Modeling of colloid-associated radionuclide transport in porous groundwater aquifers at the Gorleben site, Germany

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Results are presented which have been obtained in prediction studies on the colloid-associated transport of radionuclides through porous groundwater aquifers overlying as geochemical barrier the planned nuclear repository site at Gorleben, Germany. The studies incorporate three-phase retardation factors for $^{227}$Ac, $^{228}$Th, $^{232}$U and $^{210}$Pb in site-specific groundwater aquifers containing humic colloids and efficiencies for Brownian deposition of colloidal carriers onto immobile sedimentary grains. It is shown that colloid-bound radionuclide migration can be approximately modeled by using the basic advection-dispersion transport equation modified with three-phase retardation coefficients and colloid-chemical attachment factors due to the presence of multiple phases, i.e., fluid, colloid and immobile solid. Moreover, results of site-specific assessment studies indicate that the transport of colloid-associated radionuclides in porous groundwater aquifers overlying the Gorleben salt dome may not occur over long distances, provided that the nuclides are transported by porous flow only.

INTRODUCTION

In the Federal Republic of Germany it is intended to dispose of all types of radioactive wastes in deep geological formations. One of the sites considered for such an underground repository is the Gorleben salt dome which is located in the northern part of Germany (PSE, 1985; Röthemeyer, 1991; OECD Nuclear Energy Agency, 1999) (Fig. 1). Salt formations are suggested as important potential host rocks for nuclear repositories because of negligible permeability, extremely low water content and high thermal conductivity which expedites the dissipation of heat from high-level wastes (Brockins, 1984). However, for conservative approach reasons it is not precluded that during the post-operational phase of the repository water from the overlying strata of the salt dome and from inclusions in the rock salt may reach waste packages so that nuclides might be released (Warnecke et al., 1984, 1994). Therefore, for the performance of a long-term safety assessment the barrier function of the geological formations overlying the salt dome have been studied by batch, column and diffusion experiments (Lieser et al., 1990; Meier et al., 1992, 1993, 1994, 1995; Hollmann and Tittel, 1993; Kim et al., 1994; Warnecke et al., 1994).

Experimental investigation have mainly be focused on data characterizing the transport of released radionuclides as dissolved species. For ensuring this approach in performance assessment, however, it is necessary to test how far colloids which have been found in some Gorleben groundwaters in high concentrations (Kim et al., 1984; Kim, 1991) may facilitate the transport of radionuclides away from the repository. The significance of colloids to the migration of nuclides

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has been demonstrated by radionuclide analyses of groundwaters outside a nuclear detonation cavity (Buddemeier and Hunt, 1988; Penrose et al., 1990; McCarthy and Degueldre, 1993; Kaplan et al., 1994). According to these observations colloid-associated nuclides could be characterized by a more rapid migration in aquifer-water systems than expected from sorption data. Additionally, there is evidence in natural geochemical systems that colloidal migration of uranium and daughter species such as thorium or polonium may be important in fieldscale mobilization and accumulation processes lasting over long periods of time (Meier and Hecker, 1976; Airey and Ivanovich, 1986; Short et al., 1988; Hoocker, 1991; Payne et al., 1992; Ivanovich et al., 1992).

There are several attempts to model the colloid-mediated transport of nuclides through aquifers. The present status is that models can be used to describe approximately the migration of actinides through granite fractures (Van der Lee et al., 1992; Smith and Degueldre, 1993; Harmand and Sardin, 1994). Furthermore, models are developed for simulating the colloid-facilitated transport of nuclides through a porous medium (McCarthy and Zachara, 1989; Mills et al., 1991; Bennet et al., 1993; Artinger et al., 1998). However, the ability of these models to predict colloid-enhanced transport is limited. Models cannot (a) describe influences of environmental conditions on the coagulation of migrating colloids, (b) predict effects of physicochemical attachment of colloids to porous aquifers, especially when colloids and aquifer surfaces have a like charge, (c) simulate results of field studies concerning influences of both the size of particles and water velocity on the mobility of colloids, (d) explain discrepancies between colloid-associated nuclide transport observed in porous aquifers and estimated by using three-phase transport terms (Ryan and Elimelech, 1996).

Therefore, experiments have been carried out aimed, among other things, at data on the efficiency of reversible nuclide association with colloids in Gorleben groundwaters. Additionally, it is tested how far colloid-bound radionuclide migration through porous aquifers can be approximately described by using the advection-dispersion transport equation modified with nuclide-specific three-phase retardation factors. Moreover, the proposed model is extended to describe the impeded colloid transport by using colloid-chemical filtration parameters. The paper summarizes corresponding results.

**GEOLOGY AND HYDROCHEMISTRY**

The elevation of the Zechstein salt deposits during the Cretaceous and the Tertiary has been connected with an intensive influence on the deposition of Oligocene and Miocene sediments at the central area of the diapir. Therefore, Tertiary sediments are spread over the Gorleben salt dome area as partially fragmentary and ruptured layers of lowerer thickness than in the borderland of the dome. The sedimentary cover of this disturbed Tertiary strata comprises Quaternary sediments resulting from the deposition of sand, silt, marl and clay with an overall thickness of about 150 m to 300 m during four Pleistocene glaciations (Fig. 2).

Although sedimentary layers are not connected
Migration behavior of radionuclides in the geosphere

vertically and horizontally all over the region above the salt dome the Tertiary and Quaternary sequence of strata with irregularly arranged aquiclude and aquifuge layers can be subdivided into two main aquifers consisting of (a) Miocene brown-coal sands with aquifuge clay banks at the bottom and an alternation of sealing silt and bouldery clay banks at the topwall and

Fig. 2. (A) Boundary of the salt dome with the general flow direction of the groundwater (calculated flow time from the salt dome to the biosphere about 4000 to 17000 years). (B) Scheme of a geological cross-section of the strata overlying the Gorleben salt dome corresponding to section S–S' given in (A). Details see, e.g., PSE, 1983, 1985; Warnecke and Hild, 1988; Bundesamt für Strahlenschutz, 1990; Röthemeyer, 1991.
(b) Pleistocene glaciofluvial sediments (PSE, 1985; Röthemeyer, 1991). In agreement with the rough subdivision into two main aquifers, groundwaters are characterized by a boundary between waters of low and high mineralization at a depth of about 100 m with the highest salinity nearest to the salt dome surface (Hund, 1991).

With regard to long-term safety scenarios it is important to note that glacial erosion during the Elsterian stage resulted in the formation of glacial stream channels through Tertiary sediments to anhydrite horizons of the dome. These channels filled with aquiferous glaciofluvial sands may represent a potential discharge path for radionuclides from the repository into the overlying strata due to the convergence of the salt dome. Therefore, in a conservative approach it is assumed that in the post-operational phase nuclides might be released into the overlying aquifers by using pathways caused by thermomechanical effects in the anhydrite horizons (Warnecke et al., 1994).

The radionuclides eventually released from the repository might migrate in the flow of the groundwaters through the strata of Tertiary and particularly Quaternary sands to the biosphere (Bütow et al., 1983; Warnecke and Hild, 1988; Memmert, 1991). Among other things, in view of the migration of radionuclides with the groundwaters it should be taken into account that the Gorleben aquifers contain natural organics with dissolved organic carbon (DOC) ranging from 0.1 mg C/l up to 100 mg C/l near lignite intercalations. The components of the site-specific DOC are mainly humic and fulvic acids with colloidal properties corresponding to concentrations as high as $10^{10}$ to $10^{17}$ particles per litre (Buckau et al., 1986; Dearlove et al., 1991; Kim, 1991; Kim et al., 1992).

**Experimental**

**Experimental bases**

As basis for deriving radionuclide migration data the general advection-dispersion transport equation is used. This equation which can be commonly extended from laboratory to field situations results from the balancing of a component’s dissolved mass in an elementary volume. Under the simplifying assumption of an unidirectional flow field along the $x$ axis according to the mass conservation principle the mass change of a component in the elementary volume over time $dt$ can be expressed as

$$\frac{\partial C_L}{\partial t} = -\frac{dJ_i}{dx}.$$  \hspace{1cm} (1)

Here $C_L$ is the solute concentration and $J_i$ corresponds to the sum of the following mass fluxes which are in action when a fluid flows in a porous medium: (a) advective mass flux of a component caused by the flow of the transporting fluid ($J_a = n_v a C_L$ [mol/cm$^2$ s]), (b) mass diffusion flux caused by the concentration gradient of the component in the fluid ($J_D = -n_v D_D (\partial C_L/\partial x)$ [mol/cm$^2$ s]), (c) mechanical dispersion flux of solutes due to spatial fluctuations in velocity resulting from aquifer heterogeneities ($J_L = -n_v D_L (\partial C_L/\partial x)$ [mol/cm$^2$ s]). In these terms $n_v$ is the effective porosity available for the movement of water, $v_a$ is the mean porous velocity, $D_D$ is the molecular diffusion coefficient and $D_L$ is the longitudinal mechanical dispersion coefficient. Because of the similarity in the mathematical description of diffusion and dispersion the coefficients $D_D$ and $D_L$ may be combined in the coefficient $D_{H,L} (=D_D + D_L)$ of longitudinal hydrodynamic dispersion. Substitution of the sum of these terms into Eq. (1) yields the general form of the one-dimensional advection-dispersion equation for a porous medium

$$n_v \frac{\partial C_L}{\partial t} = -n_v v_a \frac{\partial C_L}{\partial x} + n_v D_D \frac{\partial^2 C_L}{\partial x^2} + n_v D_L \frac{\partial^2 C_L}{\partial x^2} + S = -n_v v_a \frac{\partial C_L}{\partial x} + n_v D_{H,L} \frac{\partial^2 C_L}{\partial x^2} + S.$$  \hspace{1cm} (2)

