

Conf-9409212--1

NATURAL ANALOGUE STUDIES OF THE ROLE OF COLLOIDS,
NATURAL ORGANICS AND MICROORGANISMS ON RADIONUCLIDE
TRANSPORT

John F. McCarthy
Environmental Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008, Bethel Valley Road
Oak Ridge, TN 37831-6036, USA

ABSTRACT

Colloids may be important as a geochemical transport mechanism for radionuclides at geological repositories if they are 1) present in the groundwater, 2) stable with respect to both colloidal and chemical stabilities, 3) capable of adsorbing radionuclides, especially if the sorption is irreversible, and 4) mobile in the subsurface. The available evidence from natural analogue and other field studies relevant to these issues is reviewed, as is the potential role of mobile microorganisms ("biocolloids") on radionuclide migration. Studies have demonstrated that colloids are ubiquitous in groundwater, although colloid concentrations in deep, geochemically stable systems may be too low to affect radionuclide transport. However, even low colloid populations cannot be dismissed as a potential concern because colloids appear to be stable, and many radionuclides that adsorb to colloids are not readily desorbed over long periods. Field studies offer somewhat equivocal evidence concerning colloid mobility and cannot prove or disprove the significance of colloid transport in the far-field environment. Additional research is needed at new sites to properly represent a repository far-field. Performance assessment would benefit from natural analogue studies to examine colloid behavior at sites encompassing a suite of probable groundwater chemistries and that mimic the types of formations selected for radioactive waste repositories.

INTRODUCTION

The major pathways and mechanisms of subsurface contaminant migration must be included in models of radionuclide fate and transport if attempts to assess repository performance are to succeed. This paper considers the role of natural analogue studies in evaluating the potential significance of colloidal-size (submicron) particles and natural organic matter (NOM) in radionuclide migration in the far-field outside the engineered barriers of the waste repository. Models of contaminant transport processes typically treat aquifers as a two-phase system with radionuclides partitioning between immobile solids and the mobile aqueous solution. However, evidence suggests that a third phase may exist in groundwater systems in the form of inorganic or organic colloidal material capable of adsorbing or complexing

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

radionuclides and potentially altering the rate and extent of their transport (McCarthy and Zachara 1989; McCarthy and Degueudre 1993).

The term "colloid" is formally defined as suspended material in the size range of 1- μm to 1-nm and can include inorganic materials, including mineral fragments (layer silicates, oxides, and other weatherable mineral phases) and mineral precipitates (notably iron, aluminum, and manganese oxides, hydroxides, carbonates, silicates, and phosphates, but also including colloids produced by processes of nucleation and growth of radionuclide species); "biocolloids" (bacteria and viruses); as well as NOM and other organic compounds and degradation products associated with low- and intermediate-level waste (L/LIW) streams. The emphasis on size as a criteria for defining "colloids" is somewhat problematic since measurement of fine particles is difficult. Operationally-defined size limits based on filter cut-off sizes are often used as a basis of identifying colloidal material in groundwater. However, it may be appropriate to replace the focus on operational definitions of colloid size (as will be discussed, radionuclides can complex with NOM that passes through a 1-nm filter), with an emphasize on the more fundamental issue of the geochemical transport mechanism for radionuclides. The significance of a "third phase" capable of altering radionuclide transport is more properly defined in terms of the question: What is the physicochemical form of the radionuclide in groundwater? Is the radioelement present as an ionic species (the typical assumption for modeling), or is it either: (1) adsorbed to a inorganic colloid (or existing as a homogeneous radiocolloid); (2) adsorbed to a bacteria or virus suspended in groundwater; or (3) complexed with NOM? Any of the latter three examples of radionuclide association with a "third phase" involve geochemical transport mechanisms that would invalidate modeling of radionuclide mobility as solute transport.

Existing scientific information is not sufficient to allow long-term predictions of abundance and distribution of colloidal particles in groundwater, colloid formation or mobilization under conditions typical of natural aquifers or waste repository sites, or colloid mobility in subsurface systems. Therefore, field studies at natural analogue sites are critical to determine the potential significance of colloids in the far-field environment. The far-field is emphasized because it appears to be generally assumed that compacted bentonite and other engineered barriers will minimize colloid advection from the waste package. However, the cement in barriers, backfill and encapsulation used for most L/LIW (and some transuranic) repositories are expected to produce colloids as they degrade, and little is known about the mechanisms of generation or transport of these colloids, or their potential significance to repository performance. Figure 1 identifies some of the key issues that will dictate the potential significance of colloids on repository performance. Generally, if colloids are absent, immobile, or do not adsorb radionuclides, they will not be significant to repository performance. The existing data from natural analogue studies that address these key issues will be discussed below. Although most studies have focused on inorganic colloids and NOM, the potential role of microorganisms on radionuclide transport in groundwater will be discussed later in this paper. Finally, general conclusions and uncertainties will be identified. The interested reader is also referred to reviews of

colloids in natural analogue studies presented in Ivanovich et al. (1992) and Miller et al. (1994).

NATURAL ANALOGUE STUDIES INVOLVING COLLOIDS AND NOM

Operational difficulties confound almost all studies of colloids in groundwater. For example, the act of sampling can affect the nature and amount of colloids and particles recovered, and changes in thermodynamic conditions during sample recovery (e.g., introduction of oxygen or degassing of carbon dioxide) can produce colloidal artifacts. A detailed description of colloid sampling and analysis techniques is given in McCarthy and Degueudre (1993). Despite these difficulties, a number of studies have sampled colloids with the goal of assessing their potential impact on radionuclide transport. Results will be discussed in terms of a hierarchy of questions such as that identified in Figure 1.

