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Stability and Mobility of Colloids in Opalinus Clay

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This report was prepared on behalf of Nagra. The viewpoints presented and conclusions reached are those of the author(s) and do not necessarily represent those of Nagra.

SUMMARY

The Opalinus Clay formation in northern Switzerland is currently under evaluation for its suitability as a host rock for a spent fuel, vitrified high-level waste and long-lived intermediate level waste repository. The Swiss concept of geological disposal of radioactive waste is based on a multi-barrier system. In the near field, spent fuel and vitrified high-level radioactive waste are contained in massive steel canisters surrounded by a dense bentonite clay barrier. The long-lived intermediate-level waste, on the other hand, is surrounded by cementitious materials in separate emplacement tunnels. In the far field, the host rock formation is expected to act as an effective barrier for radionuclide migration. In this report, we discuss the potential role of mobile colloidal particles in facilitating radionuclide transport through the Opalinus Clay formation (far field). Since rock fractures resulting in preferential flow paths are not expected in Opalinus Clay, we limit the discussion to convective-diffusive transport through the rock matrix.

Numerous reports in the literature have suggested that mobile colloidal particles in subsurface porous media may serve as carriers for strongly sorbing contaminants, such as many radionuclides, and thereby facilitate contaminant migration. The objective of this report is to (i) discuss the potential composition of colloidal particles in Opalinus Clay, (ii) evaluate the colloidal stability of colloids in Opalinus Clay under consideration of the pore water chemistry, (iii) discuss the potential mobility of colloidal particles in Opalinus Clay under various assumptions concerning flow conditions and colloid-matrix interactions.

The most relevant types of colloids in Opalinus Clay were inferred from the rock composition and from reference pore water chemistry. These include clay minerals, quartz, calcite, iron oxides, and organic matter. An evaluation of published data on surface charge and colloidal stability of these types of colloidal particles suggests that they would readily aggregate in Opalinus Clay pore water, which has a high ionic strength (~0.1-0.3 M) and neutral to slightly alkaline pH (~6.8-8.2).

Based on the texture of Opalinus Clay and hydrologic parameters, simple diffusion, advection, and colloid filtration calculations were conducted. Colloidal mineral particles larger than ~ 60 nm are expected to be rather immobile, since they settle by gravitational forces. Also, the mesoporous structure of Opalinus Clay is likely to limit their mobility by physical straining. Colloidal particles smaller than ~ 60 nm are expected to be removed very effectively from the pore water by diffusion and deposition to immobile matrix surfaces. Maximum travel distances (99.99 % removal) of colloidal particles, as calculated by filtration theory, are therefore below 1 m even under worst-case assumptions. In summary, the mobility of colloids in Opalinus Clay is expected to be extremely low due to the following factors: (i) high ionic strength of pore water and resulting low colloidal stability, (ii) mesoporous structure of Opalinus Clay and resulting filtration by physical straining, (iii) extremely low hydraulic conductivity and advective pore water velocity in Opalinus Clay, (iv) much slower diffusion of colloidal particles compared with dissolved radionuclide species.

In conclusion, Opalinus Clay contains various types of colloidal size particles, but their colloidal stability and mobility is expected to be extremely low due to both chemical and physical factors. Thus, colloid-facilitated transport of radionuclides in Opalinus Clay is unlikely, as long as fracture flow does not occur. If further hydrogeologic studies reveal the relevance of fracture flow, the role of colloids needs to be re-evaluated in this con-

text. The composition of Opalinus Clay organic carbon and dissolved organic carbon and its potential role in radionuclide migration through Opalinus Clay requires additional research.