Since several factors, for example radioactive de-
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Cay or sorption processes, may cause changes of solute concentration a sink/source term \( S \) (\( =n_e(\partial C_L/\partial t) \)) is added to Eq. (2). In the case of radioactive decay the term \( S \) is given by the mass decreasing rate of the considered radionuclide due to decay in a unit volume of the porous medium, i.e.,

\[
n_e \frac{\partial C_L}{\partial t} = -n_e \lambda(C_L + s). \tag{3}
\]

Here \( \lambda \) is the decay constant, \( C_L \) is the concentration of the nuclide in the free pore water [mol/ml], \( s = (\rho/n_e)C_S \) is the nuclide concentration in an unit volume of the solid phase [mol/ml], \( C_S \) is the solute concentration sorbed in the solid [mol/g] and \( \rho \) is the porous media bulk density [g/ml]. If flow of groundwater is slow enough that equilibrium concentration at the interfaces between solid and liquid phases is rapidly obtained then \( s \) given in Eq. (3) can be modified by taking into account the linear adsorption isotherm \( \partial C_S/\partial C_L = K_d \) and \( C_S = K_d C_L \), respectively, in the following manner:

\[
s = \frac{\rho}{n_e} C_S = \frac{\rho}{n_e} K_d C_L. \tag{4}
\]

Here \( K_d \) is the distribution coefficient used to quantify sorption processes which are kinetically fast in relation to groundwater velocity, reversible and independent of the concentration of sorbing solutes. The \( K_d \) parameter is given by \( K_d = C_S/C_L \) where the \( C \) values refer to nuclide concentration in the solid (\( C_S \)) and aqueous phases (\( C_L \)), respectively (Maas and Huf, 1983; McKinley and Scholtis, 1992; Jenne, 1998). Substituting \( s \) into Eq. (3) in the case of radioactive decay the sink term \( S_d \) can be written as

\[
S_d = n_e \frac{\partial C_L}{\partial t} = -n_e \lambda C_L \left( 1 + \frac{\rho}{n_e} K_d \right). \tag{5}
\]

When sorption and desorption phenomena occur at the interfaces between solid and liquid phases the term \( S_d \) can be obtained by simultaneously considering the mass balance of the nuclide with the solid and liquid phases. In this case we have

\[
n_e \frac{\partial C_L}{\partial t} = -\rho \frac{\partial C_S}{\partial t} = -\rho \frac{\partial C_S}{\partial C_L} \frac{\partial C_L}{\partial t} \quad \text{and substituting}
\]

\[
\frac{\partial C_S}{\partial C_L} = K_d \quad \text{gives} \quad S_S = \left( n_e \frac{\partial C_L}{\partial t} \right) = -\rho K_d \frac{\partial C_L}{\partial t}. \tag{6}
\]

Substituting the expressions of \( S \) (\( =S_d + S_S \)) into Eq. (2) with subsequent multiplication of both sides by \( 1/n_e \) and rearranging obtains

\[
\frac{\partial C_L}{\partial t} \left( 1 + \frac{\rho}{n_e} K_d \right) = -\nu_a \frac{\partial C_L}{\partial x} + D_{HL} \frac{\partial^2 C_L}{\partial x^2} - \lambda C_L \left( 1 + \frac{\rho}{n_e} K_d \right). \tag{7}
\]

Upon dividing through both sides of Eq. (7) by \( (1 + (\rho/n_e)K_d) \) and assuming

\[
R_f = 1 + \frac{\rho}{n_e} K_d \quad \text{or} \quad R_f = 1 + \rho_S \frac{1}{n_e} K_d, \tag{8}
\]

the basic transport equation becomes (see, e.g., Bear and Veruij, 1987; Mills et al., 1991; Sun, 1996; Lege et al., 1996)

\[
\frac{\partial C_L}{\partial t} = -\frac{\nu_a}{R_f} \frac{\partial C_L}{\partial x} + \frac{D_{HL}}{R_f} \frac{\partial^2 C_L}{\partial x^2} - \lambda C_L. \tag{9}
\]

According to this equation both the mean flow velocity and the hydrodynamic dispersion coefficient are decreased by the influence of the coefficient \( R_f \) (\( \geq 1 \)). The coefficient \( R_f \) is called the retardation factor which describes the retardation effect as result of sorption processes. The parameters \( \rho_S \) and \( \rho \) correspond to the density of the rock solids (particle density) and the porous media bulk density, respectively. By ignoring hydrodynamic
dispersion and radioactive decay the transport equation can be rearranged to give the nuclide migration velocity $v_T = \frac{dx}{dt}$ as

$$\frac{dx}{dt} = \frac{\nu_a}{R_f} \quad \text{or} \quad R_f = \frac{\nu_a}{v_T}.$$

(10)

$R_f$ values can be obtained from batch and/or column experiments by utilizing Eq. (8) and Eq. (10), respectively (see, e.g., Maas and Huf, 1983; McKinley and Scholtis, 1992).

**Experimental procedures**

As samples, sediments from selected strata overlying the Gorleben salt dome were taken by the Bundesanstalt für Geowissenschaften (BGR), Hannover, Germany, by procedures which avoid the presence of drilling agents and any change of natural particle size distribution (Warnecke and Hild, 1988). According to X-ray diffraction analysis the sediments consist of sandy loose rocks of about 95% quartz and 5% clays (mainly illite, kaolinite and montmorillonite), marlstone and clay beds. Water samples used were groundwaters taken from the same site as the sediments. The numerical designation “Gohy” corresponds to the nomenclature of drill holes which were selected within a drilling programme for obtaining samples of sediments and accompanying waters from all important aquifers on the possible nuclide migration path (Warnecke and Hild, 1988). The radionuclides investigated in this study, besides $^{226}$Ra and $^{63}$Ni, were $^{233}$U, $^{210}$Pb, $^{228}$Th and $^{227}$Ac. Ac was taken as representative of trivalent actinides such as Am$^{3+}$ and Cm$^{3+}$. For the tracer concentrations in the groundwaters a range of $10^{-5}$ to $10^{-11} \, M$ was used corresponding to the necessity to facilitate good counting statistics. Solutions obtained from distribution experiments were analyzed for the content of both $\alpha$ and $\beta$ emitting radionuclides by scintillation counting with a Packard Tri-carb Model 5000 liquid scintillation counter. Counting was done by transferring 1.0 ml of the reaction solution in 15 ml scintillators. Using several-point calibration curves radionuclide standards provided measured nuclide concentrations with relative percentage standard deviation from 1.4 to 4.5% (confidence level P = 95%). The detection limit attained was $8.2 \times 10^{-9}$ g/ml $^{233}$U, $1 \times 10^{-16}$ g/ml $^{228}$Th, $2 \times 10^{-13}$ g/ml $^{227}$Ac and $4.7 \times 10^{-8}$ g/ml $^{210}$Pb.

**Batch experiments**

Batch experiments were carried out using 25 ml polyethylene tubes generally filled with 30 grams of geologic samples and 7.0 ml of reaction solutions. The solid matrix has been pre-equilibrated with the groundwater. The mixed samples consisting of solid matrix and traced feed solution were gently agitated on a vertical rotator at five rotations per hour. Having approximately attained within contact times up to six weeks the sorption equilibrium the liquid phase was separated from the solid phase by filtration (0.45 µm). In order to obtain an insight into the action of reversible and irreversible sorption processes sorption experiments were supplemented by desorption studies. Therefore, after replacing reaction solutions of sorption studies by fresh groundwater without containing radionuclides desorption experiments have been carried out analogous to the measurement of sorption ratios. The terms $R_s$ and $R_d$ are used respectively for sorption ratios determined in sorption and desorption experiments. In the case of reversible exchange processes ($R_s = R_d$) the term $K_d$ can generally be used as an equilibrium quantity. However, in the literature the term $K_d$ has also been used as an approximation for describing sorption and desorption experiments regardless of whether equilibrium was achieved or not (see, e.g., Meyer, 1983; Allard, 1992; Rundberg, 1992; Serne, 1992). Values of $R_s$ and $R_d$ were calculated by using

$$R_s = \frac{c_a - c_e}{c_e} \frac{V}{M} \quad \text{and} \quad R_d = \frac{(c_a - c_e) - c_d}{c_d} \frac{V}{M},$$

(11)

where $c_a$ and $c_e$ are the initial and final aqueous concentrations, respectively, $c_d$ is the final aqueous concentration of desorbed radionuclides, $V$ is...
the volume of the aqueous phase and \( M \) is the mass of the solid. Data are expressed by the unit cm\(^3\)/g or m\(^3\)/kg. Experimental precision in each set was determined by analysis of double or triplicate samples for each sediment equilibrated with reaction solution. In order to minimize systematic errors due to nuclide losses by mechanisms other than sorption onto sediments (e.g., sorption onto tube walls) operational blanks consisting of the reaction solution without sediments were also analyzed. The overall percents relative standard deviation (%RSD) for replicates measured throughout the experiments ranged from 3 to 20% (\( P = 95\% \)).