Are Colloids Present? -- The presence of colloids has been examined at a fairly large number of subsurface environments, especially in the last few years since the potential role of colloids has been highlighted and more reliable methods for colloid sampling and characterization have been devised. The data base of colloid studies has been tabulated in McCarthy and Degueudre (1993). A number of studies have focused on groundwater environments considered analogues for geological repositories, including granitic formations in Switzerland, Germany, Sweden and France (Degueudre et al. 1987, 1989a, 1989b, 1990; Schlotis et al. 1993; Brutsch and Degueudre 1991; Alexander et al. 1990; Billion et al. 1991; Laaksoharju and Degueudre 1994), rhyolitic tuffs in Nevada (Buddemeier and Hunt 1988; Buckholz ten Brink et al. 1992; Kingston 1989), sedimentary deposits in Germany (Kim et al. 1984), and natural ore deposits in Brazil, Australia and Canada (Miekeley et al. 1991, 1992; Short et al. 1988; Ivanovich et al. 1988; Vilks et al. 1993). Although it is not yet possible to reliably predict the nature and abundance of colloidal particles as a function of the chemical, hydrological and mineralogical properties in a range of subsurface environments, some general relationships are beginning to develop (McCarthy and Degueudre 1993).

- Colloids appear to be ubiquitous. Although concentrations are extremely low in some systems (as low as $1-25 \mu\text{g L}^{-1}$), there is no study which demonstrates the absence of colloidal particles.
- Colloid concentrations appear to be lowest in deep, geochemically stable subsurface environments; shallow aquifer systems generally appear to have higher colloid concentrations even in the absence of geochemical instabilities.
- Regardless of the geology or depth of the geological system, higher levels of colloids are routinely associated with some hydrogeochemical perturbation. For example, in studies of a series of fractured granitic systems, colloid concentrations are 20 to 1000-fold higher in ground-water zones affected by inputs of surface water or in hydrothermal zones with large temperature and pressure gradients, compared to stable hydrogeochemical systems (Degueudre 1994). In fractured rhyolitic tuffs, colloid concentrations were several-fold higher in locations affected

by underground nuclear testing, compared to locations with similar geology but remote from the test site (Buddemeier and Hunt 1988; Buckholz ten Brink et al. 1992). Disturbances occurring on longer geological time scales can also affect colloids. A reducing ground water resulting from microbial metabolism of NOM beneath a swamp was associated with increased levels of colloids, compared to oxic zones in adjacent formations (Ryan and Gschwend 1990).

- In most cases, the composition of the colloids observed in different subsurface systems "makes sense" in terms of the geology of the formation and the nature of the geochemical perturbations. In fractured granitic systems, the observed silica and clay/mica colloids would be consistent with production of primary and secondary minerals from geochemical alteration of the parent rock, and colloids in volcanic tuffs appear to be constituents of the parent rock and alteration products. Particles in a sandstone/uranium ore formation are composed of fracture-filling minerals characteristic of the host rock.

The implications of these relationships to repository performance is significant. Assessment of the role of colloids in the dissemination of radionuclides cannot be limited to consideration of the "background" population of colloids existing prior to development of the repository. Performance evaluation needs to reflect the potential for generating new types or increased concentrations of colloids by alteration of geochemical conditions as a result of disturbances arising from the near-field environment. For example, the hyperalkaline front emerging from a degrading cementitious repository may produce colloids, as will the redox front moving away from a corroding steel canister in a high-level water repository. The redox front may pass through the bentonite into the bentonite/host rock interface as well. In addition to localized effects associated with the repository, global climatic changes could affect ionic strength and composition of recharge water, inputs of organic matter, and other factors controlling colloid formation, stability and transport.

Are Colloids Stable? -- This question encompasses two separate issues: *colloidal* stability (are the colloids suitably charged to avoid aggregation or attachment to aquifer surfaces), and *chemical* stability (colloid formation and dissolution). Studies measuring the electrophoretic mobility of colloids recovered from groundwater have found that they have fallen within a relatively small range of negative values. These data suggest that the colloids carry a large negative charge and would, therefore tend to be stable in groundwaters (Longworth et al. 1989a, 1989b; Longworth and Ivanovich 1989; Degueldre et al. 1989a, 1989b; Dearlove et al. 1990a, 1990b; Liang et al. 1993). These observations include colloids such as iron oxide, which at the groundwater pH would be expected to have a strong positive charge; the charge reversal has often been attributed to coatings of NOM on the oxide surface (Longworth et al. 1989a; Miekeley et al. 1990; 1992; Liang et al. 1993). It should be noted that even low concentrations of NOM can bring about reversal of surface charge, suggesting that concentrations of NOM in groundwater may be able to stabilize radiocolloids expected to be inherently unstable in groundwater. For

example, stable suspensions of negatively-charged ferrihydrite were formed following introduction of oxygen into a shallow sandy aquifer. The groundwater had a neutral pH and contained concentrations of only 0.5 mg-C/L of NOM, all of which was < 1-nm in size based on ultrafiltration (Liang et al. 1993). The frequent observation of iron hydr(oxide) colloids in groundwaters of pH below the expected ZPC of iron oxides, such as Alligator Rivers and Poços de Caldas, suggests that NOM or inorganic anions (such as silicate) may be important in promoting colloidal stability.

