

# ORGANIC COLLOID TRANSPORT OF RADIONUCLIDES AT GORLEBEN, WEST GERMANY.

J.P.L. Dearlove, G. Longworth, M. Ivanovich,  
Isotope Geoscience Section,  
Nuclear Physics and Instrumentation Division,  
Harwell Laboratory, Oxon, UK.

J.I. Kim, B. Delakowitz and P. Zeh  
Institute für Radiochemie,  
Technische Universität München, F.R.G.

## ABSTRACT

A study has been carried out on the Gorleben glacial sand/silt aquifer system, West Germany, to determine both the nature and actinide loading of the organic colloids present at the site and their transport characteristics. Six boreholes were sampled and two distinct groundwaters were identified, an organic-rich groundwater containing humic colloids and a saline groundwater which appears to contain mainly fulvic acid. A mixed organic-rich/saline groundwater has also been identified. There is unequivocal evidence for the association of uranium and thorium isotopes with the humic colloids in the organic-rich groundwaters. The values of the  $^{234}\text{U}/^{238}\text{U}$  activity ratio for the colloid fraction in all the boreholes sampled are different from the corresponding values for the solution phase. Uranium isotopes in the colloid fraction are therefore not in chemical equilibrium with those in solution. Other elements strongly bound to the humic colloids in the organic-rich groundwaters include lanthanides and trivalent/tetravalent metals such as Fe, Mn and Ti. Divalent alkaline earths and monovalent metals are less strongly bound.

## INTRODUCTION

Evaluation of the effect of colloids on radionuclide transport requires the characterization of the groundwater colloids present in the far-field, assessment of how they interact with the flux of radionuclides from the near-field (both as colloids and solution species) and a knowledge of colloid stability and mobility in relevant aquifers.

A study has been carried out on the Gorleben aquifer system to determine the nature and actinide loading of the organic colloids present at the site as well as their transport characteristics. Information on colloid transport was obtained by sampling six boreholes, three of which appear to intersect the same aquifer along two potential groundwater flow paths. Colloid characterization and actinide loading were determined using both tangential flow and cross flow ultrafiltration techniques which were tested and compared in an initial study of the Gorleben site [1,2] and later applied in the colloid transport study.

Samples of the aquifer geomatrix were also collected in order to compare their measured actinide isotopic activity ratios with those of relevant groundwaters. This comparison will help to identify both the source of the organic colloids and that of the natural actinides present in the groundwater. Study of the Gorleben groundwaters with their high organic content [3] represents a valuable opportunity to evaluate the effects of organic colloids on radionuclide migration in the far field.

## THE GORLEBEN SITE

The Gorleben site comprises between 150 and 300 metres of glacial sand, silt, marl and clay which overlies a salt dome with a volume of approximately  $8 \times 10^{10} \text{ m}^3$  [4]. Two

main aquifers within the Miocene and Pleistocene sands and silts are locally subdivided into four aquifers.

Two physically and chemically distinct groundwaters from the Gorleben site have been selected for the present study. One is brown, translucent, with low salinity, relatively low conductivity and is rich in organic (humic) material. The other groundwater is clear, with a low concentration of organic material, a relatively high conductivity (due to high salinity) and is derived from groundwaters leaching the salt dome. Mixed organic-rich/saline groundwaters are also studied.

## ANALYTICAL TECHNIQUES

Full details of the analytical techniques used are given in [1,2]. All samples were collected anaerobically ( $\text{N}_2 + 1\% \text{ CO}_2$  atmosphere) to prevent changes in the physical and chemical properties of the colloids through interaction with air. Unfiltered groundwaters were collected for aqueous chemistry and cross flow ultrafiltration experiments, with prefiltration being carried out in the laboratory in a  $\text{N}_2 + 1\% \text{ CO}_2$  atmosphere glove box.

Large volume samples for uranium and thorium isotopic analysis using isotope dilution/alpha spectrometry were collected in the field using an Amicon DC10LA ultrafiltration system fitted with a 1000nm prefilter and a 10,000 molecular weight (approx. 1.5nm) cut-off hollow fibre tangential flow cartridge filter. In this way, 20 liters of colloid concentrate were produced with a particle size range between 1.5nm and 1000nm [1,2], together with an ultrafiltrate. In addition, the unfiltered groundwaters were also sampled. The elemental concentration in the colloid fraction is derived by subtracting the elemental concentration in the ultrafiltrate from that in the colloid concentrate and divid-

ing the result by the concentration factor of the colloid concentrate. Any activity on the ultrafilter cartridge is removed by flushing the system with dilute NaOH and HCl solutions. Any activity on the prefilter is leached in the laboratory to yield the activity loading of the >1000nm particulates.

