

A REVIEW OF SOME GEOCOLLOID TRANSPORT STUDIES IN THE FARFIELD RELEVANT TO RADIOACTIVE WASTE DISPOSAL

G. Longworth and M. Ivanovich

Isotope Geoscience Section, B7 Harwell Laboratory, Oxon OX11 0RA, UK

ABSTRACT

The major pathway for the spread of radionuclides within the geosphere surrounding a radioactive waste repository is the groundwater. Since groundwaters contain colloidal particles which can sorb radionuclides and may be mobile, it is important to assess whether the presence of colloids will significantly change the radionuclide burden carried by the groundwater. Groundwater colloids from a variety of aquifers have been characterized in terms of their physical, chemical and actinide compositions. The partition of natural series actinides has been measured using isotope dilution alpha spectrometry, between the particulate, colloid and solution phases. When the colloids are inorganic in character the fraction of total actinide activities on the colloid phase is less than one per cent for uranium and < 10% for thorium. In the case of organic colloids/complexes, however, 80-90% of the uranium or thorium load is carried by the colloid phase. In addition, measurements of daughter/parent isotopic activity ratio demonstrate that the uranium associated with the colloid phase is not in chemical equilibrium with that in the groundwater. The transport of colloids is being studied using labelled synthetic colloids in a shallow glacial sand aquifer in which a set of ordered boreholes over a scale of several meters has been established by the British Geological Survey. The stability and transport behavior of these colloids has been established in laboratory column experiments before their use in a field tracer experiment. The implications of this work for modelling radionuclide transport in the geosphere is discussed.

INTRODUCTION

The migration of radionuclides within the geosphere at a radioactive waste repository is largely governed by movement of the groundwater. The transport models used in safety assessment studies typically include the processes of advection, diffusion and retardation by rock/water interactions. However, natural groundwaters contain colloidal particles (size range 0.001-1 μm) which may sorb or complex radionuclides. In addition, colloids with a radionuclide loading may be generated in the near field at a failure of the engineered barriers. Both these processes will affect the radionuclide burden that the flow of groundwater can transport.

Since colloids are much smaller than the pore or fracture sizes in permeable or fractured media, there is a considerable potential for colloid transport. Their large surface area per unit mass makes them effective sorption substrates. Sorption on to the aquifer matrix is governed both by their Brownian motion and by the electrostatic interactions with the matrix surface charges.

In order therefore to predict realistically the effects of mobile colloids on radionuclide migration it is necessary:

- a. to characterize the groundwater colloids present in the far field, and in particular to measure their radionuclide loading,
- b. to assess how the colloids interact with the flux of radionuclides from the near field (both as colloids and as solution species), and
- c. to study colloid stability and transport in relevant water bearing geological formations.

The work described here is concerned mostly with field sampling of groundwater colloids from differing aquifers and their characterization in terms of physical, chemical and actinide composition. In one instance, the measurements at a shallow glacial sand aquifer, together with laboratory column studies are intended to provide the information required to set up a field tracer experiment using synthetic colloids, designed to measure colloid mobility at that site. The results of the tracer field experiments should serve as the basis for setting up a colloid transport model of relevance to radioactive waste safety assessment.

Work on understanding the nature and properties of natural groundwater colloids and their association with radionuclides has only been carried out relatively recently. The subject is complex due to the variety of colloid types based, for example on iron oxides, clay minerals, detrital silica, calcite and organic macromolecules such as humic substances. Radionuclides may form colloids directly (real colloids), or be associated with naturally occurring colloids (pseudocolloids). In addition, their small size and high relative surface area, with consequent high reactivity, (which can lead to aggregation or dissolution under changing chemical conditions), means that great care must be taken in their sampling from aquifers, and in their subsequent characterization in the laboratory.

TECHNIQUES

The activities of the longer lived actinides in the natural decay series originating with ^{238}U , ^{232}Th and ^{235}U , can be measured in mineral phases and in groundwater down to ~ 10 ppt, using isotope dilution/alpha spectrometry. In addition, determinations of daughter/parent activity ratios and their divergence from unity, expected for secular equilib-

rium, will give an idea of the geochemical history of the system studied.