The chemical stability of colloids (i.e., considering colloid formation and dissolution) over long times is more difficult to assess directly. Erosion of fracture-lining mineral (formed by geochemical alteration of primary minerals along fractures or by mechanical crushing) is postulated as the source of colloids in many formations (McCarthy and Degueldre 1993; Vilks et al. 1991, 1993). It is reasonable to expect that colloids can form or disappear due to advection into zones with different geochemical conditions. For example, iron oxide particles recovered from groundwater at the Osamu Utsumi mine were thought to be generated at depth by the upflowing, reducing waters, and not by downward migration of material from the surface during rainfall (Miekeley et al. 1990, 1992). The presence of ferrous phosphate colloids downgradient from a sewage infiltration site is consistent with equilibrium solubility calculations suggesting supersaturation with respect to this product within a plume of phosphate (from detergents in the sewage) flowing through an iron-rich aquifer (Gschwend and Reynolds 1987). Similar processes were postulated at a natural analogue site. Uranium colloids were found at Alligator Rivers, yet dissolved uranium concentrations were far below saturation for any U(VI) species. It was suggested that U-colloids could only form by precipitation in pockets of supersaturation, which might only occur where groundwater is in contact with U-rich rock for extended periods. Colloids formed by such a process would be short-lived since they would become unstable as soon as the water pocket moved away from the rock and mixed with generally more oxidizing groundwater (Miller et al. 1994).

Do Colloids Take Up Radionuclides and Is Uptake Reversible? -- Two types of analogue studies address these issues: "traditional" analogue studies involving geological formations containing naturally-occurring radionuclides or their analogues, and "anthropogenic" analogue sites created by disposal of radionuclides or by nuclear detonations. The latter studies, while providing little information about the long-term geological behavior of radionuclides, do provide information on processes relevant to speciation and transport in physically and chemically heterogeneous natural systems over periods of 25- to 50 years. The results of both types of studies clearly indicate that radionuclides do associate with colloidal species. For example, in studies at Cigar River (Vilks et al. 1993), Whiteshell Research Area (Vilks et al. 1991), Alligator Rivers (Ivanovich et al. 1988; Short et al. 1988; Seo et al. 1992), Grimsel, Reskajeage and Drigg (Longworth et al. 1989a) and Poços de Caldas (Miekeley et al. 1990; 1992), both uranium and thorium were associated with the colloidal phase. As might be expected, of the total concentrations of these radionuclides in the groundwater, the colloids accounted for a much larger fraction of the less soluble

thorium, compared to only a few percent of the uranium. Rare earth elements (REE) show an affinity for colloids that is intermediate between uranium and thorium (Miekeley et al. 1990, 1992). Cobalt, cerium and europium were associated with inorganic colloids outside a nuclear detonation cavity at the Nevada Test Site (Buddemeier and Hunt 1988). Plutonium and americium were adsorbed to colloids in an alluvial aquifer three kilometers downgradient from a liquid waste outfall at Los Alamos National Laboratory. Humic colloids in Gorleben contained large numbers of trace heavy metals that are natural homologues of actinides and some fission products, and association of americium with humics was demonstrated (Kim et al. 1984). Champ et al. (1984) concluded that a number of radionuclides (including Co, Ce, Cs, Eu, Sb, Zr, Fe, Ni, I, Pu and possibly Am) in waste plumes at Chalk River Nuclear Laboratories were associated with organic ligands. The exception to the common observation of radionuclide association with colloids was in the hyperalkaline groundwaters at the Maqarin area of Jordan, where it was shown that uranium was not associated with colloids (Alexander 1992).

Alpha-emitting radionuclides, probably americium and curium, in groundwater downgradient of disposal trenches at the Oak Ridge National Laboratory appear to be associated with low molecular weight components of NOM. All the NOM and alpha-radioactivity pass through a 1-nm (3000 mol. wt.) filter. Although this size fraction is generally considered "dissolved" rather than colloidal, the <1-nm groundwater NOM could be isolated by adsorption on DEAE-cellulose anion exchange media. Step input of base mobilized the NOM from the column. The radioactivity co-eluted with the NOM, suggesting that the radionuclides were complexed with the NOM in the groundwater. In laboratory studies, ^{241}Am in a solution free of NOM was input to the DEAE column; the radionuclide did not elute with base but could be eluted with acid (J. F. McCarthy and J. D. Marsh, Oak Ridge National Laboratory, unpublished data). These results suggest that 1-nm may not always be an appropriate size cut-off for defining "colloidally-bound" radionuclides, especially when complexation with organics is possible. For example, at Alligator Rivers, the ^{230}Th and ^{232}Th in the "dissolved" phase (operationally defined as <18-nm in that study) was two- to three orders of magnitude above the solubility limit, probably because of trace organic complexation (Short et al. 1988). Association of radionuclides with even low molecular weight NOM has the potential to invalidate thermodynamic modeling based on assumptions that radionuclides passing through certain filter sizes are truly ionic species.

Evidence of reversibility of binding of radionuclides to colloids is based largely on data from uranium-series disequilibrium studies. It should be noted, however, that interpretation of data concerning the reversibility of adsorption can be controversial since it is difficult to distinguish processes of adsorption versus precipitation. Furthermore, it is not clear to what extent the composition of the interior of a particle (which may not interact with the water) biases interpretation of adsorption phenomena at the particle-water interface. While underlying mechanisms may be difficult to distinguish, natural analogue studies can help evaluate the extent of exchange of radionuclides between colloidal and aqueous phases in groundwater.

The $^{234}\text{U}/^{238}\text{U}$ activity ratios for solution and *inorganic* colloidal phases are generally very similar, indicating that uranium in the two phases is in equilibrium (Longworth et al. 1989a, 1989b; Longworth and Ivanovich 1989; Degueldre et al. 1989; Dearlove et al; 1990a, 1990b). In contrast, corresponding activity ratios for humic colloids at Gorleben are significantly different, suggesting that the U bound to the humic colloids do not interact significantly with the groundwater. In studies along flow paths from uranium ore deposits, the U activity ratios of the solution and colloidal phases are similar near the ore bodies and diverge downgradient with a significant rise only in solute activity ratios. Colloids having lower ratios than groundwater probably contain ^{238}U inherited from the rock matrix (Vilks et al. 1993; Short et al. 1988). Generally, $^{230}\text{Th}/^{234}\text{U}$ ratios in solution are very low because of the low solubility of Th. Colloidal $^{230}\text{Th}/^{234}\text{U}$ ratios are also generally well below 1.0, indicating that ^{234}U had not been sorbed onto particles long enough for ^{230}Th to come into secular equilibrium with its parent (Vilks et al. 1991, 1993; Short et al. 1988; Longworth et al. 1989a). Short et al. (1988) noted that in transects of wells at Alligator Rivers, the ^{232}Th levels were independent of ^{230}Th levels and locations. Since the ^{232}Th is ubiquitous and present before any radiogenic thorium is available for solution, this isotope dominates the trace equilibrium processes of adsorption/precipitation and complexation. These authors suggested that there was considerable hysteresis in the process of thorium adsorption on colloids. Additional evidence for limited desorption of strongly adsorbed radionuclides was presented by Penrose et al. (1990). Plutonium and about half of the americium associated with groundwater colloids did not undergo significant exchange over a period of several days after solutions were spiked with other isotopes of the same elements.