**Column experiments**

In our studies flow-through column experiments have been performed by using columns with a diameter of 20 mm which are packed with sandy sediments to a height of 120 mm. Tracers are injected as a pulse. By evaluating the peak centroid velocities in the column effluents obtained by monitoring the concentration of the non-sorbing tracer \(^3\)H\(\text{HO}\) and the tested radionuclide, respectively, the mean flow velocity \( v_\text{a} \) of the water and the mean flow velocity \( v_\text{T} \) of the nuclide have been derived. By using these velocities the sorption behavior of radionuclides in the presence or absence of colloids could be expressed by the factor \( R_f = v_\text{a} / v_\text{T} \) (see, e.g., Hoeffner, 1983; Moser, 1983; Klotz and Lang, 1992).

**Determination of electrical charges at sediments and colloids**

The electrical charges of pore surfaces and colloids have been recognized to be important in explaining colloid stability and transport (Ramsey, 1988; Feng et al., 1994; Sätmark et al., 1994). These charges can be derived from zeta-potentials which are experimentally accessible by electrokinetic measurements (Meier et al., 1991, 1994; Feng et al., 1994; Evans and Wennerström, 1994). In our study electroosmotic and electrophoretic methods have been used: (a) Electroosmosis experiments are based on the movement of the mobile double-layer liquid phase adjacent to charged surfaces caused by an externally applied electrical field. In accordance with this mechanism zeta-potentials, \( Z_e \), of sediment-groundwater systems are derived from measurements of the electroosmotic volume flow of water through sediment containing columns packed between two electrodes (see Meier et al., 1991). (b) In electrophoresis experiments motion of charged colloids follows in electrical fields from the balance between viscous and electrical forces. Thus, the zeta-potential, \( Z_C \), of colloids can be derived from the measurement of their electrophoretic mobility. In this study the electrophoretic mobility in terms of zeta-potential has been determined by using the commercially available photon correlation spectrometer (PCS) Zetasizer 3 (Malvern Instruments), i.e., by measuring the Doppler shift of laser light scattered by moving colloidal particles (see, e.g., Fourest et al., 1994).

**Measurement of colloid sizes**

The size of colloids was measured with the Zetasizer 3 system by analyzing the fluctuations of laser light scattered by particles in suspensions. Fluctuations in light scattering arise from the Brownian diffusion of the colloids. Therefore, by using an autocorrelation function (see, e.g., Triay et al., 1991) from fluctuation signals diffusion coefficients \( D_P \) can be derived which are related to particle sizes by the Stokes-Einstein equation (see Eq. (20)). Aqueous colloidal suspensions must not be modified for analyzing in the PCS system (Sätmark and Albinsson, 1992; Feng et al., 1994; Fourest et al., 1994).

**RESULTS AND DISCUSSION**

**Bases of colloid-facilitated radionuclide transport**

Any colloid-enhanced transport of low-solubility radionuclides through site-specific groundwater aquifers requires the following conditions (Ryan and Elimelech, 1996): (1) stable colloids are present in groundwaters of the aquifer horizons at concentrations of about 1–100 mg/l, (2) radionuclide species associate strongly with site-specific colloids, (3) colloids and colloid-
bound radionuclides migrate with the groundwater stream through the site-specific aquifers. The following results are consistent with the given criteria.

Properties of colloids in Gorleben groundwaters

Complementary to studies demonstrating the presence of metal loaded humic acids at concentrations as high as 150 mg C/l in Gorleben groundwaters (Kim, 1991; Kim et al., 1992) the colloidal behavior of humic substances could be confirmed and characterized by PCS parameters:

1. In agreement with the microanalytical characterization of colloids separated in ultrafilters of different sizes (Kim, 1991) the polydisperse character of Gorleben groundwater colloids could be confirmed by using the PCS technique. For instance, in groundwater from the drill-hole Gohy 1281 (=10 mg C/l DOC) prefiltered through a 400 nm Nucleopore filter a mixture of colloids corresponding to size groups with a mean diameter of 172, 124 and 24 nm have been detected. Owing to the observed small sizes which correspond to a high colloid surface area humic colloids of Gorleben groundwaters can be considered as effective sorbents of nuclides.

2. The zeta-potential of groundwater colloids belonging to Gorleben aquifers with water of low salinity (i.e., ionic strength $I \leq 0.1$ mol/l) is negative. However, in deep aquifers with highly mineralized groundwater the colloidal particles are less negatively charged (see Table 1). The observed values indicate that humic colloids in groundwaters of low salinity will be stable for a long time because of repulsive electrostatic forces which are effective among negatively charged colloids. (see, e.g., Feng et al., 1994; Geckeis et al., 1998). Additionally, repulsive forces between colloids and aquifer solids which are likely charged negative, exist (see Ramsey, 1988; Meier et al., 1991). The values also indicate that in saline groundwaters near the salt dome, even in the case of high DOC concentrations, only small amounts of colloids will be present on account of the compression of the diffuse double-layer resulting in flocculation by van der Waals attraction.

Association of radionuclide species with humic colloids

Basic relationships

For describing quantitatively the effectiveness of nuclide association with humic colloids which depends on the strong complexation of humic acids with metal ions (Kim, 1991; Choppin, 1988, 1992; Moulin et al., 1992) and the influence of large surface areas of colloidal suspensions on their adsorption capacity (Ramsey, 1988; Sätmark and Albinsson, 1992; Read et al., 1994) solute-colloid partition coefficients, $K_C$ [ml/g], are used. Values of this coefficient, defined as the ratio of nuclide concentration per gram of colloid to its concentration per 1 ml water, are obtainable in batch experiments.

An important precondition for these studies is that in the course of batch experiments colloidal particles are not sorbed by the solid matrix. Because of repulsive electrostatic forces resulting from negative charges of both the humic colloids (see Table 1) and groundwater bearing sediments (see Meier et al., 1991, 1994) this requirement is met. There are several studies indicating corre-

Table 1. Zeta-potential $Z_C$ of colloids in Gorleben aquifer-groundwater systems

<table>
<thead>
<tr>
<th>Depth [m]</th>
<th>Sediment</th>
<th>Water Gohy</th>
<th>$I$ [mol/l]</th>
<th>DOC [mg/l]</th>
<th>pH</th>
<th>$Z_C$ [mV]</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Sand 2</td>
<td>2131</td>
<td>0.005</td>
<td>3.0</td>
<td>7.1</td>
<td>$-10.1 \pm 1.6$</td>
<td>e</td>
</tr>
<tr>
<td>83</td>
<td>Sand 7</td>
<td>1281</td>
<td>0.09</td>
<td>10.9</td>
<td>7.6</td>
<td>$-8.1 \pm 1.6$</td>
<td>e</td>
</tr>
<tr>
<td>85</td>
<td>Marl 8</td>
<td>1281</td>
<td>0.09</td>
<td>7.5</td>
<td>7.3</td>
<td>$-10.5 \pm 2.0$</td>
<td>e</td>
</tr>
<tr>
<td>131</td>
<td>Sand 11</td>
<td>1341</td>
<td>0.19</td>
<td>7.7</td>
<td>7.0</td>
<td>$-4.3 \pm 1.4$</td>
<td>n</td>
</tr>
<tr>
<td>187</td>
<td>Sand 13</td>
<td>1092</td>
<td>1.03</td>
<td>3.4</td>
<td>7.0</td>
<td>$-1.5 \pm 1.4$</td>
<td>e</td>
</tr>
</tbody>
</table>

Note: $n =$ natural groundwater. $e =$ equilibrated sediment-groundwater. Single standard deviation in $Z_C$. 


sponding influences of repulsive double-layer interactions (see Prieve and Ruckenstein, 1977; Christenson, 1988; Ramsey, 1988; Ryan and Elimelech, 1996). For instance, goethite (FeOOH) colloids are effectively pushed away from quartz sand grains at pH 10.5 owing to similar negative charges of both the colloid and quartz surfaces (Sätmärik et al., 1994). Surface charge heterogeneities of solids containing minor oppositely-charged domains with attractive double-layer behavior may not affect the stability of colloids in batch experiments due to small efficiencies of collisions between particles and surface domains (McCarthy and Zachara, 1989; Ryan and Elimelech, 1996). However, in column experiments (Kim et al., 1994) and field-scale transport, respectively, an attenuation in concentration of colloids cannot be excluded because deposition may be favored by contacts occurring between moving particles and heterogenous surfaces of the entire granular medium (Stumm, 1992; Ryan and Elimelech, 1996). The repulsion of colloids from solids makes possible to estimate partition coefficients, $K_C$, for “in situ” conditions. On the one hand, nuclide concentration sorbed to the solid phase ($C_S$ [mol/g]) is defined by

$$C_S = K_{eff} (C_L + C_L K_C c_C). \tag{12}$$

Here $K_{eff}$ represents the observable (effective) distribution coefficient [ml/g] and the parenthesis the mobile phase concentrations consisting of (a) the dissolved nuclide concentration ($C_L$ [mol/ml]) and (b) the concentration of nuclides sorbed to mobile colloids ($C_L K_C c_C$ [mol/ml]) which are not attached onto the solid phase. On the other hand, by reorganizing Eq. (12) and insertion the distribution coefficient $K_d = C_d/C_L$ measured in colloid-free solutions the observable distribution coefficient may be given in accordance with Morel and Gschwend (1987) and Stumm (1992) by

$$K_{eff} = K_d / (1 + K_C c_C). \tag{13}$$

This equation suggests that the effective distribution coefficient for describing the sorption equilibrium of radionuclide species between sedimentary grains, humic colloids and aqueous solution is decreasing with increasing concentration of colloidal particles ($c_C$ [g/ml]).