ZUSAMMENFASSUNG

Die geologische Formation Opalinuston in der Nordschweiz wird derzeit auf seine Eignung als Wirtgestein für ein Endlager von abgebrannten Brennelementen, verglasten hochaktiven Abfällen und langlebigen mittelaktiven Abfälle untersucht. Das schweizerische Konzept zur geologischen Endlagerung radioaktiver Abfälle beruht auf einem System mehrerer Barrieren. Im Nahfeld sind die Brennelemente und verglasten hochradioaktiven Abfälle in massiven Stahlbehältern gelagert, die wiederum von einer Barriere aus verdichtetem Bentonit umgeben sind. Andererseits sind die langlebigen mittelaktiven Abfälle, die in separate Stollen eingelagert werden, von Zementmaterialien umgeben. In der Geosphäre wird davon ausgegangen, dass das Wirtgestein eine wirksame Barriere für die Migration von Radionukliden darstellt. In diesem Bericht diskutieren wir die mögliche Rolle von Kolloiden beim Transport von Radionukliden durch Opalinuston (Geosphäre). Da nicht davon ausgegangen wird, dass Störungszonen im Opalinuston präferentielle Fliesspfade darstellen, beschränken wir die Diskussion auf den konvektiv-diffusiven Transport durch die Gesteinsmatrix.

Zahlreiche Studien deuten darauf hin, dass mobile kolloidale Partikel im porösen Untergrund als Träger für stark sorbierende Schadstoffe, wie z.B. viele Radionuklide, dienen können, und dadurch die Migration der Schadstoffe beschleunigen. Die Ziele dieser Studie sind (i) die Zusammensetzung möglicher Kolloide im Opalinuston zu bestimmen, (ii) ihre kolloidale Stabilität im Opalinuston unter Berücksichtigung der Zusammensetzung des Porenwassers zu beurteilen und (iii) die potentielle Mobilität von kolloidalen Partikeln im Opalinuston unter verschiedenen Annahmen betreffend der Fliessbedingungen und der Kolloid-Matrix-Interaktionen zu diskutieren.

Relevante Typen von Kolloiden im Opalinuston wurden von der Zusammensetzung des Gesteins und des Referenzporenwassers abgeleitet. Dazu gehören Tonmineralien, Quarz, Kalzit, Eisenoxide, und organische Substanzen. Eine Auswertung von publizierten Daten zur Oberflächenladung und kolloidalen Stabilität dieser Kolloidtypen deutet darauf hin, dass diese im Porenwasser des Opalinustons mit seiner hohen Ionenstärke (~ 0.1-0.3 M) und seinem neutralen bis basischen pH (~ 6.8-8.2) schnell aggregieren würden.

Basierend auf der Textur von Opalinuston und hydrologischen Parametern wurden einfache Diffusions-, Advektions- und Kolloidfiltrationsrechnungen durchgeführt. Kolloidale Mineralpartikel grösser als ~ 60 nm sind wahrscheinlich immobil, da sie aufgrund der Gravitation sedimentieren. Zudem begrenzt die mesoporöse Struktur des Opalinustones ihre Mobilität durch physikalische Filtration. Kolloidale Partikel kleiner als ~ 60 nm dürften durch Diffusion und Deposition an der immobilen Matrixoberfläche sehr effizient aus dem Porenwasser entfernt werden. Selbst Filtrationsrechnungen unter äusserst konservativen Annahmen ergaben für kolloidale Partikel maximale Transportdistanzen (99.99 % Partikelfiltrierung) von weniger als 1 m. Zusammenfassend wird die Mobilität von Kolloiden im Opalinuston als sehr gering eingeschätzt, aufgrund der folgenden Faktoren: (i) Hohe Ionenstärke des Porenwassers und daraus resultierende geringe kolloidale Stabilität dispergierter Partikel, (ii) mesoporöse Struktur des Opalinustones und infolgedessen physikalische Filtration von Kolloiden, (iii) extrem tiefe hydraulische Leitfähigkeit und Fliessgeschwindigkeit im Opalinuston, (iv) wesentlich langsamere Diffusion von Kolloiden als von gelösten Radionukliden.

Opalinuston enthält also verschiedene Typen von Partikeln, die potentiell Kolloide bilden können. Die kolloidale Stabilität und Mobilität dieser Partikel wird aber aufgrund

chemischer und physikalischer Faktoren als sehr gering eingeschätzt. Daher ist ein beschleunigter Transport von Radionukliden durch mobile Kolloide im Opalinuston sehr unwahrscheinlich, solange kein präferentieller Wasserfluss in Störungszonen auftritt. Sollten weitere Studien zeigen, dass in Störungszonen ein wesentlicher Wasserfluss auftreten kann, so müsste die Rolle von Kolloiden in diesem Zusammenhang neu beurteilt werden. Weitere Forschungsarbeiten sind nötig, um die Zusammensetzung der organischen Substanzen im Opalinuston und ihren Einfluss auf die Migration von Radionukliden besser beurteilen zu können.