In summary, colloids appear to be capable of binding a large number of radioelements and sorption appears to be generally inversely related to solubility. Solution and colloidal phases appear to be in equilibrium for weakly adsorbing species such as uranium, suggesting its binding is readily reversible. There is evidence suggesting that more strongly adsorbed elements such as thorium, and possibly plutonium, are not in equilibrium with the solution phase and that the association of the radionuclide with colloids is not readily reversible.

Are Colloids Mobile? -- There is evidence both for and against the transport of colloids. Much of the data suggesting that colloids are mobile derive from observations of movement of radionuclides downgradient of an "anthropogenic" source. Coles and Ramspott (1982) found much more rapid migration of ruthenium in the field than expected from batch adsorption studies. A well 91 m from a nuclear detonation cavity at the Nevada Test Site was pumped to induce flow into the well from the cavity. No radioactivity was observed for 2 years, but, with further pumping, the concentration of both ^3H (a nonreactive tracer of water flow) and ^{106}Ru increased at the same rates, suggesting that both traveled at the same velocity from the detonation cavity. Laboratory measurements of the equilibrium sorption coefficient (K_d) for Ru with rock and water from the site predicted that the Ru should have traveled 30,000-fold slower than the ^3H -water (i.e., the Ru should have moved

only 3 cm during the time the ^3H -water migrated 91 m) (Coles and Ramspott 1982). Although laboratory K_d 's have proven to be poor predictors of field behavior, the unretarded transport of Ru contrasts with its expected behavior as a solute, suggesting that colloids may have been involved in its transport. Also at the Nevada Test Site, Buddemeier and Hunt (1988) demonstrate the presence of inorganic colloidal particles (3 to 50 nm) with sorbed transition metals (manganese and cobalt) and lanthanide (cerium, europium) radionuclides. The colloids were recovered from ground water inside a nuclear detonation cavity and also from a well in a permeable fractured lava and tuff formation 300 m from the cavity. Plutonium and americium were associated with siliceous colloids (25-450 nm) in a shallow alluvial aquifer at Los Alamos National Laboratory (Penrose et al. 1990). Filterable particles (>400 nm) containing radionuclides of Co, Zr, Ru, Cs, and Ce were recovered from contaminant plumes in ground water at the Chalk River Nuclear Laboratory (Champ et al. 1984).

Additional evidence of long-distance subsurface transport of natural colloids was obtained in a fractured formation at Menzenschwand in the Black Forest of Germany. The Mg:Ti ratio and REE signature of colloids recovered from the granite groundwater differed significantly from that of the host granite, but appeared to reflect that of a neighboring gneiss several kilometers upgradient (Alexander et al. 1990).

Other data suggest that colloid transport is quite limited. At the Cigar River uranium deposit site, U and Ra contents of colloids in the ore and surrounding clay zones are significantly higher than in colloids from the sandstone, suggesting the clay is an effective barrier to colloid migration (Vilks et al. 1993). Similar results at Alligator Rivers and Morro de Ferro also suggest that colloids have a limited capacity for migration since the concentrations of colloid-bound radionuclides outside the ore body are low (Miekeley et al. 1992; Ivanovich et al. 1988; Short et al. 1988).

Some cautions should be noted in interpreting any of these data. Nuclear detonations at the Nevada Test Site undoubtedly promoted fracturing of the formation, and the extensive transport at the Los Alamos site involved a permeable alluvial aquifer. The long distance transport at the Menzenschwand site should perhaps also not be over-emphasized as the flow system is unusual (relatively wide, coated fractures) and the presence of the mine induced fast groundwater flow. Conversely, the studies showing limited transport are also not perfect analogues for the far-field environment. The reduction in colloid migration by the clay halo around the Cigar Lake ore deposit suggest that engineered barriers of clay may be effective, but says less about the potential role of colloids for transport of radionuclides once they reach the far-field environment. Likewise, although the Morro de Ferro study concluded that colloids were not transported, the ore zone lies in the unsaturated zone, and this must obviously affect the degree of retention of colloids in the system. Unfortunately, the general conclusions of these studies must be that no conclusion concerning the movement of colloids is proven.

ROLE OF "BIOCOLLOIDS" (Bacteria and Viruses) ON RADIONUCLIDE TRANSPORT

Microbiota can be significant at geological repositories and concern about their effect on corrosion of the waste form and engineered barriers is real. However, this paper will address another microbial issue: concern that bacteria and viruses can adsorb radionuclides and potentially enhance radionuclide migration if the biocolloids are mobile in the far-field environment. Bacteria have been shown to biosorb metals and radionuclides, probably due at least in part to the presence of polysaccharides in cells walls that undergo ion exchange with metals in solution. Available evidence suggests that different species of bacteria can exhibit wide variations in biosorption capacity. However, for at least some microorganisms including common soil bacteria, biosorption capacity for thorium is comparable in magnitude to thorium sorption to groundwater colloids (Tsezos and Volesky 1981). Given the fact that autochthonous microbial populations exist in host formations and that repository construction is likely to introduce additional biomass, the potential role of microbes as vectors for radionuclide transport cannot be dismissed *a priori*.