**Results** For testing the influence of humic colloids on the distribution of nuclides between solid and aqueous phases of site-specific samples sorption and desorption coefficients (Eq. (11)) have been measured as a function of colloid concentration. The studies were carried out using batch reaction techniques as described above. As standards for humic colloids Fluka-HA, Gohy-573-HA (Kim et al., 1991) and Aldrich humic acid (Aldrich-HA) were used. The complexation behavior of humic acids extracted from the Gorleben groundwater (e.g., Gohy-573-HA) and purchased from Aldrich Co. (Aldrich-HA) are comparable (Kim et al., 1991). Moreover, Aldrich-

<table>
<thead>
<tr>
<th>Colloid</th>
<th>Ra$^{2+}$/Fluka-HA</th>
<th>Ni$^{2+}$/Fluka-HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_C$ [g/ml]</td>
<td>Sediment 2220/Water 2220</td>
<td>Sediment 2220/Water 2220</td>
</tr>
<tr>
<td>—</td>
<td>$R_s$ [ml/g]</td>
<td>$R_i$ [ml/g]</td>
</tr>
<tr>
<td>$10^{-6}$</td>
<td>139 ± 2</td>
<td>190 ± 15</td>
</tr>
<tr>
<td></td>
<td>146 ± 2</td>
<td>200 ± 7</td>
</tr>
<tr>
<td>$10^{-5}$</td>
<td>171 ± 2</td>
<td>245 ± 9</td>
</tr>
<tr>
<td>$10^{-4}$</td>
<td>180 ± 14</td>
<td>158 ± 12</td>
</tr>
</tbody>
</table>

Note: Arithmetic mean ± one standard deviation of two replicates.
HA consists of colloids as proven in our laboratory by PCS parameters concerning the colloid sizes \((d_C = 363 \text{ nm and } 82 \text{ nm})\) and colloid charges \((Z_C = -24.2 \pm 0.4 \text{ mV and } -7.2 \pm 0.3 \text{ mV})\). Studies have been performed with concentrations \(c_C\) of \(0, 10^{-6}, 10^{-5}\) and \(10^{-4}\) [g/ml] in order to span the range of colloid concentrations found in Gorleben groundwaters (Kim, 1991).

Batch measurements concerning the association of selected radionuclides with humic colloids indicate (a) for \(Ra^{2+}\) and \(Ni^{2+}\) no significant influence of humic colloids on sorption and desorption at any of the investigated colloid concentrations and sediments (Table 2), (b) for \(UO_2^{2+}\) and \(Pb^{2+}\) mostly a decrease of \(R_S\) and \(R_d\) coefficients on sandy sediments in the concentration range of humic colloids between \(10^{-5}\) and \(10^{-4}\) [g/ml] (Table 3), (c) for \(Ac^{3+}\) decreasing \(R_S\) and \(R_d\) coefficients on sandy sediments with increasing concentration of humic colloids above \(10^{-6}\) g/ml (Table 4), (d) for \(Th^{4+}\) an influence of humic colloids on sorption and desorption with \(R_S\) and \(R_d\) values ranging from \(10^3\) to \(10^4\) ml/g to about 40 ml/g for an increase in colloid concentration from \(10^{-6}\) to \(10^{-4}\) g/ml (Table 4). In addition to these results, a strong decrease of \(R_S\) in the presence of humic colloids is reported for \(Am^{3+}\) by Artinger et al. (1998). In groundwaters of high ionic strength \((I = 1.03 \text{ mol/l})\) no influence of the colloidal humic standards on the sorption of any of the investigated nuclides could be observed (Table 5). This difference to waters of low ionic strength can be explained by the decrease in colloid concentrations resulting from the flocculation of colloids in saline waters (see, e.g., Kim et al., 1984; Feng et al., 1994).

Table 3. Dependence of \(R_S\) and \(R_d\) on the concentration of humic colloids in the sandy sediment Gohy 2220 with groundwater Gohy 2220 \((I = 2.6 \cdot 10^{-3} \text{ mol/l})\) for \(UO_2^{2+}\) and \(Pb^{2+}\); \(pH = 7; \text{ V/M} = 2.33\)

<table>
<thead>
<tr>
<th>Colloid Concentration</th>
<th>(c_C) [g/ml]</th>
<th>(R_S) [ml/g]</th>
<th>(R_d) [ml/g]</th>
<th>(R_S) [ml/g]</th>
<th>(R_d) [ml/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment 2220/Water 2220</td>
<td>(UO_2^{2+}/Aldrich-HA)</td>
<td>(Pb^{2+}/Aldrich-HA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>112</td>
<td>658</td>
<td>194 ± 11</td>
<td>362 ± 57</td>
<td></td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>111 ± 1.2</td>
<td>691 ± 46</td>
<td>216 ± 7</td>
<td>888 ± 112</td>
<td></td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>123 ± 1.5</td>
<td>611 ± 90</td>
<td>244 ± 17</td>
<td>484 ± 136</td>
<td></td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>12.35 ± 0.19</td>
<td>11.97 ± 1.36</td>
<td>9.9 ± 0.7</td>
<td>11.6 ± 0.04</td>
<td></td>
</tr>
</tbody>
</table>

Note: Arithmetic mean ± one standard deviation of two replicates.

Table 4. Dependence of \(R_S\) and \(R_d\) on the concentration of humic colloids in the sandy sediment Gohy 2220 with groundwater Gohy 2220 \((I = 2.6 \cdot 10^{-3} \text{ mol/l})\) for \(Ac^{3+}\) and \(Th^{4+}\); \(pH = 7; \text{ V/M} = 2.33\)

<table>
<thead>
<tr>
<th>Colloid Concentration</th>
<th>(c_C) [g/ml]</th>
<th>(R_S) [ml/g]</th>
<th>(R_d) [ml/g]</th>
<th>(R_S) [ml/g]</th>
<th>(R_d) [ml/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment 2220/Water 2220</td>
<td>(Ac^{3+}/Aldrich-HA)</td>
<td>(Th^{4+}/Aldrich-HA)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>—</td>
<td>239 ± 4</td>
<td>943 ± 1</td>
<td>(3.1 ± 0.8)(\cdot 10^3)</td>
<td>(1.06 ± 0.06)(\cdot 10^4)</td>
<td></td>
</tr>
<tr>
<td>(10^{-6})</td>
<td>235 ± 26</td>
<td>744 ± 76</td>
<td>(2.54 ± 0.08)(\cdot 10^3)</td>
<td>(3.67 ± 0.46)(\cdot 10^3)</td>
<td></td>
</tr>
<tr>
<td>(10^{-5})</td>
<td>60 ± 1</td>
<td>337 ± 32</td>
<td>236 ± 22</td>
<td>542 ± 1.6</td>
<td></td>
</tr>
<tr>
<td>(10^{-4})</td>
<td>13 ± 1.8</td>
<td>7.9 ± 1.1</td>
<td>43 ± 13</td>
<td>36 ± 8</td>
<td></td>
</tr>
</tbody>
</table>

Note: Arithmetic mean ± one standard deviation of two replicates.
The observed influence of colloid concentrations on sorption and desorption of radionuclides in groundwater-aquifer systems (see, also, Ticknor et al., 1996) may provide the basis for estimating the strength of association of nuclides with colloids. For an estimation of the association coefficient $K_C$, Eq. (13) can be modified in the following manner:

$$K_C = \left[\frac{K_d}{K_{eff}} - 1\right] / c_C.$$  (14)

That is, $K_C$ values may be obtainable from $K_d/K_{eff}$ ratios by linear regression analysis of $\log(K_d/K_{eff} - 1)$ vs. $\log c_C$ plots (see Fig. 3) or by calculating $K_d/K_{eff}$ ratios at relatively high colloid concentrations in the case of lower association efficiencies. In Table 6 $K_C$ values which were derived by using Eq. (14) are listed.