Laboratory cross flow (flat bed) ultrafiltration was carried out using Nuclepore 1000, 400, 100 and 30nm and Amicon XM300 (approx. 15nm), YM10 (approx. 1.5nm) and YM2 (approx. 1nm) filters. All pore sizes are quoted manufacturers nominal specifications. These were used to study metal ion loading and colloid population studies on size fractionated samples [5].

Colloid size fractionation in the field was carried out using three cut-off size ultrafilters (1.5nm, 3nm and 1000nm), preceded by a 1000nm prefilter. In this way three colloid concentrates were produced with colloid size fractions of 1.5nm to 1000nm (GoHy2227-1), 3nm to 1000nm (GoHy2227-2) and 100 to 1000nm (GoHy2227-3).

## RESULTS AND DISCUSSION

Groundwaters rich in organic (humic) material were collected from boreholes GoHy532, GoHy1271, GoHy2211 and GoHy2227 (Tables I and II). They are all brown, translucent, with DOC (Dissolved Organic Carbon) concentrations from 30 to 100 mgC/litre and conductivity from 950 to 5,000  $\mu$ S/cm. Groundwater from borehole GoHy1231 is saline and clear, with a DOC of 4 mgC/litre and a conductivity of 24,600  $\mu$ S/cm. The groundwater from borehole GoHy2226 appears to be a mixture of the organic-rich and saline groundwaters. It is brown, translucent with a DOC concentration of 49 mgC/litre and conductivity of 11,700  $\mu$ S/cm.

### Colloid Characterization

Both colloid sizes and concentrations are directly related to the chemical nature of DOC and its concentration [1]. The colloid populations for the organic-rich groundwaters from the Gorleben site measured by LPAS vary from  $9 \times 10^{15}$  to  $5 \times 10^{16}$  particles/litre for the 1.5 to 30nm particle size range. In the saline groundwater the overall colloid population is of the order of  $10^{12}$  particles/litre and in the mixed groundwater (GoHy2226) it is  $3 \times 10^{13}$  particles/litre.

The percentage of humic acid in the total humic material in sample GoHy2227 (86%) is similar to the percentage of DOC trapped on a 2nm cross flow ultrafilter (81%) It is probable, therefore, that the smaller particles passing through the ultrafilter consist of fulvic acid while the larger, filtered particles comprise humic acid [1]. Since 75% of the DOC in the saline groundwater (GoHy1231) passes through a 2nm ultrafilter it may be assumed that most of the organic material in this groundwater consists of fulvic acid.

Analyses of the organic-rich groundwaters (samples GoHy532, GoHy1271, GoHy2211 and GoHy2227) show that the 1.5nm to 1000nm colloid fraction contains 70 to 80% of the uranium and more than 90% of the Th present in the unfiltered groundwater (Tables I and II). The remaining fraction occurs in the ultrafiltrate. This is clear evidence for the association of uranium and thorium with organic groundwater colloids. Analysis of sample GoHy2227 shows that 81% of the DOC and (80+/-6)% of the 3+ and 4+ valency metals (including lanthanides) are removed by a 2nm cross flow ultrafilter [1]. Only (10.6+/-1)% of the 2+ valency metals are removed by the same ultrafilter. The similarity between the proportion of DOC, uranium, thorium and 3+/4+ metals removed by ultrafiltration indicates that all these metals appear to be complexed with organic substances, identified as humic acid, and occur in the groundwater as humic colloids [3]. Similar results are obtained for the other organic-rich groundwaters [8].

Analysis of the cross flow ultrafiltration measurements shows that the largest colloid fraction in the organic-rich groundwaters occurs in the 1 to 15nm size range [1]. This has been confirmed in the field, tangential flow ultrafiltration study. There the percentages of uranium and thorium isotopic activities between the colloid fraction and ultrafiltrate in samples 3nm to 1000nm and 100 to 1000nm size ranges are similar (Table II). A higher proportion of the uranium and thorium isotopes occur in the 1.5nm to 1000nm colloid fraction (GoHy2227-1) than in the 3nm to 1000nm and 100 to 1000nm colloid fraction (GoHy2227-2 and GoHy2227-3). This indicates that a higher proportion of the isotopes of uranium and thorium are colloid bound in the 1.5 to 3nm size range. This range has the largest surface area for potential complexation with metal ions in solution.

In groundwaters from borehole GoHy1231 the fraction of uranium and thorium associated with colloids is <20% of the total concentration, the majority (>80%) being present in the ultrafiltrate [1]. Since the organic substance in this groundwater is predominantly fulvic acid, which is not filterable at 1.5nm, a proportion of the uranium and thorium in the ultrafiltrate may be associated with this fulvic acid, which behaves chemically like humic in terms of metal ion complexation and organic particle generation [1]. This however can only be confirmed with further work on the sub 1.5nm particles.