Transport of microorganisms includes processes that govern transport of inorganic colloids (size, shape, surface charge), as well as additional biological processes. Secretion of exocellular polysaccharides can increase "stickiness" of bacteria and make detachment more difficult, while sloughing of daughter cells from attached bacteria can promote advection of bacterial biomass. Bacteria can alter their transport properties (changes in size or surface characteristics) in response to environmental conditions, further complicating predictions of the rate and extent of biocolloid migration.

Field data suggest that transport of biocolloids can occur very rapidly and over long distances, in at least some locations. The mechanism of transport in these cases may involve travel through highly transmissive zones of preferred flow. For example, bacteria injected into ground water have been reported to travel up to 920 m at rates of 200 to 350 m d⁻¹, and viruses injected into a well migrated 680 m downgradient at a rate estimated between 36-180 m d⁻¹ (Keswick et al. 1982). Yeast cells injected into a well moved 7 m in a sand and gravel aquifer in less than 48 h, and moved faster than nonreactive tracers of ground-water flow such as iodide and bromide (Wood and Ehrlich 1978). Likewise, Harvey et al. (1989) observed that bacteria injected into a sandy aquifer eluted slightly ahead of the nonreactive tracer. Of perhaps greater relevance to repository environments, McKay et al. (1993) demonstrated that viruses (bacteriophage, 26- to 65-nm diameter) were transported rapidly in a low permeability clay-rich till (hydraulic conductivity of 10⁻¹⁰ to 10⁻⁶ m s⁻¹). In this trench-to-trench tracer migration study, phage were detected in seepage collectors in a downgradient trench 4-m from the source trench with 1-2 days. The large contrast in the transport velocity of the phage (2- to 5-m d⁻¹) and the bromide tracer (0.01- to 0.07-m d⁻¹) was attributed to extensive diffusion of the solute, but not the phage into the pore water of the clay matrix. Only a small fraction of the viruses were recovered, however. The attenuation was attributed to biological inactivation of the phage and, more importantly, to attachment to fracture walls and diffusion into larger pores.

These short-term field observations may be of limited significance to deep geological repositories. The U.S. Department of Energy's Subsurface Science Program is initiating a more relevant field study on microbial transport and microbial ecology in deep subsurface environments at the Cerro Negro site in the Rio Puerco area of New Mexico (USDOE 1994). The goals of the study are to determine the mechanisms and environmental conditions by which microorganisms are maintained in the subsurface for extended periods, as well as the mechanisms and conditions by which they are transported through the deep subsurface over long periods and distances. At the Cerro Negro site, a volcanic intrusion penetrated through a thick Cretaceous sequence of marine sediments that included low permeability shale with interbedded tongues of sandstone. The heat from the igneous intrusion 3.4 million years ago would have sterilized the rock near the intrusion and created a gradient along which there may have been differential survival of any microorganisms present. Once the sediments around the intrusion became saturated again, recolonization may have occurred if 1) suitable microbial inoculum and transport vectors existed, 2) physical parameters permit microbial transport, and 3) geochemical conditions in the altered zone support microbial populations. The purpose of the research is to determine if the sterilized sediments are still sterile or if microorganisms have been able to re-establish themselves in the last several million years. Results may be relevant to assessing microbial activity, survival and transport at nuclear repositories.

SUMMARY AND CONCLUSIONS

Thus far, natural analogue studies have demonstrated that many radioelements or their analogues do adsorb to organic and inorganic colloids present in groundwater. Field studies of groundwater colloids suggest that colloids are ubiquitous. However, colloid concentrations, especially in geochemically stable deep groundwaters, appear to be quite low and may be insufficient to affect radionuclide transport (Vilks et al. 1993; Smith 1993; Smith and Degueldre 1993). Even if colloid populations are low, they may have the potential to affect radionuclide transport if the colloids are stable (with respect to both colloidal and chemical stability), if adsorption onto them is irreversible, and if physical transport pathways exist in the formation surrounding the repository.

The very fact that colloids can always be found in every site sampled suggests that colloids are stable, with rates of colloid loss balanced by colloid generation. Of potentially greater concern is the effect of geochemical changes on colloid formation in the far-field environment. Several studies have documented significant increases in colloid abundance in both deep and shallow systems affected by altered geochemical conditions (McCarthy and Degueldre 1993). Such changes could result from advection across groundwater interfaces, or be induced either anthropogenically by the disturbances originated from the repository, or naturally due to unforeseeable geological or climatic changes.

Concern about the effect of colloids is not diminished by uranium-series disequilibrium studies that suggest the strongly adsorbing radionuclides such as thorium are not readily desorbed over long periods. Significant hysteresis in

adsorption/desorption could significantly accelerate contaminant migration; the transport of the contaminant would then be strongly dependent on the extent of colloid-aquifer media interaction (Smith and Degueudre 1993).

Field studies to date have not been notably successful in proving or disproving the potential of colloids for transport. Examples of analogue sites where colloid mobility seems limited (e.g., Cigar Lake and Morro de Ferro) are balanced by other examples demonstrating transport in fractured formations (Menzenschwand) and a clay till (McKay et al. 1992).