Table 6. Analysis of the dependence of sorption/desorption ratios on colloid concentration

<table>
<thead>
<tr>
<th>Nuclide species</th>
<th>Sample Gohy</th>
<th>HA</th>
<th>Analysis</th>
<th>$r^2$</th>
<th>$s$</th>
<th>$K_d$ ($c_C = 0$) [ml/g]</th>
<th>$K_C$ [ml/g]</th>
<th>Number of data points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th$^{4+}$</td>
<td>2220</td>
<td>A</td>
<td>R</td>
<td>0.94</td>
<td>1.17</td>
<td>6.85·10$^3$</td>
<td>8.37·10$^6$</td>
<td>6</td>
</tr>
<tr>
<td>Th$^{4+}$</td>
<td>2220</td>
<td>F</td>
<td>R</td>
<td>0.93</td>
<td>1.26</td>
<td>4.48·10$^3$</td>
<td>8.74·10$^6$</td>
<td>6</td>
</tr>
<tr>
<td>Ac$^{3+}$</td>
<td>2220</td>
<td>A</td>
<td>R</td>
<td>0.94</td>
<td>1.39</td>
<td>591</td>
<td>1.80·10$^7$</td>
<td>6</td>
</tr>
<tr>
<td>Ac$^{3+}$</td>
<td>2220</td>
<td>F</td>
<td>R</td>
<td>0.93</td>
<td>1.42</td>
<td>673</td>
<td>1.93·10$^7$</td>
<td>6</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>5</td>
<td>G</td>
<td>R</td>
<td>0.91</td>
<td>0.97</td>
<td>6.0·10$^3$</td>
<td>2.25·10$^5$</td>
<td>6</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>2220</td>
<td>A</td>
<td>S</td>
<td>—</td>
<td>—</td>
<td>278</td>
<td>2.4·10$^5$</td>
<td>—</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>2220</td>
<td>A</td>
<td>S</td>
<td>—</td>
<td>—</td>
<td>358</td>
<td>3.1·10$^5$</td>
<td>—</td>
</tr>
<tr>
<td>UO$_2^{2+}$</td>
<td>2220</td>
<td>F</td>
<td>S</td>
<td>—</td>
<td>—</td>
<td>234</td>
<td>5.1·10$^5$</td>
<td>—</td>
</tr>
</tbody>
</table>

Samples: Sandy sediments (Gohy 2220/8–14 m, Gohy 5/45 m) with groundwaters Gohy 2220 ($I = 2.6·10^{-3}$ mol/l) and Gohy 1281 ($I = 9·10^{-2}$ mol/l). Nuclides: $^{228}$Th, $^{227}$Ac, $^{210}$Pb, $^{233}$U. Humic acids (HA) as colloid standards: A = Aldrich-HA; F = Fluka-HA; G = Gohy-573-HA. pH = 7. Analyses by using Eq. (14): S = evaluation of single $K_d/K_{eff}$ ratios at $c_C = 10^{-4}$ g/ml; R = regression analysis by using $K_d/K_{eff}$ ratios in the range of $c_C = 0–10^{-2}$ g/ml (i.e., 0–100 mg/l) in sets of 0, $10^{-3}$, $10^{-2}$ and $10^{-1}$ g/ml with the parameters $r^2$ (squared correlation coefficient).
complexation of tri- and tetravalent actinides in natural waters up to pH = 7–8.

**Mobility of colloid-associated radionuclides**

From data given in Tables 3 and 4 it can be seen that in systems with a relatively high content of humic colloids the differences between $R_s$ and $R_d$ coefficients are generally not significant. According to this observation an adsorption equilibrium between colloids-solute and immobile matrix-solute can be considered as being approximately established in many cases (see, however, Artinger et al., 1998). Consequently, the retardation equation used for describing two-phase transport (Eq. (8)) may be modified in the presence of colloids by incorporation of nuclide-colloid partition coefficients $K_C$. That is, if nuclide ions do both associate with mobile colloids and sorb to stationary sediments the three-phase retardation factor will be expressed as follows (see, e.g., Mills et al., 1991; Ryan and Elimelech, 1996):

$$R_{f3} = 1 + \left( \frac{\rho}{n_e} \right) K_{eff} = 1 + \left( \frac{\rho}{n_e} \right) K_d \frac{1}{1 + K_{CC} c_C}$$

where

$$R_{f3} = \frac{v_{groundwater}}{v_{colloid-bound nuclide}}.$$

In conformity with Eq. (15) the effect of humic colloids on the migration of radionuclides has been observed in dynamic laboratory experiments. Thus, it could be shown by Meier et al. (1992) that the rate of diffusion of Pb$^{2+}$ through sandy sediments (Gohy 2220) increases significantly in the presence of Aldrich humic colloids. Additionally, column experiments with the water/sediment system Gohy 1012 rich in humic colloids (Kim, 1991) have demonstrated that mobilities of Th$^{4+}$ and Pb$^{2+}$ are greater than those anticipated in a two-phase system. By comparing centroid velocities of Th$^{4+}$ and Pb$^{2+}$ species with the water velocity traced by $^3$HHO three-phase retardation factors $R_{f3} = 2.6$ ($K_{eff} = 0.46 \text{ ml/g}$) and $R_{f3} = 16$ ($K_{eff} = 4.5 \text{ ml/g}$), respectively, have been found by us (see Warnecke et al., 1994, and Fig. 4). Moreover, retardation factors in the order of $R_{f3} = 1$ have been found for humic colloid-bound Am$^{3+}$ in column experiments (Artinger et al., 1998).

By using two-phase and three-phase retardation expressions (Eqs. (8), (10), (11)) the effect...
of colloids on the migration velocity of nuclides may be predicted by taking as a basis (a) groundwater flow-rates \( v_a \), (b) sediment ratios \( \rho/n_e \), (c) \( K_d \) values for nuclides interactions with immobile sediments, and (d) \( K_C \) values derived in batch experiments. For example, based on \( v_a = 100 \) m/a, \( \rho/n_e = 4 \) and \( K_d = 6.85 \times 10^3 \) ml/g \( (R_{f2} = 2.7 \times 10^4) \) the \( \text{Th}^{4+} \) migration velocity is predicted to be only \( 3.64 \times 10^{-3} \) m/a, whereas in the presence of humic colloids at concentrations of \( 10^{-4} \) g/ml (100 mg/l) and \( K_C = 8.37 \times 10^6 \) ml/g \( (R_{f3} = 22) \) the velocity of \( \text{Th}^{4+} \) species would be at \( 2.97 \) m/a, i.e., around 800 times greater than the predicted two-phase transport velocity.

**Assessment of unimpeded colloid-facilitated radionuclide transport**

**Transport equation for colloid-bound nuclide migration**  
Colloid-facilitated transport of radionuclides implies that colloids migrate through porous aquifer-groundwater zones like non sorbing conservative tracers, such as \( ^3 \)THHO, without noticeable retardation. Thus, the mobility of colloids as potential carriers for nuclides is determined by the same hydrological factors which control flow rates and flow paths of groundwater. However, for simplicity of the colloid-associated transport of radionuclides in the present work following approximations are used: (1) the advective-dispersive transport in the aquifer zones overlying the Gorleben salt dome is considered to be one-dimensional neglecting the influence of transverse effects because groundwater velocities along the porous migration paths are usually higher than transverse velocities to adjacent formations (see Hadermann, 1980; Hadermann and Roesel, 1985; Warnecke and Hild, 1988; Hund, 1991; Warnecke et al., 1994), (2) complexation of nuclide species with important aqueous reactions, e.g., hydrolysis and carbonate complexation, are assumed to remain spatially and temporally constant because in accordance with the “constant \( K_d \) model” each zone of the waterpath from the repository to the biosphere might be approximately characterized by an unique \( K_d \) value for each radionuclide (see, e.g., Serne, 1992; Warnecke et al., 1994), (3) radionuclides which belong to chains of successive decays as parent species or as members of radioactive series will be considered without their decay products because on this often used approach analytical solutions to the transport problem are possible (see, e.g., Hadermann and Patry, 1980; Hadermann and Roesel, 1985; Van der Lee et al., 1992). In addition, with regard to the movement of dissolved nuclides which preferentially sorb to conservatively migrating colloids Eq. (9) has to be modified by substituting the two-phase retardation factor \( R_{f2} (=R_{f2}) \) for the three-phase retardation factor \( R_{f3} \). Consequently, by presupposing that the properties of aquifers remain constant in time, i.e., blocking effects of porous media are disregarded, the unimpeded colloid-bound transport of nuclides through porous groundwater zones at the Gorleben site might be approximately described by the modified transport equation (Eq. (9)).

The initial and boundary conditions for solving this equation are: (a) \( C = 0 \) at \( t = 0 \) and for any \( x \geq 0 \) by taking into account that \( x = 0 \) at the geosphere inlet for nuclides released from the repository into the potential waterpath. This waterpath is approximated by an one-dimensional transport system along the \( x \)-coordinate. (b) \( C = 0 \) at the outer boundary \( (x = \infty) \) of aquifer zones at \( t \geq 0 \). (c) \( C = C_0 \) at \( x = 0 \) for \( t \geq 0 \) where \( C_0 \) corresponds to the total dissolved source concentration of any radionuclide released at constant rate during the post-operational phase. \( C_0 \) values (e.g., for \( ^{232} \)Th we have \( C_0 = 10^{-6} \) mol/l within a release period of \( 10^7 \) years) may be derived from tables of radioactive repository inventories (Hadermann and Roesel, 1985; Memmert, 1991). Additional conditions demand that porous aquifer zones are homogenous and isotropic, shapes of aquifer boundaries are regular and three-phase nuclide partitions are defined by reversible and linear sorption processes (see, e.g., Mills et al., 1991; Bennet et al., 1993).

With these conditions in the case of continuous inflow of radionuclides into colloid-containing groundwater-aquifer zones the solution of Eq.
(9) (see Ogota and Banks, 1961; Van Genuchten and Alves, 1982; Sun, 1996; Lege et al., 1996) can be written as

$$C(x,t) = \frac{C_0}{2} \left[ \exp\left(\frac{v_f - u}{2D}\right)^x \text{erfc}\left(\frac{Rx - ut}{2\sqrt{DRt}}\right) + \exp\left(\frac{v_f + u}{2D}\right)^x \text{erfc}\left(\frac{Rx + ut}{2\sqrt{DRt}}\right) \right]$$

(16)

where $u = \left(\frac{v_f}{n_e}\right)^2 + 4\lambda D^{1/2}$ and

$$\text{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_z^{\infty} e^{-t^2} dt$$

is the error function complement $(1 - \text{erf}(z))$.

