**	0.00	3.23
$UO_2(OH)_2^0$	0.10	0.06	0.12	0.06	0.00	0.26	0.00	0.15
$UO_2CO_3^0$	**19.39**	**1.16**	**20.41**	**1.35**	0.18	**68.13**	0.18	**68.13**
$UO_2(CO_3)_2^{2-}$	**67.73**	**40.46**	**65.58**	**43.12**	0.02	**8.46**	0.00	**4.96**
$UO_2(CO_3)_3^{4-}$	**9.80**	**58.27**	**8.47**	**55.38**	0.0	0.02	0.00	0.01
UO_2Cl^+	**1.91**	0.01	**2.30**	0.01	0.02	**5.46**	0.00	**3.16**
UO_2F^+	0.14	0.00	**1.76**	0.00	0.00	**1.22**	0.00	0.71
$UO_2SiO(OH)_3^+$	0.04	0.00	0.05	0.00	0.00	**1.00**	0.00	0.58
UO_2HEDTA^-	-	-	**1.76**	0.00	-	-	0.00	**40.44**
$(UO_2)_2EDTA(OH)^-$	-	-	0.03	0.00	-	-	0.0	0.73
U in Oxidation State V								
UO_2^+	0.00	0.00	0.00	0.00	**8.63**	0.00	0.02	0.00
U in Oxidation State IV								
$U(OH)_4$	0	0	0	0	**91.10**	0.00	**5.72**	0.0
U(EDTA)	-	-	0.00	0.00	-	-	**93.76**	0.0

Uranium concentration 9.45×10^{-7}M
* EDTA concentration 4.6×10^{-5} M

Table 7 Calculated Uranium Speciation in Broubster Groundwater. Oxidising conditions. (Eh=400mV)

Species	No Organics		EDTA (1.28×10^{-4} Molal)	
	pH=6.5	pH=7	pH=6.5	pH=7
U in Oxidation State VI				
UO_2^{2+}	0.01	0.00	0.01	0.00
UO_2OH^+	0.15	0.05	0.15	0.05
$UO_2(OH)_2$	0.11	0.11	0.11	0.11
$UO_2CO_3^0$	**11.32**	**3.49**	**11.31**	**3.49**
$UO_2(CO_3)_2^{2-}$	**83.59**	**81.48**	**83.60**	**81.47**
$UO_2(CO_3)_3^{4-}$	**4.84**	**14.89**	**4.85**	**14.92**
UO_2Cl^+	0.00	0.00	0.00	0.00
$UO_2H(EDTA)^-$	0.00	0.00	0.01	0.00
$(UO)_2(EDTA)(OH)^-$	0.00	0.00	0.00	0.00

Uranium concentration 9.45×10^{-7}M

6. DISCUSSION

6.1 The Needle's Eye Silt-Groundwater System

6.1.1 Effect of pH on speciation and sorption

A study of the results of speciation modelling using the NE/42 composition shows that :-
(i) All the uranium is present in the VI oxidation state.
(ii) Speciation changed markedly as the pH was increased from 6.0 to 7.0. Thus at pH 6 the main species were the neutral and divalent carbonates whereas at pH 7 the main species were the divalent and tetravalent carbonates.
Note In the experiments at pH 6 small amounts of acid were added to keep the pH constant. This could have led to dissolution of carbonates and altered the speciation. However, the effect is probably small and no attempt was made to model this effect.

The measured distribution ratios between 10^2 and 10^3 ml/g imply significant sorption. It is possible that the small amount of cationic uranium present is responsible for this sorption as re-equilibration would occur as soon as it was sorbed. A continuous cycle of sorption and re-equilibration could lead to sorption of this magnitude.

Alternatively, in the absence of cationic uranium species the most likely mechanism for sorption of the uranium carbonates is ligand exchange of carbonate anions for solid-phase hydroxyls at oxide surfaces. Lieser and Tybusch (1988) have suggested a series of reactions in which sorption of uranium carbonates is by displacement of carbonate ligands e.g.