Additional research is needed at new sites to properly represent a repository far-field. As noted by Miller et al. (1994), different basement groundwaters exist at many sites. In Swiss granites, water chemistry ranges from deep reducing NaCl-type water to shallower oxidizing Ca-HCO₃-type waters. Likewise, inhomogeneities in groundwater compositions exist at the UK Sellafield site and the Precambrian Fennoscandian Shield, and colloids crossing these boundaries may become unstable. Performance assessment would benefit from natural analogue studies to examine colloid behavior at sites encompassing a suite of probable groundwater chemistries and that mimic the types of formations selected for radioactive waste repositories.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the help and insights of R. Alexander and C. Degueudre. Support was provided by the Subsurface Science Program, Environmental Sciences Division, Office of Health and Environmental Research, U.S. Department of Energy (U.S. DOE), and the encouragement of the Program Manager, F. J. Wobber, is gratefully acknowledged. The Oak Ridge National Laboratory (ORNL) is managed by Martin Marietta Energy Systems, Inc., under Contract No. DE-AC05-84OR21400 with the U.S. DOE.

REFERENCES

Alexander, W. R. (editor) "A Natural Analogue Study of Cement Buffered Hyperalkaline Groundwaters and their Interaction with Sedimentary Host Rock," Nagra Technical Report NTB 91-10, Nagra, Wettingen, Switzerland (1992).

Alexander, W. R., R. Brüttsch, C. Degueudre, and B. Hofmann. "Evaluation of Long Distance Transport of Natural Colloids in a Crystalline Groundwater," Paul Scherrer Institute, Internal Report, TM-43-90-20 (1990).

Billion, A., M. Caceci, G. Della Mea, T. Dellis, J. C. Dran, V. Moulin, S. Nicholson, J. C. Petit, J. D. F. Ramsay, P. J. Russell, and M. Theyssier. "The Role of Colloids in the Transport of Radionuclides in Geological Formations," Nuclear Science and Technology, Commission of the European Communities, CEC Report: EUR 13506 EN (1991).

Brüttsch, R., and C. Degueudre. "Kolloide von Mineralwasser Eglisau III. Probenahme und Charakterisierung Phase 2," Paul Scherrer Institute, Internal Report TM-43-90-38, Würenlingen and Villigen, Switzerland (1990).

Brütsch, R., C. Degueldre, and H. J. Ulrich. "Kolloide im Thermalwasser von Bad Zurzach," Paul Scherrer Institute, Internal Report TM-43-91-19 (1991).

Buchholtz ten Brink, M. S. Martin, B. Viani, D. K. Smith, and D. Phinney. "Heterogeneities in Radionuclide Transport: Pore Size, Particle Size, and Sorption," *Concepts in Manipulation of Groundwater Colloids for Environmental Restoration*, J. F. McCarthy and F. J. Wobber, Eds. (Chelsea, MI: Lewis Publishers, Inc., 1992).

Buddemeier, R. W., and J. R. Hunt. "Transport of Colloidal Contaminants in Groundwater: Radionuclide Migration at the Nevada Test Site," *Appl. Geochem.* 3(5):535-548 (1988).

Champ, D. R., J. L. Young, D. E. Robertson, and K. H. Abel. "Chemical Speciation of Long-Lived Radionuclides in a Shallow Groundwater Flow System," *Water Pollut. Res. J. Can.* 19(2):35-54 (1984).

Coles, D. G., and L. D. Ramspott. "Migration of Ruthenium-106 in a Nevada Test Site Aquifer: Discrepancy Between Field and Laboratory Results," *Science* 215(5): 1235-1237 (1982).

Dearlove, J. P. L., G. Longworth, and M. Ivanovich. "Improvement of Colloid Sampling Techniques in Groundwater and Actinide Characterization of the Groundwater System at Gorleben (FRG) and El Berrocal (E)," Harwell Laboratory, United Kingdom Atomic Energy Authority-AEA D&R 0066 (1990).

Dearlove, J.P.L., G., Longworth, M. Ivanovich, J.-I. Kim, B. Delakowitz, and P. Zeh. Sampling and characterisation of groundwaters at the Gorleben site FRG. Phase 1: Results for groundwaters GoHy 2227 and GoHy 1231. AEA Report D&R 0059 (1990b).

Dearlove, J.P., 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. In *Radiochimica Acta.*, 52/53, 83-89 (1991).

Degueldre, C. "Colloid Properties in Groundwater from Crystalline Formations," NAGRA NTB 92-05 and Paul Scherrer Institute, Report, Würenlingen and Villigen, Switzerland (1994).

Degueldre, C., G. Longworth, V. Moulin, P. Vilks, C. Ross, G. Bidoglio, A. Cremers, J. Kim, J. Pieri, J. Ramsay, B. Salbu, and U. Vuorinen. "Grimsel Colloid Exercise: An International Intercomparison Exercise on the Sampling and Characterization of Groundwater Colloids," Paul Scherrer Institute, Internal Report TM-36, Würenlingen and Villigen, Switzerland (1989a).

Degueldre, C., B. Baeyens, W. Görlich, J. Riga, J. Verbist, and P. Stadelmann. "Colloids in Water from a Subsurface Fracture in Granitic Rock, Grimsel Test Site, Switzerland," *Geochim. Cosmochim. Acta.* 53:603-610 (1989b).

Degueldre, C., R. Keil, M. Mohos, B. Van Eygen, and B. Wernli. "Study of the Leuggern Groundwater Colloids," Paul Scherrer Institute, Internal Report TM-43-90-69, Würenlingen and Villigen, Switzerland (1990).

Degueldre, C., and B. Wernli. "Characterization of the Natural Inorganic Colloids from a Reference Granitic Ground Water," *Anal. Chim. Acta.* 195:211-223 (1987).

Gschwend, P. M., and M. D. Reynolds. "Monodisperse Ferrous Phosphate Colloids in an Anoxic Groundwater Flume," *J. Contam. Hydrol.* 1:309-327 (1987).

Harvey, R. W., L. H. George, R. L. Smith, and D. R. LeBlanc. "Transport of Fluorescent Microsphere and Indigenous Bacteria Through a Sandy Aquifer: Results of Natural- and Forced-Gradient Tracer Experiments," *Environ. Sci. Technol.* 23:51-56 (1989).