Here $D (=a \cdot v_a)$ is the hydrodynamic dispersion coefficient, $a$ is the (longitudinal) dispersivity, $v_f (=v_a \cdot n_e)$ is Darcy’s velocity (with $v_a =$ mean porous velocity), $\lambda$ is the decay constant, $C$ is the total mobile phase concentration of nuclides (i.e., dissolved concentration plus concentration adsorbed to mobile colloids) and $R$ is the factor $R_f$ given in Eq. (15). When radionuclides are released into groundwater-aquifer systems as a pulse of the length $t_0$ time/distance changes of nuclide concentrations are given by

$$C(x,t,t_0) = C(x,t) - C(x,t-t_0).$$

(18)

Usually, the dependence of the relative concentration, $C/C_0$, on travel time for certain migration distances is plotted as breakthrough curve in order to obtain an insight into influences of sorption and other parameters on the time change in concentration at any boundaries (see, e.g., Sigg and Stumm, 1994). As an alternative, the variation of $C/C_0$ over the migration length at fixed travel times, i.e., concentration-distance profiles, may also be plotted.

**Modeling of the colloid-associated radionuclide transport**

For testing the colloid-nuclide transport equation data may be used which have been obtained within the scope of the Gorleben-site investigation programme (Warnecke and Hild, 1988; Warnecke et al., 1994). Among others, parameters, such as $C_0$, $v_f$, $K_d$, $n_e$, $a$, $c_C$ and path-lengths, are taken from (a) values of the radionuclide inven-

<table>
<thead>
<tr>
<th>Description</th>
<th>Symbol</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length of model segments of the aquifer zone</td>
<td>$x$</td>
<td>100–1000 m</td>
</tr>
<tr>
<td>Effective porosity of the matrix</td>
<td>$n_e$</td>
<td>0.36</td>
</tr>
<tr>
<td>Density of the rock solids</td>
<td>$\rho_S$</td>
<td>2.6 kg/m$^3$</td>
</tr>
<tr>
<td>Flow rate (Darcy velocity) of Gorleben groundwater</td>
<td>$v_f$</td>
<td>16–48 m/a</td>
</tr>
<tr>
<td>Model flow rates</td>
<td>$v_f$</td>
<td>66–378 m/a</td>
</tr>
<tr>
<td>Longitudinal dispersivity</td>
<td>$a$</td>
<td>3–50 m</td>
</tr>
<tr>
<td>Mean diameter of sediment grains</td>
<td>$d$</td>
<td>200 $\mu$m</td>
</tr>
<tr>
<td>Radius of sediment grains</td>
<td>$a_C$</td>
<td>100 $\mu$m</td>
</tr>
<tr>
<td>Colloidal particle sizes</td>
<td>$r_p$</td>
<td>10–200 nm</td>
</tr>
<tr>
<td>Colloid concentrations</td>
<td>$c_C$</td>
<td>0–100 mg/l</td>
</tr>
<tr>
<td>Association constant onto humic colloids (mean values)</td>
<td>$K_c$</td>
<td>Th: 8.5·10$^6$ ml/g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ac: 1.9·10$^7$ ml/g</td>
</tr>
<tr>
<td>Attachment (collision) efficiency over the range of tested Gohy aquifers (see Table 9)</td>
<td>$\alpha_d$</td>
<td>2.73·10$^{-4}$–9.07·10$^{-6}$</td>
</tr>
</tbody>
</table>
tory in combination with solubility data (see, e.g., Memmert, 1991), (b) hydrogeological data obtained in site-specific programmes (PSE, 1983, 1985; Bundesamt für Strahlenschutz, 1990; Hund, 1991; Röthemeyer, 1991), (c) migration experiments (Meier et al., 1993, 1994; Warnecke et al., 1994), (d) relationships which hold for performance assessment scales (Luckner and Schestakow, 1986; Grindrod et al., 1994) and (e) studies on groundwater colloids (Kim et al., 1984; Kim, 1991). Some of these parameters are given in Table 7.

Results of modeling colloid-bound nuclide transport by using Eqs. (16)–(18) indicate among others: (1) the travel time of thorium from any source to aquifer boundaries at distances of about 1000 m may be decreased from thousands to hundreds of years by humic colloids within the site-specific range of colloid concentrations because Th\(^{4+}\) species are more effectively sorbed to humic colloids than to sandy sediments (see Fig. 5), (2) the mobility of Ac\(^{3+}\) species may be significantly affected when colloids are increased from \(c_C = 0\) to \(c_C \geq 20\) mg/l as shown by an increase in \(C/C_0\) values and a drop of travel time because of high \(K_C\) values (see Fig. 6).

The results obtained are consistent with results of particle migration simulations given in literature (Eichholz et al., 1982; Mills et al., 1991). This implies that in the presence of colloids a large reduction of nuclide travel times and an increase of nuclide concentrations at the outlet of aquifer horizons must be taken into account when nuclide-colloid sorption exceeds nuclide-sediment sorption. That is, the protective effect of porous sediments against the migration of radioactive nuclides must be considered when nuclide-colloid transport exceeds nuclide-sediment transport.

**Fig. 5.** Influence of humic colloid concentration \((c_C = 0, 5, 25, 100\) mg/l\) on \(c/t\) curves of \(^{232}\)Th calculated with Eqs. (16) and (17) for porous groundwater systems with the parameters: \(x = 1000\) m (segment of the sandy sediment Gohy 2220). \(K_C = 8.5 \cdot 10^6\) ml/g. \(K_d = 6.8 \cdot 10^3\) ml/g. \(v_f = 66.15\) m/a. \(\rho = 2.6\) g/ml. \(n_e = 0.36.\) \(a = 50\) m. \(\lambda_{232} = 4.92 \cdot 10^{-11}\) a\(^{-1}\).

**Fig. 6.** Breakthrough curves calculated with Eqs. (16)–(18) for the colloid-associated transport of \(^{227}\)Ac released by a pulse of the length \(t_0 = 10\) a. Parameters: \(x = 400\) m (segment of the sandy sediment Gohy 2220). \(K_C = 1.8 \cdot 10^7\) ml/g. \(K_d = 230\) ml/g. \(v_f = 66.15\) m/a. \(\rho = 2.6\) g/ml. \(n_e = 0.36.\) \(a = 15\) m. \(\lambda_{227} = 3.2 \cdot 10^{-2}\) a\(^{-1}\). Humic colloid concentrations \(c_C = 0, 2, 5, 20\) mg/l \((0, 2 \cdot 10^{-6}, 5 \cdot 10^{-6}, 2 \cdot 10^{-5}\) g/ml)
contaminants to the biosphere can be low in the presence of colloids. Consequently, it is important to consider within the framework of safety assessment studies attenuation mechanisms of colloid-bound radionuclides by physicochemical filtration processes.

**Attenuation of colloid-associated nuclide transport in porous aquifers**

**Bases of physicochemical colloid deposition in porous media**

Although repulsive electrostatic forces will resist the attachment of colloids to aquifer surfaces of like net charge field-scale migration of colloids may be generally limited in porous media by the process of physicochemical deposition (McCarthy and Degueldre, 1993; Ryan and Elimelech, 1996). According to the underlying classical filtration theory (Yao et al., 1971; Tobaison and O’Melia, 1988; O’Melia and Tiller, 1993; Elimelech et al., 1995; Ryan and Elimelech, 1996) deposition of submicron colloids from flowing groundwater involves:

1. The convective Brownian diffusion of colloids (<1 µm) to stationary particle surfaces. This process can be described by the dimensionless rate at which colloids collide with immobile grains (diameter \( d = 2a_c \) [m]) of porous media without taking electrical double layer interaction into account, i.e., by the single collector efficiency \( \eta_0 \) (Yao et al., 1971; Spielman and Friedlander, 1974; O’Melia and Tiller, 1993; Elimelech et al., 1995):

\[
\eta_0 = 4.04B^{1/3} \left( \frac{v_j d}{D_p} \right)^{-2/3}
\]

where \( B = 1.26 \left( \frac{1 - \gamma^5}{w} \right) \); \( w = 2 - 3\gamma + 3\gamma^5 - 2\gamma^6 \);

\[
\gamma = \frac{z_{el}}{N} - n_e \quad \text{and} \quad D_p = \frac{kT}{6\pi r_p \eta_v}.
\]

Here \( B \) is a dimensionless flow parameter with which the particle capture by a single isolated grain can be corrected by the particle capture within porous packed bed systems (Happel, 1958; Yao et al., 1971; McDowell-Boyer et al., 1986). For this, according to Happel (1958) the granular medium is approximately treated as an assemblage of identical grains (radius \( a_c \)) surrounded in each case by a shell of aqueous fluid. In this model used in many particle deposition studies (Levich, 1962; Yao et al., 1971; Tien, 1989; Elimelech et al., 1995) (a) the radius \( b \) of the fluid envelope is given under the condition that the overall porosity, \( n_e \), of the porous system is maintained for the individual grains, i.e., \( b = a_c(1 - n_e)^{-1/3} \), and (b) the flow field is described by the porosity-dependent parameters \( \gamma = a_c/b \) and \( w \) which are derived from the stream function of a low flow around a spherical grain in porous media. For \( n_e \) values of 0.31–0.36 which are typical for Gohy aquifer sands (Kim et al., 1994) \( B \) is about 80–44. \( D_p \) [m²/s] is the intrinsic diffusion coefficient of colloids with \( k = \) Boltzmann constant \( (1.4 \times 10^{-23} \text{ kg m}^2\text{s}^{-2}\text{K}^{-1}) \), \( \eta_v = \) water viscosity \( (1.05 \times 10^{-3} \text{ kg m}^{-1}\text{s}^{-1}; T = 298 \text{ K}) \), \( T = \) temperature [K], \( r_p = \) radius of the colloidal species [m].