Since the sensitivity limit of alpha spectrometry is often close to the colloid actinide activity levels, it is necessary to concentrate colloidal particles from large volumes of groundwater (10^2 - 10^3 l). This may be achieved using an ultrafiltration system, in the recirculation mode with a sealed atmosphere. Such a system is based on the use of a large area tangential flow ultrafiltration cartridge [1]. In this way, most of the groundwater, containing particles less than the filter cutoff size—the ultrafiltrate, is drawn off. The remaining solution contains the colloids at a higher than natural concentration: the colloid concentrate.

Many techniques have been developed for the physical and chemical characterization of colloids (2 and 3). As a general rule, there are difficulties associated either with the invasive nature of the techniques, or with their application to studies of natural colloids, of relatively low concentration (10^8 - 10^{12} particles/l) and with a broad distribution of particle sizes.

Elemental analysis of geocolloids is conveniently carried out using inductively coupled plasma emission spectrometry (ICPES). An approximate value for the precision in the measurement of concentration for each element can be obtained from the standard deviation determined from measurements on several aliquots of the starting solution. In the case of studies of concentrates of colloids in aqueous solution (ultrafiltrate), analysis of the colloid composition depends upon the difference between measurements on concentrate and ultrafiltrate, and is therefore subject to increased error.

The colloid population may be assessed in terms of colloid size and concentration using Scanning Electron Microscopy (SEM). Although this technique is both simple and direct, it is restricted to particle sizes greater than about 0.05-0.08 μ m. In addition, identification of colloids using Energy Dispersive X-ray Spectrometry (EDX) is limited by the relatively large area from which the X-rays are emitted (~ a few μ ms) and by extraneous scattering from the sample. Both of these difficulties may be overcome using Transmission Electron Spectroscopy (TEM), although sample preparation is then more difficult.

Microelectrophoresis is used to determine the colloid mobility which may be related to the zeta potential [4]. This in turn can give information about the stability since colloids with higher zeta potential would be expected to be more stable.

Before carrying out a field tracer test using synthetic colloids to get a direct measure of colloid transport, it is necessary to assess the hydraulic properties of the matrix in laboratory column experiments. This also serves to develop

and test the preparation, characterization and labelling of monodisperse colloids.

RESULTS

Uranium series disequilibrium studies were carried out at a series of aquifers: slate, granite, glacial sand, sandstone [3], and the sand/sediment layers overlying a salt dome (Gorleben) [5].

The colloids characterized at these aquifers were all inorganic in character, except for those from Gorleben which were organometallic (humic) colloids [6]. The concentrations of inorganic colloids are in the range 10^9 - 10^{11} particles/l as determined from scanning electron microscopy (lower limit ~0.05 μ m). At these levels the sensitivity of ICP/ES measurements is usually insufficient to allow them to be used to determine the elemental composition of the colloids. However, a calculation for the silica colloids from the granite aquifer, leads to a weight concentration of ~50 μ g/l. Apart from silica colloids there is evidence from SEM measurements for the presence of iron oxide and clay mineral colloids.

Laser Induced Photoacoustic Spectrometry (LPAS) has been used to measure groundwater colloid concentrations for sizes down to 1 nm [7]. In the case of the humic colloids, a much higher concentration of 10^{17} particles/l was found [6].

Mean electrophoretic mobility values in the range $-(1$ to $3) \times 10^{-8}$ $\text{m}^2\text{s}^{-1}\text{v}^{-1}$ were obtained, indicating that the colloids in each case were stable and negatively charged [3].

The activity levels for primordial isotopes of uranium (^{238}U) and thorium (^{232}Th) in the groundwaters are in the range 0.4-40 mBq/l (10^{-10} - 10^{-8} mol/l) (U) and 0.004-0.21 mBq/l (4×10^{-12} - 2×10^{-10} mol/l) (Th) for the inorganic colloids (Table I). The corresponding concentrations for the organic colloids are 7.2 mBq/l (U) and 5.8 mBq/l (Th). There is thus a large enrichment of the thorium in the latter, DOC-rich water [6]. Also shown in Table I are the activities of uranium and thorium associated with the colloid (0.001-1 μ m) and particulate phases (>1 μ m).