Ivanovich, M., P. Duerden, T. Payne, T. Nightingale, G. Longworth, M.A. Wilkins, S.E. Hasler, R.B. Edgehill, D.J. Cockayne, and B.G. Davey. Natural analogue study of the distribution of uranium series radionuclides between the colloid and solute phases in the hydrogeological system of the Koongarra uranium deposit, Australia. (ed. Harwell). (1988).

Ivanovich, M. A. G. Latham, G. Longworth, and M. Gascoyne. "Applications to Radioactive Waste Disposal Studies", *Uranium-series Disequilibrium: Applications to Earth, Marine and Environmental Sciences*, M. Ivanovich and R. S. Harmon, Eds. (Oxford: Clarendon Press, 1992).

Keswick, B. H., D. S. Wang, and C. P. Gerba. "The Use of Microorganisms as Groundwater Tracers: A Review," *Ground Water* 20:142-149 (1982).

Kim, J. I., G. Buckau, F. Baumgartner, H. C. Moon, and D. Lux. "Colloid Generation and the Actinide Migration in Gorleben Groundwaters," *Mater. Res. Soc. Symp. Proc.* 26:31-40 (1984).

Kingston, W. L. "Characterization of Colloids Found in Various Groundwater Environments in Central and Southern Nevada," M.S. Thesis, University of Nevada, Reno, NV (1989).

Laaksoharju, M., and C. Degueldre. "Colloids from the Swedish Granitic Groundwater," SKB-Technical Report; in press (1994).

Liang, L., J. F. McCarthy, L. W. Jolley, J. A. McNabb, and T. W. Mehlhorn. Iron dynamics: transformation of Fe(II)/Fe(III) during injection of natural organic matter in a sandy aquifer. *Geochim. Cosmochim. Acta*, 57:1987-1999 (1993).

Lieser, K. H., B. Gleitsmann, and Th. Steinkopff. "Colloid Formation and Sorption of Radionuclides in Natural Systems," *Radiochim. Acta.* 40:39-47 (1986).

Longworth, G. and M. Ivanovich. (1989), The Sampling and Characterisation of Natural Groundwater Colloids: Studies in Aquifers in Slate, Granite and Glacial Sand. (Harwell Laboratory Ukaea), *Safety Studies Nirex Radioactive Waste Disposal*

Longworth, G., C. A. M. Ross, C. Degueldre, and M. Ivanovich. "Interlaboratory Study of Sampling and Characterization Techniques for Groundwater Colloids," Harwell Laboratory Report AERER-13393 (1989a).

Longworth, G., M.A. Wilkins, and M. Ivanovich. Characterisation of natural colloids in a shallow glacial aquifer and their radionuclide leaching (ed. W. Lutze and R.C. Ewing). In *Mat. Res. Soc. Symp. Proc.*, 127, 755-61 (1989b).

McCarthy, J. F., and J. M. Zachara. "Subsurface Transport of Contaminants," *Environ. Sci. Technol.* 23(5):496-503 (1989).

McCarthy, J. F. and C. Degueldre. 1993. Sampling and characterization of groundwater colloids for studying their role in the subsurface transport of contaminants. IN J. Buffle and H. van Leeuwen (Eds.) Environmental Particles, Volume II. Lewis Publishers, Chelsea MI. Chapter 6, pp. 247-315.

McKay, L.D., J.A. Cherry, R.C.Bales, Y.T. Moyasar, and C.P. Gerba. A Field Example of Bacteriophage as Tracers of Fracture Flow. In *Environ. Sci. Technol.*, 27, 1075-1079 (1993).

Miekeley, N., H. Coutinho de Jesus, C. Porto da Silveira, and C. Degueldre. "Chemical and Physical Characterization of Suspended Particles and Colloids in Water from Osamu Utsumi Mine and Morro do Ferro Analog Study Sites," NAGRA (NTB 90-27), SKB (TR 90-18), Poços de Caldas, Brazil. NAGRA Technical Report NTB 90-27 (Wettingen, Switzerland, and SKB Report TR-90-18 (Stockholm, Sweden) (1991).

Miekeley, N., H. Coutinho de Jesus, C.L. Porto da Silveira, and C. Degueldre, (1992). Chemical and physical characterization of suspended particles and colloids in waters from the Osamu Utsumi mine and Morro do Ferro analogue study sites, Pocos de Caldas, Brazil (Elsevier Science Publishers). In *Journal of Geochemical Exploration.*, 45, 409-437.

Miller, W., R. Alexander, N. Chapman, I. McKinley, and J. Smellie. 1994. Natural Analogue Studies in the Geological Disposal of Radioactive Wastes" (1994). ed Elsevier, *Studies in Environmental Science* 57.

Penrose, W. R., W. L. Polzer, E. H. Essington, D. M. Nelson, and K. A. Orlandini. "Mobility of Plutonium and Americium Through a Shallow Aquifer in a Semiarid Region," *Environ. Sci. Technol.* 24(2):228-234 (1990).

Ryan, J. N., Jr., and P. M. Gschwend. "Colloid Mobilization in Two Atlantic Coastal Plain Aquifers," *Water Resour. Res.* 26(2):307-322 (1990).

Schlotis, A., Degueldre, A. Laube and P. Gorez. Colloid Characterization and Geochemical Modeling of Groundwaters from a Potential Radioactive Waste Repository Site in Central Switzerland. Fourth International Conference on the Chemistry and Migration of Actinides and Fission Products in the Geosphere, Charleston, South Carolina (1993).

Seo, T, R. Edis, and T.E. Payne. A Study of Colloids in Groundwaters at the Koongarra Uranium Deposit. In *CEC Nuclear Science and Technology Report, EUR 11725, Commission of European Communities*, 71 (1994) .