(1) $2(>SOH) + UO_2(CO_3)_3^{4-} <=> (>SO)_2UO_2(CO_3)_2^{4-} + HCO_3^- + H^+$
or
$SOH + SO^- + UO_2(CO_3)_3^{4-} <=> (>SO)_2UO_2(CO_3)_2^{4-} + HCO_3^-$

(2) $2(>SOH) + UO_2(CO_3)_2^{2-} <=> (>SO)_2UO_2(CO_3)^{2-} + HCO_3^- + H^+$
or
$SOH + SO^- + UO_2(CO_3)_2^{2-} <=> (>SO)_2UO_2(CO_3)^{2-} + HCO_3^-$

(3) $2(>SOH) + UO_2(CO_3) <=> (>SO)_2UO_2 + HCO_3^- + H^+$
or

$$SOH + SO^- + UO_2(CO_3)OH^- <=> (>SO)_2UO_2 + HCO_3^-$$

The high iron and manganese content of the associated water and the fact that iron hydroxides precipitated out on exposure to air indicates that the surfaces of the minerals in the silt may have been coated with iron and manganese oxyhydroxides. Sorption of anions should, therefore, increase as the pH decreases below the ZPC. The observed behaviour, therefore, supports the hypothesis that uranium carbonates were sorbed onto oxide surfaces.

The results of the kinetic experiments may indicate that speciation changes are also involved. Figure 3a is a graphical representation of the predicted speciation at the two pH values studied and Figure 3b is a graph of % sorbed *vs.* time for the first five hours only. At both pH values the percentage sorbed within the first 15 minutes corresponds roughly to the amount of $UO_2(CO_3)_2^{2-}$. This could conceivably indicate that the rapidly sorbed species is the divalent carbonate with the other species either being sorbed more slowly or being converted to $UO_2(CO_3)_2^{2-}$ and then sorbed. At pH 7-8 subsequent sorption exhibits first order kinetics reaction whereas at pH 6.0 this was not the case.

It should be pointed out that this discussion is highly speculative. The relationship between the amount sorbed and one particular species could be chance. Furthermore, the results of speciation modelling, although useful, should always be treated with caution. Their accuracy depends on the accuracy of the data base. A small change in the relative stability constants for the different carbonate species results in large changes in their relative concentrations. Databases are continually being updated but, particularly for the actinides, there are numerous uncertainties.

6.1.2 Effect of water composition

(i) Oxidising conditions: Even at Eh 400 mV the calculated speciation in groundwater NE/33 was markedly different from that in groundwater NE/42 . In the absence of organics the main difference was the higher proportion of neutral $UO_2(CO_3)^0$. In the presence of 4.6×10^{-5} M EDTA 40% of the uranium appears to be complexed as $UO_2H(EDTA)$ and it is likely, therefore, that complexation with natural organic material would have occurred.

(ii) Reducing conditions: The effect on speciation of reducing the Eh to 0 mV is dramatic, with none of the uranium now being in the +6 oxidation state. Actinides in the +4 oxidation