2. The attachment of charged colloidal particles to grain surfaces of like net charge by the interaction of double layer repulsion and van der Waals attraction. This process will be described by an empirical attachment efficiency \( \alpha_d \) (also termed collision efficiency) which specifies the fraction of collisions with aquifer grains resulting in irreversible deposition by the influence of surface charge heterogeneities (McCarthy and Zachara, 1989; Song and Elimelech, 1994; Elimelech et al., 1995; Ryan and Elimelech, 1996), i.e., \( \alpha_d = \eta/\eta_0 \). Here, \( \eta \) is the overall single removal efficiency resulting from the interaction between colloids and aquifer grain surfaces, \( \eta_0 \) corresponds to the single collector efficiency which can be calculated by Eqs. (19) and (20).

**Attachment efficiency \( \alpha_d \)**

**Determination** Theories are not able to predict \( \alpha_d \) in the presence of double layer repulsion or steric interaction (Elimelech et al., 1995). However, \( \alpha_d \) may be derived from packed-bed column
studies if the assumptions hold: (a) colloid transfer from the convective fluid flow to the boundary layer of granular collectors by diffusion (Yao et al., 1971; O’Melia and Tiller, 1993), (b) steady state distribution (∂c/∂t = 0) of colloids between flowing aqueous phase and grain surfaces (Yao et al., 1971; Spielman and Friedlander, 1974), and (c) negligible permeability reduction of packed beds by colloid accumulation (Hunt et al., 1987). In this case, according to Yao et al. (1971), O’Melia and Tiller (1993) and Elimelech et al. (1995) the concentration of colloids, c_C = c, in the effluent of the column is obtained as

\[
\frac{c}{c_0} = \exp\left(\frac{3}{2d}(1-n_e)\eta_0\alpha_d x\right) = \exp(-\lambda_d x)
\]

where \(\lambda_d = \frac{3}{4a_c}(1-n_e)\eta_0\alpha_d\). (21)

That is, \(\alpha_d\) becomes (O’Melia, 1990; Elimelech et al., 1995)

\[
\alpha_d = -\frac{4a_c}{3(1-n_e)\eta_0 x} \ln \frac{c}{c_0}.
\]

Here, \(c_0\) is the influent concentration of colloids, \(c/c_0\) corresponds to the recovery of injected colloids and \(\lambda_d\) is the so-called filter coefficient which in its inversed form, \(1/\lambda_d [\text{m}]\), corresponds to a distance over which the colloid concentration is reduced to 0.37\(c_0\) (Iwasaki, 1937; Hunt et al., 1987).

**\(\alpha_d\) values of model colloids** In the case of diffusion as dominant colloidal transport mechanism to aquifer surfaces \(\alpha_d\) values given in literature are usually in the range of \(10^{-3}\) to \(1\) (Ryan and Elimelech, 1996). \(\alpha_d\) values were mostly derived from deposition experiments for suspensions of submicron latex particles in laboratory columns containing spherical glass beads uniform in size (Elimelech and O’Melia, 1990; Elimelech, 1992; O’Melia and Tiller, 1993; McCarthy and Degueldre, 1993; Elimelech et al., 1995). Field studies on the deposition are rather limited up to now. Nevertheless, it seems noticeable that \(\alpha_d\) values observed in field experiments on the passage of microspheres through a sandy aquifer are considerably uniform and in the same order as those derived in laboratory experiments (Harvey et al., 1989; McCarthy and Degueldre, 1993). Moreover, results obtained with latex colloids indicate that chemical parameters, such as electrolyte concentration and pH, via surface potentials of colloids and solid media will be the main factors in controlling colloid-solid attachment according to (Elimelech, 1992)

\[
\alpha_d = A \frac{\alpha H}{\varepsilon_0 \varepsilon Z_C Z_S}.
\]

(23)

Here \(\varepsilon_0\) is the permittivity of free space \((8.854 \times 10^{-12} \text{[As V}^{-1}\text{m}^{-1}]\)), \(\varepsilon\) is the dielectric constant of water \((78.5; T = 298 \text{K})\), \(\kappa\) is the inverse Debye length of the double layer \((=3.29 \times 10^9\text{[m}^{-1}]\)), \(I\) is the ionic strength \([\text{mol/l}]\), \(H\) is the Hamaker constant \((=10^{-20} \text{VAs})\) and \(Z_C, Z_S\) are the zeta-potentials of colloids and solids \([\text{V}]\), respectively. Site-specific factors, such as roughness of interacting colloids and aquifer surfaces, charge heterogeneity of the surfaces (Ryan and Elimelech, 1996) and steric (non-electrostatic) effects (O’Melia and Tiller, 1993) may be covered with the empirical constant \(A\).

**Estimation of \(\alpha_d\) values of humic colloids** \(\alpha_d\) values for describing the deposition of colloids in groundwater aquifers are not known to us at present. However, there are results of experiments carried out with natural inorganic and organic colloids which demonstrate the applicability of theoretical approaches as a function of flow-rate, pH and charge on the removal of colloids (Eichholz et al., 1982; Read et al., 1994; Sätmark et al., 1994). With regard to Gorleben aquifers results may be of importance which have been obtained by Kim et al. (1994) with groundwater rich in humic colloids (borehole Gohy 2227/128 m containing \(=5 \times 10^{17}\) colloids per litre) and Pleistocene sand comparable to the borehole aquifer. The data from these experiments indicate: (1) that \(^{152}\text{Eu}^{3+}\)
and $^{241}$Am$^{3+}$ migrate through the columns without marked retardation (i.e., $R_f$ is close to 1) since trivalent actinide ions analogous to Ac$^{3+}$ preferentially sorb to humic colloids relative to aquifer sands, (2) that in conformity with Eqs. (19) and (21) $c/c_0$ values of colloids and colloid-bound radionuclides, respectively, seem to decrease by slowing down water flow-rates (Table 8).

Based on the published data by using Eq. (22) the attachment efficiency, $\alpha_d$, for humic colloids migrating through the investigated Gorleben aquifer may be available (see Table 8). Moreover, because the sediment-groundwater system Gohy 11/1341 (depth 131 m) is comparable to that of the aquifer Gohy 2227 (depth 128–130 m) the empirical constant $A$ (Eq. (24)) may be derived. With $\alpha_d = 2.73 \cdot 10^{-4}$ (Table 8) and double layer parameters characterizing the system Gohy 11/1341 (Table 9) a value of $A = 1.68 \cdot 10^{-7}$ is obtained. Therefore, by means of Eq. (23) with both the constant $A$ and the site-specific parameters $Z_C$, $Z_S$, $\kappa$ and $H$ attachment efficiencies for humic colloids in various Gorleben aquifers may be derived as approximate values (see Table 9). According to the given $\alpha_d$ values being around $10^{-5}$ to $10^{-4}$ attachment efficiencies of humic colloids to porous groundwater aquifers seem to be smaller than $\alpha_d$ values of submicron latex particles observed by Elimelech (1992) and McCarthy and Degueldre (1993) in studies on the transport of charged artificial colloids through sandy aquifers ($\alpha_d = 4 \cdot 10^{-2}$) or packed-bed columns of uniform glass beads ($\alpha_d = 10^{-1}$–$10^{-2}$).

### Modeling of the impeded colloid-bound nuclide transport

An analytical approximation for describing the impeded colloid-bound transport of radionuclides through porous groundwater aquifers may be based on (a) the Brownian deposition of colloidal carriers, and (b) the advective-dispersive transport of colloid-bound nuclides assuming steady state flow (Nielsen et al., 1986). That is, on the one hand analogous to Eq. (21) the relative concentration of colloid-bound radionuclides associated with the deposition of colloidal carriers can be described by

$$C(x,t)_{t>0}/C_0 = \exp(-\lambda_d x)$$  \hspace{1cm} (24)

for any $x > 0$ (Iwasaki, 1937; Hunt et al., 1987).

### Table 8. Attachment efficiencies for the deposition of humic colloids (traced with Eu-152 and Am-241) on the groundwater aquifer Gohy 2227 calculated by using Eq. (22). Data concerning flow-rates and $c/c_0$ ratios were taken from Kim et al. (1994).

<table>
<thead>
<tr>
<th>Flow rate [m/a]</th>
<th>$c/c_0$</th>
<th>$\alpha_d$</th>
<th>Nuclide</th>
</tr>
</thead>
<tbody>
<tr>
<td>378</td>
<td>0.91</td>
<td>2.90 $\cdot$ 10^{-4}</td>
<td>Eu-152</td>
</tr>
<tr>
<td>76.69</td>
<td>0.75</td>
<td>3.06 $\cdot$ 10^{-4}</td>
<td>Am-241</td>
</tr>
<tr>
<td>66.15</td>
<td>0.71</td>
<td>3.30 $\cdot$ 10^{-4}</td>
<td>Eu-152</td>
</tr>
<tr>
<td>16.38</td>
<td>0.64</td>
<td>1.69 $\cdot$ 10^{-4}</td>
<td>Eu-152</td>
</tr>
<tr>
<td>mean $\alpha_d$</td>
<td>(2.73 $\pm$ 0.71)$\cdot$ 10^{-4}</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: $x = 0.5$ m; $n_e = 0.36$; $r_p = 100$ nm; $T = 298$ K. The mean diameter of the Pleistocene sand was estimated as $d = 0.04$ cm by using the mercury penetration method according to Stanley-Wood (1979).