Short, S. A., R. T. Lowson, and J. Ellis. " $^{234}\text{U}/^{238}\text{U}$ and $^{230}\text{Th}/^{234}\text{U}$ Activity Ratios in the Colloidal Phases of Aquifers in Lateritic Weathered Zones," *Geochim. Cosmochim. Acta.* 52:2555-2563 (1988).

Smith, P.A. A Model for Colloid Facilitated Radionuclide Transport Through Fractured Media. (Nagra, Wettingen) *Technical Report 93-32* (1993).

Smith, P. A., and C. Degueldre. "Colloid Facilitated Transport of Radionuclides Through Fractured Media," *J. Contamin. Hydrol.* 13:143-166 (1993).

Tsezos, M and B. Volesky. Biosorption of Uranium and Thorium. *Biotechnol. Bioengineering* 23:583-604 (1981).

USDOE. "Draft of the Science Investigation Plan: Cerro Negro Field Site, Seboyeta, New Mexico," Office of Health and Environmental Research, Subsurface Science Program, U.S. Department of Energy, Washington, D.C. (1994).

Vilks, P, H. G. Miller, and D. C. Doern. "Natural Colloids and Suspended Particles in the Whiteshell Research Area and Potential Effects on Radiocolloid Formation," *Appl. Geochem.* 6:565-574 (1991).

Vilks, P, J. J. Cramer, D. B. Bachinski, D. C. Doern and H. G. Miller. "Studies of Colloids and Suspended Particles, Cigar Lake Uranium Deposit, Saskatchewan, Canada," *Appl. Geochem.* 8: 605-616 (1993).

Wood, W. W., and G. G. Ehrlich. "Use of Baker's Yeast to Trace Microbial Movement in Ground Water," *Ground Water* 16:398-403 (1978).

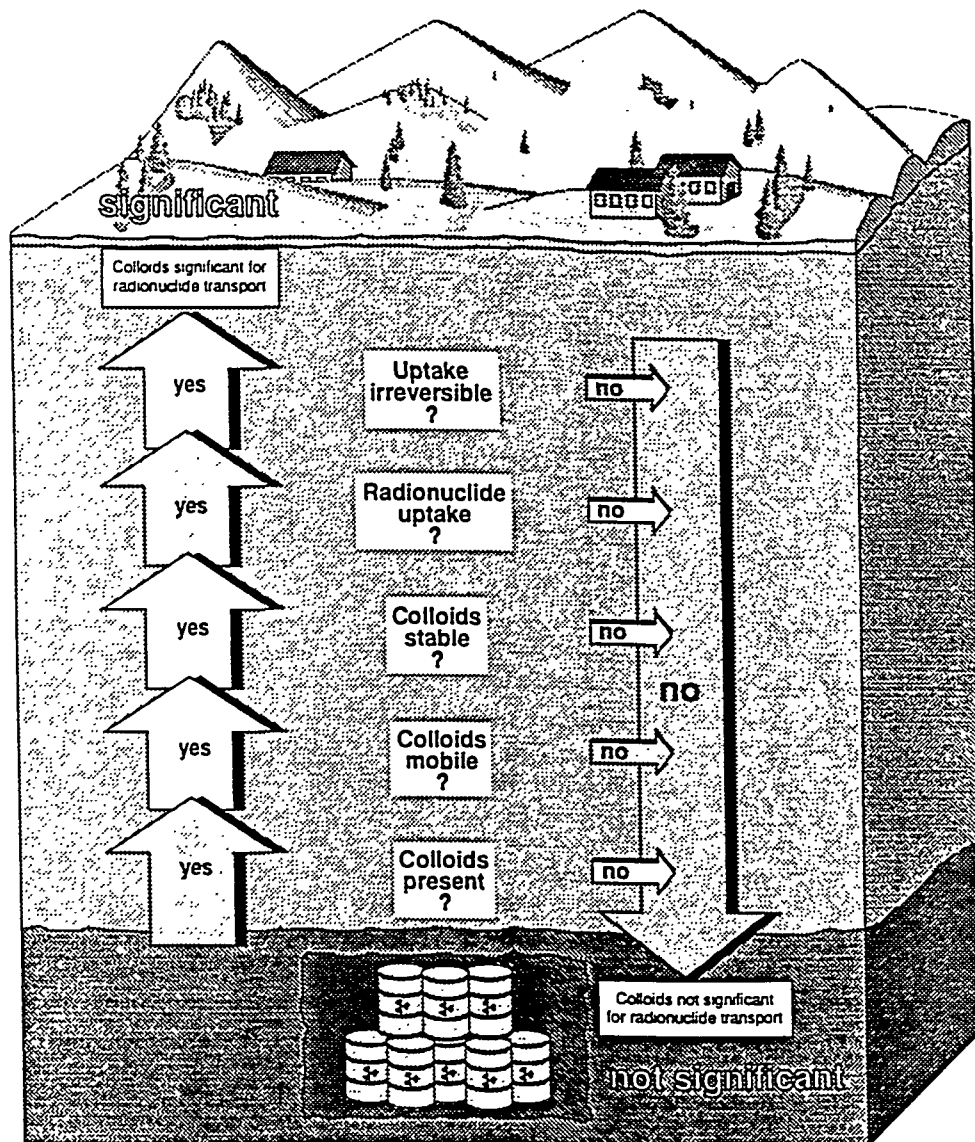


Figure 1. Diagram illustrating the general issues that need to be considered in assessing the significance of colloids to repository performance (Miller et al. 1994). The simplicity of the diagram makes it a useful didactic tool. However, it should be noted that the questions are inter-related and cannot be answered as simply as is suggested by the arrows. For example, irreversible uptake becomes less important when higher concentrations of colloids are present or if colloids have a large adsorption capacity. Similarly, colloid stability and mobility are interdependent since stability must be compared with the time required for colloids to transport radionuclides to the accessible biosphere.