The concentrations of uranium and thorium on the humic colloids in the organic-rich groundwaters are higher than those found on inorganics (eg. silica, iron oxyhydroxide and clay particle) colloids [6]. The organic-rich Gorleben groundwaters also contain a higher total concentration of thorium than groundwaters containing inorganic colloids [6]. The total calculated mass of humic acid in sample GoHy2227 is approximately 158 mg/litre [1]. This is large in comparison with other Gorleben groundwaters [7]. The

TABLE I

Comparison of Radionuclide and DOC Concentrations and Conductivity in Unfiltered Groundwaters and Isotopic Partition for U and Th Isotopes and Isotopic Ratios Between Colloid Fraction and Solution for Boreholes Which are Thought to Intersect the Same Aquifer

Unfiltered groundwaters.

	U (nmol/litre)	Th	DOC (mg/litre)	Conductivity ( $\mu$ S/cm)
GoHy532	1.3 +/- 0.1	3.5 +/- 0.1	30	975
GoHy1271	1.7 +/- 0.1	5.8 +/- 0.2	44	3190
GoHy2211	4.7 +/- 0.1	8.1 +/- 0.2	100	5000

Isotopic partition (%).

	$^{238}\text{U}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{232}\text{Th}$	$^{228}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$
GoHy532							
CF*	77	69	96	98	87	1.2	1.3
+/-	6	5	7	8	6	0.1	0.1
Sol**	23	31	4	2	13	1.8	0.09
+/-	2	2	1	1	1	0.1	0.01
GoHy1271							
CF	86	77	87	93	69	1.0	1.0
+/-	6	6	6	8	5	0.1	0.1
Sol.	14	23	13	7	31	2.1	0.4
+/-	1	1	1	1	2	0.2	0.1
GoHy2211							
CF	82	78	84	94	67	1.4	0.8
+/-	5	5	5	6	4	0.1	0.1
Sol.	18	22	16	6	33	1.8	0.5
+/-	1	1	1	1	2	0.1	0.1

\* CF = Colloid fraction    \*\* Sol. = solution (ultrafiltrate)

mass of uranium and thorium in the organic-rich groundwaters ranges from 0.3 to 0.8  $\mu$ g/litre for uranium and 1.0 to 2.1  $\mu$ g/litre for thorium. In the mixed organic-rich/saline groundwater the mass of uranium and thorium on the organic colloids is 0.2 and 0.6  $\mu$ g/litre respectively.

#### Colloid Transport

The  $^{234}\text{U}/^{238}\text{U}$  activity ratios (AR) for the colloid fraction and the ultrafiltrate in the organic-rich groundwaters are significantly different (Tables I,II). In terms of uranium isotopes, this suggests that the colloids are not in chemical equilibrium with the solution. In the saline groundwater

TABLE II  
Isotopic Partition (%) for Colloid Size Fractination of Sample GoHy2227

	$^{238}\text{U}$	$^{234}\text{U}$	$^{230}\text{Th}$	$^{232}\text{Th}$	$^{228}\text{Th}$	$^{234}\text{U}/^{238}\text{U}$	$^{230}\text{Th}/^{234}\text{U}$
GoHy2227-1 1.5 - 1000nm							
CF*	83	70	82	96	60	1.3	0.9
+/-	6	5	6	7	4	0.1	0.1
Sol**	16	30	18	4	40	2.9	0.4
+/-	1	1	1	1	3	0.2	0.1
GoHy2227-2 3 - 1000nm							
CF	52	30	46	84	19	0.9	1.1
+/-	4	2	4	6	1	0.1	0.1
Sol.	48	70	54	16	81	2.3	0.6
+/-	4	4	2	1	4	0.1	0.1
GoHy2227-3 100 - 1000nm							
CF	63	43	56	87	30	1.1	1.0
+/-	5	3	4	6	2	0.1	0.1
Sol.	37	57	44	13	70	2.5	0.6
+/-	2	3	2	1	4	0.1	0.1

\* CF = Colloid fraction \*\* Sol. = solution (ultrafiltrate).

with low organic content (GoHy 1231) no difference was observed between the  $^{234}\text{U}/^{238}\text{U}$  ratio in the colloid and solution phase, greater than the relatively large error due to the low uranium concentrations in these samples [1].

The boreholes GoHy532, GoHy1271 and GoHy2211 are thought to intersect the same aquifer at depths of between 65 and 85 metres. The subsurface geology, interpreted from borehole logs, shows that the sand/silt aquifer between boreholes GoHy532 and GoHy2211 is inclined with groundwater flow from borehole GoHy532 to GoHy2211. Boreholes GoHy1271 and GoHy2211 are of similar depth and no groundwater flow data are available. The concentration of uranium, thorium and DOC and the conductivity in the unfiltered groundwater increase from borehole GoHy532 to GoHy1271 to GoHy2211 respectively (Table I). The concentrations of the other colloid-bound elements display a similar trend. The partition of uranium and thorium isotopes between the colloid fraction and ul-

trafiltrate in each of the three boreholes is approximately the same (Table I).