Fig 3a. Effect of pH on uranium speciation Groundwater NE/42 = 4.6e-5M EDTA

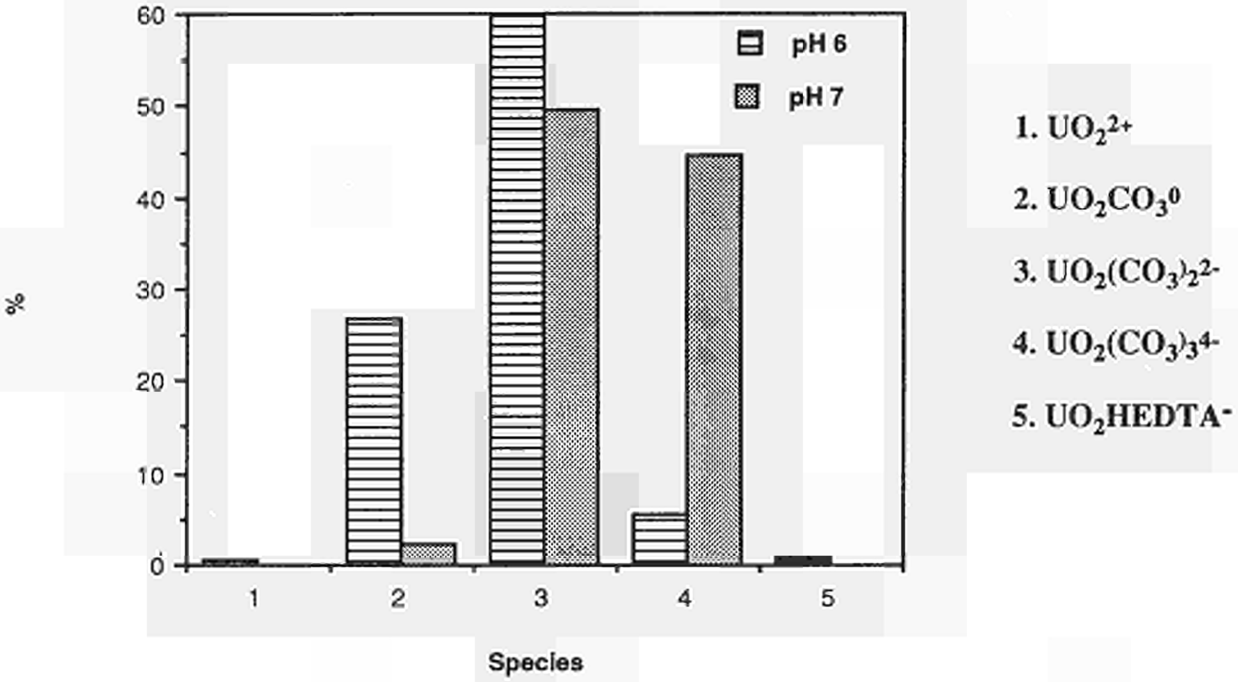
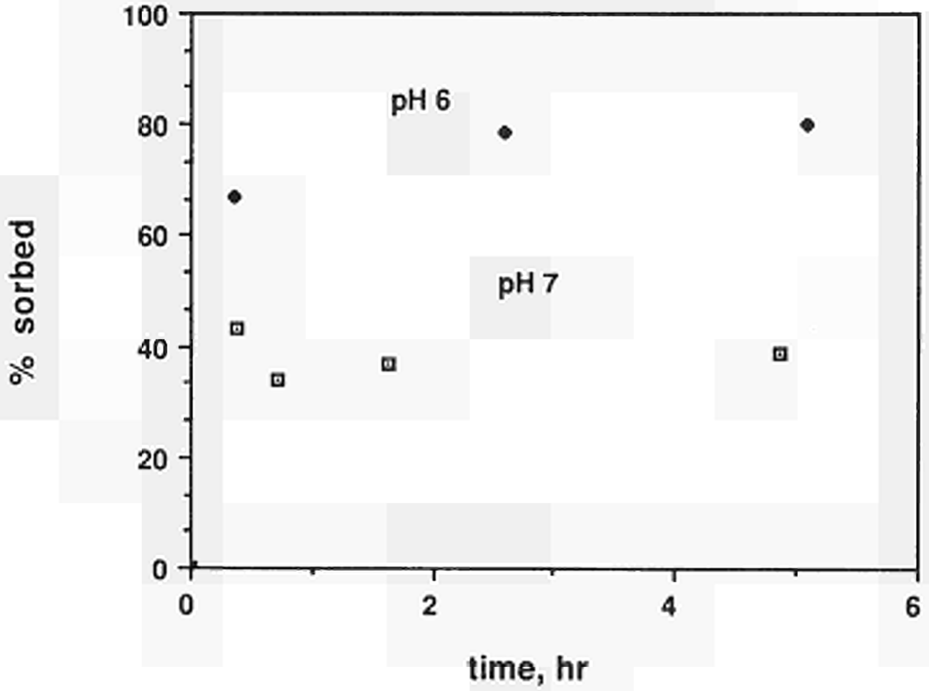


Fig 3b. Sorption of U-233 on Needle's Eye silt from groundwater NE/42



state tend to be strongly sorbed (e.g. Allard, 1984) and there can be little doubt that, at this Eh, distribution ratios in the absence of organic material will be high i.e. > 10^4ml/g.

The effect that organic complexation would have on uranium mobility would depend on the nature of the organic complexes formed. If they are part of the matrix (e.g. in peat) then the uranium would be fixed. If, however, complexes are formed with fulvic and humic acids their mobility would depend on their charge and size. The TOC concentration in waters NE/42 and NE/33 (Table 1) were high and if a significant fraction of this carbon was humic/fulvic acids then complexation might enhance solubility.

6.2 The Broubster Peat - Groundwater System

6.2.1 Inorganic ligands only

Read (1988) (also Read and Hooker, 1989) modelled the uranium speciation in eight samples of Broubster groundwater using the PHREEQE code and two sets of thermodynamic data; the preliminary project database from CHEMVAL/MIRAGE (Read and Broyd 1988) and an NEA compilation, based largely on the work of Schweingruber (1981). In the absence of organic matter, the results obtained with the two data sets were similar. Uranium (VI) carbonates were by far the most abundant species, hydroxy and sulphate complexes never exceeding 10% of the total concentration. With the CHEMVAL database the 1:1 $UO_2CO_3^0$ complex appeared to be relatively more important than the negatively charged carbonates $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$ whereas with the NEA database the divalent $UO_2(CO_3)_2^{2-}$ predominated.