Table II shows the fraction (in percent) of total activity in the fluid associated with the colloid phase for all the longer-lived actinides. These range from 0.04-0.3% (U) and 0.1-10% (Th) for the inorganic colloids but are very much higher (80-90%) for the organic colloids [6].

The daughter/parent activity ratio $^{234}\text{U}/^{238}\text{U}$ obtained for inorganic colloids and the solution (ultrafiltrate) are indistinguishable (Table III) [3]. This indicates that uranium in the two phases is in chemical corresponding values for the organic groundwater are however markedly different for colloids and solution (Table III) [6]. This suggests that the latter colloids are highly stable, and do not interact appreciably with the groundwater.

TABLE I
Natural Actinide Activity Levels in Grounwater and In Colloid and Particle (> 1µm) Phases.

Aquifer	Colloid Activity		Particle Activity		Total Activity	
	U	Th	U	Th	U	Th
	(mBq/l)					
Slate	0.06	0.001	0.24	0.003	18	0.33
Granite	0.001	0.003	0.005	0.001	0.44	0.10
Glacial sand	0.04	0.002	0.39	0.04	40	0.12
Sandstone	0.001	0.0002	0.0004	0.00005	3.3	0.004
Sand/sediment alluvium (Gorleben GoHy 2227)	6.4	5.4	0.014	0.052	7.2	5.8

TABLE II
Fractions of Total Actinide Isotopic Activities Associated with Colloid Phase

Aquifer	²³⁸ U	²³⁴ U	²³⁰ Th (%)	²³² Th	²²⁸ Th
Slate	0.2*	0.2	3.5	3.3	1.0
Granite	0.3	0.2	9.0	2.9	0.4
Glacial sand	0.1	0.1	2.4	1.6	0.4
Sandstone	<0.04	<0.04	4	9	<0.1
Sand/sediment alluvium (Gorleben GoHy 2227)	88.9 ±1.7	84.2 ±2.3	83.8 ±5.1	92.9 ±12	67.8 ±3.5

* Errors on ²³⁸U, ²³⁴U ~0.1%
²³⁰Th, ²³²Th, ²²⁸Th ~1%

TABLE III
²³⁴U/²³⁸U Activity Ratios for Groundwater Colloid and Solution Phases

Aquifer	²³⁴ U/ ²³⁸ U Activity Ratio Colloids	²³⁴ U/ ²³⁸ U Activity Ratio Solution
Glacial sand	1.4 ± 0.1*	1.39 ± 0.02
Sand/sediment alluvium (GoHy 2227)	1.46 ± 0.03	2.4 ± 0.3

* All errors are lo uncertainties due to nuclear counting statistics only.

Prior to carrying out a field tracer test of colloid mobility at a glacial sand aquifer, samples of monodisperse haematite ($0.5 \mu\text{m}$ and $0.1 \mu\text{m}$ in diameter) were prepared. Laboratory column experiments were carried out using 21.5 cm columns filled with glacial sand and the appropriate natural groundwater (ionic strength $3.51 \times 10^{-3} \text{M}$) [8]. The percentage of colloids transmitted by the column was small ($\sim 1\%$). They emerged at the same time as a nonsorbing species (bromide) implying that the colloids either stuck irreversibly to the sand particles or they did not. Similar experiments using a groundwater of lower ionic strength ($0.91 \times 10^{-3} \text{M}$) gave a larger transmission ($\sim 7\%$) and it was observed that the transmission fraction was inversely proportional to the aggregation rate. Thus, as expected the transmission rate decreased with increasing ionic strength. Further experiments using both latex and natural humic colloids indicated as expected that both the aggregation rate and the fraction sorbed within the column decreased with increasing colloid charge.