### Table 9. Estimated attachment efficiencies for the deposition of humic colloids in Gorleben groundwater aquifers. Calculation with Eq. (23) by using the double layer data of colloids, $Z_C$ (Table 1), and sediments, $Z_S$, the empirical constants $A = 1.68 \cdot 10^{-4}$ and $H = 10^{-20}$ VAs.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Depth [m]</th>
<th>$Z_C$ [mV]</th>
<th>Water Gohy $Z_S$ [mV]</th>
<th>$\kappa$ [m$^{-1}$]</th>
<th>$\alpha_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand 2</td>
<td>8</td>
<td>−2.9</td>
<td>2131</td>
<td>−10.1</td>
<td>2.3 $\cdot$ 10^{6}</td>
</tr>
<tr>
<td>Sand 7</td>
<td>83</td>
<td>−5.8</td>
<td>1281</td>
<td>−8.1</td>
<td>9.8 $\cdot$ 10^{6}</td>
</tr>
<tr>
<td>Marl 8</td>
<td>85</td>
<td>−18.5</td>
<td>1281</td>
<td>−10.5</td>
<td>9.8 $\cdot$ 10^{6}</td>
</tr>
<tr>
<td>Sand 11</td>
<td>131</td>
<td>−2.9</td>
<td>1341</td>
<td>−4.3</td>
<td>1.4 $\cdot$ 10^{6}</td>
</tr>
</tbody>
</table>
On the other hand, the relative concentration associated with the equilibrium transport of colloid-bound radionuclides is given by Eq. (16). As groundwater velocities through porous Gorleben aquifers are low relative to instantaneous adsorption or exchange reactions the components of the groundwater aquifers (dissolved radionuclides, colloids, solid matrix) may be considered as being equilibrated at all points along the flow path (Mills et al., 1991; Bennet et al., 1993). Therefore, in the case of continuous inflow of nuclides into aquifers, the analytical solution for the combined processes can be approximately written as the product of the expressions on the right-hand sides of Eq. (16) (where $F(x,t)$ corresponds to the factor given in square brackets) and Eq. (24) for the initial condition $C(x,0) = 0$ and the boundary conditions $C(0,t) = C_0$, $C(\infty, t) = 0$ and $C(x, t \gg 0) = C_0 \exp(-\lambda_d x)$ (see Lucas, 1980):

$$C(x,t)_{t>0} / C_0 = \frac{1}{2} F(x,t) \exp \left[ -\frac{3(1-n_e) x}{2d} - 4.04B^{1/3} \left( \frac{v_f d}{D_p} \right)^{2/3} \alpha_d \right]$$

(25)

That is, as a correction factor for colloid deposition the exponential term $\exp(-\lambda_d x)$ may be used where $\lambda_d$ is given by Eq. (21). The mobile concentration of radionuclides, expressed as $C$, corresponds to the dissolved nuclide concentration plus nuclide concentration associated with mobile colloids (Mills et al., 1991). The symbols of the other parameters are the same as defined above. Blocking effects may be disregarded (Hunt et al., 1987; McDowell-Boyer et al., 1986; Ryan and
When nuclides are released into aquifers as a pulse of the length $t_0$ an analogous correction of Eq. (18) by the term $\exp(-\lambda d x)$ is necessary.

Simulation of field-scale colloid-associated radionuclide transport

In order to test the applicability of Eq. (25) results of field studies concerning, among others, the influences of both the particle size and the water velocity on the mobility of colloid-bound nuclides have been simulated (see, e.g., McCarthy and Zachara, 1989). Parameter values are based on data taken from Gorleben database and results obtained in this paper (Table 7). Following results may provide an insight into colloid-facilitated transport phenomena when electrochemical repulsive forces are important between colloidal carriers and sedimentary grains: (1) in accordance with Eq. (25) migration distances may be strongly reduced by a change of colloids with diameters of around 400 nm to smaller ones (Fig. 7), (2) the total recovery, $C/C_0$, of colloid-bound nuclides may decrease by many orders of magnitude (e.g., from 80% to below $10^{-10}$%) by an increase within a decade of $\alpha_d$ as shown in concentration-time profiles calculated for $\text{Ac}^{3+}$ for the parameters $\alpha_d = 2 \cdot 10^{-5}$ (Fig. 8), (3) the total recovery, $C/C_0$, of colloid-associated radionuclides can be strongly reduced with decreasing groundwater flow rates, e.g., from 5% to below $10^{-11}$%, as demonstrated for $\text{Th}^{4+}$ in Fig. 9 for water velocities decreasing from 78.7 m/a to 13.2 m/a. Moreover, an analogous influence of water velocity on $C/C_0$ values of colloid-bound actinides observed in column experiments with aquifer sands (Kim et al.,...
1994) could be approximately modeled by means of Eq. (25).

With regard to the safety assessment of the colloid-associated nuclide transport in Gorleben aquifers it is important to note that migration distances, travel times and total mobile phase concentrations of radionuclides may be predicted within individual aquifer segments. As an example, Fig. 10 shows concentration-distance profiles for colloid-bound $^{232}$Th migrating through site-specific groundwater aquifers at depths of 131, 85, 83 and 8 m, respectively, which are characterized by $\alpha_d$ values of $2 \times 10^{-4}$, $9 \times 10^{-6}$, $3.7 \times 10^{-5}$ and $1.3 \times 10^{-5}$ (Table 9). The groundwater velocity corresponds to $v_f = 48$ m/a which is in the order of the highest flow-rates observed in Gorleben aquifers (Bundesamt für Strahlenschutz, 1990). That is, the migration distances of colloid-bound thorium may be between about 20 m and 600 m.

**Influence of fractures on colloid-bound nuclide transport**

The migration of radionuclides may exclusively occur at the Gorleben site through porous groundwater aquifers. **Fractured** rock barriers can be largely neglected as parts of the travel path (Warnecke and Hild, 1988; Bundesamt für Strahlenschutz, 1990; Warnecke et al., 1994). This property is very important for the safety of the planned repository. Fractures would operate as largely unprotected travel paths because (a) migration of nuclides may mainly depend on the advective-dispersive transport of solutes and (b) diffusion of dissolved species into the adjacent porous matrix can be efficient as protective barrier only if solute-matrix diffusion coefficients are not smaller than $D = 10^{-9}$ cm$^2$/s (see, e.g., Grisak and Pickens, 1980; Tang et al., 1981). Consequently, as colloidal carriers are characterized by both matrix diffusion coefficients $D \ll 10^{-9}$ cm$^2$/s and very small interactions with fracture surfaces, colloid-bound nuclides would migrate without any remarkable attenuation with velocities which are close to fracture water velocities (see, e.g., Van der Lee et al., 1992; Stumm, 1992; Vilks and Bachinski, 1994; Harmand and Sardin, 1994; Sahimi, 1995; Grindrod and Lee, 1997).

**CONCLUSION**

In conclusion it can be stated that the advection-dispersion transport equation modified by colloid-chemical factors allows one to predict approximately the migration of colloid-bound radionuclides through porous media. For the application of the modified transport equation as key parameters three-phase retardation factors, $R_f$, describing the association of radionuclides to mobile colloids relative to stationary solids and attachment efficiencies, $\alpha_d$, quantifying the collection of colloids on immobile grain surfaces must be known.

Results concerning the range of the key parameters $R_f$ and $\alpha_d$ point to the potential importance of colloids for the radionuclide transport in subsurface groundwater: Firstly, according to results obtained in batch experiments three-phase retardation factors of actinides in groundwaters containing humic colloids may be much more smaller than two-phase retardation factors because of a more effective sorption of nuclide species (e.g., $\text{Ac}^{3+}$) to mobile colloids than to stationary sandy and marly sediments. Secondly, collision efficiencies, $\alpha_d$, available or evaluated from published field and column tests for submicron latex particles, suspensions of inorganic colloids and humic colloids from Gorleben groundwater aquifers indicate that colloid-solid matrix interactions in geochemical barriers appear to be generally given by values not lower than around $10^{-5}$.

Therefore, in porous groundwater aquifers the migration of colloid-associated radionuclides may be controlled to a large extent by the Brownian collection of the colloidal species on stationary granular surfaces. Consequently, in spite of the high mobility of colloids only short transport distances of colloid-bound nuclides have to be expected. Because the Gorleben strata mainly consist of porous aquifers, any transport of colloid-bound nuclides through fractured rocks characterized by a low tendency for the retardation and re-
tention of colloids may be largely excluded.

In consideration of these facts and site-specific experimental data predictive simulation studies on long-term safety aspects of the planned repository at Gorleben, Germany, have been carried out. It is shown that the transport of some leached waste radionuclides, such as Ac$^{3+}$ and Th$^{4+}$, which will be eventually associated with site-specific humic colloids may take place in the porous groundwater aquifers overlying the Gorleben salt dome over finite distances of tens to hundreds meters only.

The results and methods discussed in this paper should be generally taken in assessment studies concerning the influence of inorganic and organic colloidal particles into account as carriers of leached waste components from radioactive repositories through porous groundwater aquifers to the biosphere.

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