RÉSUMÉ

La formation d'argiles à Opalinus du nord de la Suisse est actuellement étudiée en vue de la construction d'un dépôt pour éléments combustibles usés, déchets de haute activité vitrifiés et déchets de moyenne activité à vie longue. Le concept suisse pour le stockage des déchets radioactifs repose sur un système de barrières multiples. Dans le champ proche, les éléments combustibles usés et les déchets de haute activité vitrifiés sont confinés dans des conteneurs en acier massif entourés par une barrière de bentonite compactée. Les déchets de moyenne activité à vie longue sont stockés dans des galeries séparées et enrobés de ciment. Dans la géosphère, la roche d'accueil sert de barrière à la migration des radionucléides. La présente étude concerne la capacité potentielle des particules colloïdales mobiles à transporter les radionucléides dans les argiles à Opalinus (géosphère). Posant comme hypothèse que, dans les argiles à Opalinus, les zones de fractures ne constituent pas des voies d'écoulement préférentielles, seul le transport par convection-diffusion dans la matrice rocheuse a été étudié.

De nombreuses études suggèrent que, dans des sols poreux, les particules colloïdales mobiles pourraient servir de vecteur à des polluants fortement sorbants, par exemple à de nombreux radionucléides, et par là faciliter les processus de migration. Ce rapport a pour objectifs (i) l'étude de la composition potentielle des particules colloïdales dans les argiles à Opalinus, (ii) l'estimation de la stabilité des colloïdes dans les argiles à Opalinus, en fonction de la composition chimique des eaux interstitielles, (iii) l'étude de la mobilité potentielle des particules colloïdales dans les argiles à Opalinus, en variant les paramètres relatifs aux conditions d'écoulement et aux types d'interaction entre les colloïdes et la matrice rocheuse.

Les types de colloïdes présents dans les argiles à Opalinus ont été déduits de la composition de la roche et de l'eau interstitielle de référence: il s'agit de particules minérales argileuses, de quartz, de calcite, d'oxydes de fer et de matières organiques. Les données publiées sur la charge de surface et la stabilité de ces types de particules colloïdales permettent de conclure que celles-ci formeraient rapidement des agrégats dans l'eau interstitielle des argiles à Opalinus, qui a une force ionique élevée (~ 0.1-0.3 M) et un pH neutre à faiblement alcalin (~ 6.8-8.2).

Sur la base de la texture des argiles à Opalinus et des paramètres hydrologiques, des calculs de diffusion simple, d'advection et de filtrage des colloïdes ont été effectués. Les particules colloïdales minérales d'une taille supérieure à ~ 60 nm ont une mobilité relativement faible, car elles se sédimentent en raison de la force de gravitation. Par ailleurs, la structure mésoporeuse des argiles à Opalinus tendra à limiter la mobilité de ces particules par filtrage physique. Les particules colloïdales d'une taille n'excédant pas ~ 60 nm devraient, par le biais des processus de diffusion, migrer de l'eau interstitielle vers des surfaces immobiles de la matrice où elles se déposeraient. Les distances maximales sur lesquelles les particules colloïdales peuvent être transportées (pour un filtrage de 99.99 % des particules), telles qu'elles ont été calculées, sont en conséquence inférieures à 1 m, même dans les scénarios les plus conservateurs. En résumé, on considère que la mobilité des colloïdes dans les argiles à Opalinus est très faible, pour les raisons suivantes: (i) la force ionique élevée de l'eau interstitielle, avec pour conséquence une stabilité colloïdale réduite, (ii) la structure mésoporeuse des argiles à Opalinus qui entraîne un filtrage physique des colloïdes, (iii) une conductivité hydraulique et une vitesse advective de l'eau interstitielle très basses dans les argiles à

Opalinus, (iv) une vitesse de diffusion des particules colloïdales bien inférieure à celle des radionucléides dissous.