In this work uranium speciation was modelled in groundwater of the actual composition and pH values used in the sorption experiments. Only oxidising conditions (Eh 400mV) were considered. Once again the PHREEQE code and the Harwell/Nirex database (Hatches, 1988) was used. The results obtained in the presence and in the absence of EDTA are given in Table 7. Speciation in the absence of organic complexants is similar to that predicted by Read (1988) using the NEA database i.e. about 80% of the uranium is present as $UO_2(CO_3)_2^{2-}$ at both pH 6.5 and 7.0 with the remainder divided between $UO_2CO_3^0$ and $UO_2(CO_3)_3^{4-}$. At pH 6.5 there is three times as much $UO_2CO_3^0$ as $UO_2(CO_3)_3^{4-}$ whereas at pH 7.5 there is three times as much $UO_2(CO_3)_3^{4-}$ as $UO_2CO_3^0$.

6.2.2 Organic ligands present

A variety of methods have been applied to the numerical evaluation of the binding of metals to humic and fulvic acids (Falck, 1988). The calculations often assume that the metal ion (M) is the central species and the humic molecule (A) binds to it to form MA_i complexes. It is not always obvious whether the metal binds to groups on one or a number of different humic molecules. Given the size of the organic polyelectrolyte anions and the number of binding groups per molecule it is not unlikely that only one humic acid molecule is involved. Experimental studies have been interpreted assuming that in aquatic fulvic and humic acids, a mixture of 1:1 and 1:2 metal:carboxylate complexants can account for the metal binding (Choppin, 1988). Such complexation requires two stability constants, β_1 and β_2, for monodentate and bidentate complexation, respectively. This is not to be seen as a sequential addition since the assumption is that the two types of complexes are present simultaneously and independently.

Read (1988) attempted to model uranium-humate speciation assuming that all organic carbon is present as humic acid, that aqueous complexation takes place via a straightforward metal-ligand ion-association reaction and that humic acid is completely dissociated ($\alpha = 1$) with a unit negative charge at the soil water pH of 5 to 7.

It was concluded that uranium humate complexation is strongly pH dependent. Using the CHEMVAL database and U-humic acid formation constants from Shanbhag & Choppin (1981) ($\log \beta_1 = 7.67$ and $\log \beta_2 = 11.57$) there was a pH edge between 5.3 and 6.3 over which uranium-humate complexation decreased from around 100% to zero as the carbonate ligands competed more successfully for U(VI). Using the NEA database and humic acid formation constants from Kim (1986) ($\log \beta_1 = 6.3$ and $\log \beta_2 = 10.2$) the pH edge shifted upwards by two pH units.

In this study, the effect of adding EDTA (overall uranium-EDTA complex formation constant $\log K = 17.5$) rather than humic acids was modelled. An amount of EDTA equivalent to the organic carbon in the groundwater appeared to have little effect, indicating that complexation with humates probably would not have occurred at either the experimental pH values of 6.5

and 7.0 or the field value of 5.3. It is difficult to compare the results by the three different models since so much depends on the value assumed for the uranium-organic stability constants. The pH range 5 to 7 appears to be a critical region (it may reflect the second deprotonation step of carboxylic acids) and stability constants in Broubster groundwater itself will have to be determined before more certainty can be achieved.

In the distribution-ratio experiments described above (section 4.2) uranium was strongly sorbed. Clearly, peat competed successfully with carbonates for the uranium. This is presumably because in these experiments (and in peat bogs) the concentration of organic ligands is orders of magnitude higher than the carbonate concentration.