DISCUSSION

It is difficult to obtain accurate values for the weight concentration of inorganic colloids in groundwaters from number of particles per unit volume concentrations, since the lower limit of detection is $\sim 0.05 \mu\text{m}$ for most techniques, with the exception of LPAS. In addition the conversion to weight concentration requires identification of the colloid compositions. Attempts have been made (e.g. by Vilks [9]) to determine the weight concentration gravimetrically, and have yielded a value $\sim 170 \mu\text{g/l}$ ($0.01\text{--}5 \mu\text{m}$) for a granitic groundwater [9]; the value reported here ($50 \mu\text{g/l}$ for particles $> 0.05 \mu\text{m}$) is consistent with this result. For the organic colloids at Gorleben the DOC level of the water can be $\sim 100 \text{mg C/l}$, and 80-90% of this is associated with the colloid phase [6].

For inorganic colloids the fractions of total actinide activities associated with the colloid phase are small ($< 0.5\%$ for uranium isotopes) and 1-10% for thorium isotopes. However, in the case of humic colloids $\sim 90\%$ uranium and thorium activities are present on these colloids, and the overall thorium level is $\sim 10\text{--}1000$ times higher than in the inorganic water studies.

Before being able to assess the overall contribution of colloids to radionuclide transport, it is necessary to study the production of additional colloids at a breach in the engineered barriers, as well as how natural colloids interact with the flux of radionuclides released, and to determine colloid transport in the far field.

Preliminary measurements of colloid mobility in laboratory columns of glacial sand provide the basis for the equivalent field tracer experiments using an ordered borehole array. These should be carried out for several aquifer types to get an idea of the range of colloid mobilities.

Groundwater colloids, appear to be capable of transporting a significant proportion of mobile actinides. This is particularly true for humic colloids. Therefore, their presence requires a new approach to modelling radionuclide transport which would treat each rock/water system as a threephase system comprising (1) rock substrate, (2) groundwater/pore water, and (3) colloids. In such a case colloids would be treated as reactive components in a filtration model which would, in turn, be built into a coupled transport/geochemistry model. To provide a rational basis for such a model, the following ought to be considered: aggregation of colloids and attachment to matrix, attachment of metal ions to colloids, interactions between metal ions and dissolved humics, and adsorption of humics on matrix. The future work should address the question of the nature of the threephase interaction processes.

CONCLUSIONS

1. Total actinide activities in groundwater, measured in slate, granite, and glacial sand aquifers are $0.4\text{--}40 \text{mBq/l}$ (U) and $0.004\text{--}0.3 \text{mBq/l}$ (Th). The percentage activities on the colloid phase are: $0.1\text{--}0.4\%$ (^{238}U , ^{234}U), $1\text{--}9\%$ (^{230}Th), $2\text{--}4\%$ (^{232}Th) and $0.1\text{--}1\%$ (^{228}Th).
2. Total actinide activities in organic (humic) rich groundwater are 7.2mBq/l (U) and 5.8mBq/l (Th). Percentage activities on the humic colloid phase are $80\text{--}90\%$ (^{238}U , ^{234}U , ^{230}Th and ^{232}Th) and 70% (^{228}Th).
3. Colloid concentrations in these groundwaters are $10^9\text{--}10^{11}$ particles/l, above the detection limit $\sim 0.05 \mu\text{m}$. The weight concentration of silica colloids in a granitic groundwater $\sim 50 \mu\text{g/l}$.
4. There is evidence that uranium in inorganic groundwater colloids is in equilibrium with that in solution. This has been shown not to be the case for humic colloids.
5. Laboratory column experiments in glacial sand demonstrate that sorption of synthetic colloids increases with increasing ionic strength and decreasing colloid charge. These studies provide the basis for a field tracer measurement of colloid transport, which will yield input parameter values for a colloid transport model.
6. The significance of colloids in radionuclide migration will depend upon the production of additional colloids at a breach of the engineered barriers in a repository, and on the interaction between natural colloids and radionuclides released as soluble species.

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