The values obtained for the activity ratios of the colloid fraction in samples GoHy532, GoHy1271 and GoHy2211 range from 1.0 +/- 0.1 to 1.4 +/- 0.1 and overlap to within 2 sigma errors. Thus there is no clear indication for a common source for the organic colloids. Higher precision measurements using mass spectrometry are required to resolve this point. The lack of chemical equilibration for the uranium isotopes between the colloid fraction and the solution is clearly a result which requires further investigation, including dating of the groundwaters, and measurements of the uranium and thorium isotopic ratios and stable isotopes for potential colloid source material.

#### Mixing Of Organic-rich and Saline Groundwaters

Mixing between organic-rich groundwaters and high salinity groundwaters leaching the underlying salt dome, has lead to a reduction in divalent (2+) colloid-bound elements

(Ca, Sr, Mg, Mn) in the mixed groundwater (GoHy2226), in comparison with the organic-rich groundwaters. The relative concentration of uranium and thorium between the colloid fraction and the ultrafiltrate in the mixed groundwater is also reduced. Therefore mixing of organic-rich and saline groundwaters produces a lower actinide loading on the organic colloids in the mixed groundwater.

### CONCLUSIONS

- 1) The measurement of the partition of uranium and thorium activities between the colloid fraction and solution phase gives clear evidence for the association of uranium and thorium with humic colloid fraction in organic-rich groundwaters.
- 2) Corresponding  $^{234}\text{U}/^{238}\text{U}$  activity ratios show that with respect to uranium isotopes, the colloids are not in equilibrium with the solution phase, for the organic-rich groundwaters.
- 3) The actinides, lanthanides and trivalent/tetravalent elements analyzed are more strongly bound to the humic colloids than the divalent alkaline earth and monovalent metal ions.
- 4) The mass of uranium on the humic colloid fraction in the organic-rich groundwater sample (GoHy 2227) ranges from 0.3 to 0.8  $\mu\text{g/L}$  and the mass of thorium ranges from 1.0 to 2.1  $\mu\text{g/L}$ .

### ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support of the CEC's R&D program on radioactive waste management (CoCo-Club, MIRAGE project) and the UKAEA Underlying Research Program at Harwell Laboratory. Thanks are also due to the PTB, Braunschweig (FRG) for supporting this study. We would also like to thank Miss S. Hasler of Harwell Laboratory and H. Silaff, Dr. B. Frieg, D. Weselow, H. Fahrman and H. Stegemann from the

DBE at the Gorleben site for their assistance in the collection of the groundwater samples.

### REFERENCES

1. J.P.L. Dearlove, G. Longworth, M. Ivanovich, J.I. Kim, B. Delakowitz and P. Zeh, "A Study of Groundwater-Colloids and Their Geochemical Interactions With Natural Radionuclides in Gorleben Aquifer Systems," *Radiochimica Acta* (In press) (1989).
2. J.P.L. Dearlove, G. Longworth, M. Ivanovich, J.I. Kim, B. Delakowitz and P. Zeh, "Sampling and Characterization of Groundwaters at the Gorleben site, F.R.G. Phase I: Results for Groundwaters GoHy2227 and GoHy1231," Harwell Report AERE-R 13628 (In press) (1989).
3. J.I. Kim, G. Buckau and W. Zhuang, "Humic Colloid Generation of Transuranic Elements in Groundwater and Their Migration Behavior," *Mat. Res. Soc. Symp. Proc.* 84, 747-756 (1987).
4. W. Jaritz, O. Bornemann, W. Giesel and H. Vierhuff, "Geoscientific Investigation of the Gorleben Site," IAEA-SM-289/44 (1986).
5. P. Zeh, "Charakterisierung von Grundwasserkolloiden," Diplomarbeit, Techn. Univ. Munchen. Unpublished (1989).
6. G. Longworth and M. Ivanovich, "A Review of Some Geocolloid Transport Studies in the Far-field Relevant To Radioactive Waste Disposal," Tucson Waste Management '90 (1990).
7. J.I. Kim and G. Buckau, "Huminstoffuntersuchungen an Gorleben grundwassern," RCM Report RCM01688. (1988).
8. J.I. Kim, G. Buckau and R. Klenze, "Natural Colloids and Generation of Actinide Pseudocolloids in Groundwater," in *Analogues in Radioactive Waste Disposal* (B. Come, N.A. Chapman, eds), Graham and Trotman, 289-299, (1987).