7. SELECTION OF VALUES FOR MIGRATION MODELLING

Further work is clearly needed if accurate values for the stability constants are to be obtained covering the whole range of materials and conditions known to exist in the field at Needle's Eye and Broubster. At Needle's Eye it is essential that measurements are made under anoxic conditions with material that has not been exposed to air. In the absence of such information provisional estimates of suitable distribution coefficients for use in simple modelling calculations are:-

(1) Broubster Peat:

The measured distribution ratios at pH 6.5 and 7.5 were > 10^4 ml/g .
Van Der Weijden and Van Leeuwen (1985) found that the distribution ratio ranged from 2.7×10^4 ml/g at pH 3.1 to 5.7×10^5ml/g at pH 4.6. All these determinations were made in air and it can be assumed, therefore, that they are minimum values. Suggested values for modelling purposes are, therefore,

Best estimate 10^5ml/g: Range 10^4 to 10^6ml/g

2) Needle's Eye Silt

(i) Oxidising conditions	pH=6	Best estimate 10^3 ml/g:	Range 10^2 to 10^4ml/g
	pH=7	Best estimate 10^2 ml/g:	Range 10 to 10^3ml/g
(ii) Reducing conditions	pH 4 to 8	Best estimate >10^4ml/g	

8. SUMMARY AND CONCLUSIONS

Sorption of ^{233}U from natural groundwater onto Needle's Eye silt and Broubster peat was studied under atmospheric conditions and different pH regimes.

Two different sets of experiments were carried out with Needle's Eye silt. In the first, the pH was maintained at 6.0 by the addition of HCl. In the second, the pH was allowed to drift from its initial value of 6.7 to 7.9. Distribution ratios at pH 6.0 were higher than at pH 6.7-7.9. At both pH values an initial rapid sorption was followed by slow sorption but only at pH 6.7-7.9 did the slow sorption follow first order kinetics during the first week.

In order to explain these observations speciation modelling was carried out. This showed that under the experimental conditions used the uranium should be present as a mixture of negatively charged and neutral carbonates with the proportions of each species differing markedly at pH 6.0 and 7.0. It is postulated that sorption of uranium carbonates is by displacement of carbonate ligands in a series of surface-complexation reactions with oxide surfaces.

The Needle's Eye groundwater used in the sorption experiments was very different in composition from that in the field because it had been stored in air and iron and manganese oxyhydroxides had precipitated out. Uranium speciation in a groundwater, taken from the same horizon but analysed immediately after collection was , therefore, modelled under both reducing (Eh=0 mV) and oxidising (Eh=400 mV) conditions. It seems probable that in the field, even under oxic conditions, sorption and organic complexation will be higher than in the laboratory experiments. At zero Eh most of the uranium should be reduced to the IV state and strongly sorbed. If organic material is available complexation is likely to be complete.

Distribution ratios for Broubster peat were greater than 10^4 ml/g at pH values of both 6.5 and 7.0. Speciation modelling indicated that carbonate complexation should dominate in the groundwater but given sufficiently strong interaction with the solid substrate then, as a result of mass action, complexation/sorption will probably be nearly complete.

Finally an attempt was made to estimate likely distribution coefficients for use in migration modelling. It is suggested that , until ranges are narrowed by further work , the silt layers at Needle's Eye be divided into three Eh and pH regimes *viz*

(i) oxidising with pH 6.5 to 8.0 Best estimate 10^2 ml/g . Range 10^1 to 10^3 ml/g
(ii) oxidising with pH 6.5 to 4.0 Best estimate 10^3 ml/g . Range 10^2 to 10^4 ml/g
(iii) reducing (Eh ≤ 0mV): pH 4 to 8 Best estimate >10^4ml/g. Range 10^3 to 10^6ml/g

For peat layers at both sites suggested values for modelling purposes are:

Best estimate >10^4ml/g. Range 10^3 to 10^6ml/g .

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EUR 12891 — **Sorption studies of uranium in sediment-groundwater systems from the natural analogue sites of Needle's Eye and Broubster**

J. J. Higgo, W. E. Falck, P. J. Hooker

Luxembourg: Office for Official Publications of the European Communities

1990 — VIII, 30 pp. — tab., fig. — 21.0 × 29.7 cm

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Catalogue number: CD-NA-12891-EN-C

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This report describes the results of sorption experiments designed to provide essential data for migration modelling. Sorption of ^{233}U from natural groundwater onto peat from Broubster and silt from Needle's Eye was studied under atmospheric conditions and different pH regimes. The temperature was maintained at 10°C and, in the case of Needle's Eye silt, the kinetics of sorption were followed. The results were analysed in conjunction with speciation modelling in an attempt to understand the sorption mechanisms and to extrapolate the findings to cover the range of conditions likely to be met in the field.

This work is part of the CEC project Mirage — Second phase, research area 'Natural analogues'.

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