En conclusion, les argiles à Opalinus contiennent différents types de particules pouvant constituer des colloïdes, mais leur stabilité et leur mobilité seront probablement très réduites en raison de différents facteurs physiques et chimiques. De ce fait, dans les argiles à Opalinus, la probabilité que les colloïdes facilitent le transport des nuclides est très faible – pour autant que les fractures ne constituent pas des voies d'écoulement. Si des études hydrogéologiques ultérieures mettaient en évidence des fractures pouvant servir de voies d'écoulement, le rôle des colloïdes devrait être revu. La composition du carbone organique et du carbone organique dissous dans les argiles à Opalinus, ainsi que leur rôle potentiel pour la migration des radionucléides dans les argiles à Opalinus, nécessitent par ailleurs des études complémentaires.

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SYMBOLS

α	attachment efficiency
ρ	density of water (1000 kg m^{-3})
λ	filter coefficient (in m^{-1})
ϕ	porosity (in m^3 m^{-3})
η	single collector efficiency
μ	viscosity (1x10^{-3} kg m^{-1} s^{-1} for water at 293 K)
η_0	single collector efficiency at $\alpha = 1$
η_D	single collector efficiency due to diffusion
η_G	single collector efficiency due to gravity
η_I	single collector efficiency due to interception
$\delta h/\delta x$	hydraulic gradient (in m m^{-1})
ρ_p	particle (colloid) density (in kg m^{-3})
A_S	porosity dependent parameter of Happel's model
C	concentration (at t, x)
C_0	source concentration (at x = 0, t>0)
C_C	colloid concentration in solution (in kg m^{-3})
D_0	bulk diffusion coefficient (in m^2 s^{-1})
d_c	filter-bed single collector diameter (in m)
D_e	effective diffusion coefficient (in m^2 s^{-1})
d_p	particle (i.e. colloid) diameter (in m)
f_C	fraction of colloid-bound nuclide in solution
g	gravitational acceleration (9.81 m s^{-2})
k	Boltzmann constant (1.38x10^{-38} m^2 kg s^{-2})
K	hydraulic conductivity (in m s^{-1})
K_C	sorption coefficient for nuclide sorption to colloids (in m^3 kg^{-1})
L_T	travel distance (for specified degree of colloid removal, in m)
Pe	Péclet number
T	temperature (in K, set at 293 K)
t	time (in s)
v_d	Darcy velocity (in m s^{-1})
v_p	pore water velocity (in m s^{-1})
v_s	settling velocity (in m s^{-1})
x	position (in m)

1   INTRODUCTION

Argillaceous rocks such as Opalinus Clay are under evaluation in several countries as potential host rock formations for the geological disposal of nuclear waste because of their low permeability and their self-healing properties (Bonin, 1998; Gautschi, 2001; Mazurek, 2001). The Opalinus Clay formation in the Zürcher Weinland (northern Switzerland), at a depth of approximately 600 - 700 m below surface and with a thickness of about 100 m, is considered as a potential host rock for a repository for spent fuel, vitrified high-level radioactive waste, and long-lived intermediate level radioactive waste. As an additional source of information on Opalinus Clay properties, a rock laboratory is operated at Mont Terri in Switzerland (Thury & Bossart, 1999). Site-specific information for the Zürcher Weinland is available from the borehole near Benken and from geophysical measurements, including 3D seismics.

In the assessment of the barrier function of host rocks, the migration of radionuclides is usually modelled as a two-phase system. Radionuclides are either dissolved in the mobile aqueous phase as free ions or complexed species, or they are associated with the immobile solid phase as adsorbed or precipitated species. However, mobile colloidal particles as a third phase could represent a potential transport carrier for strongly sorbing contaminants, which, based on their sorption behavior, would otherwise be considered immobile (Honeyman, 1999; Kretzschmar ET AL., 1999; McCarthy & Zachara, 1989). Numerous field studies have shown that colloids are ubiquitous in environmental systems (McCarthy & Degueldre, 1993). Colloids can also be generated in the repository near field (Bates et al., 1992). For colloid-facilitated contaminant transport to be an important transport mechanism, several conditions must be fulfilled: (1) colloidal particles must be present in relevant concentrations in the pore water, (2) the particles must remain dispersed in the pore water over long time periods, i.e., they must be chemically and colloidally stable, (3) the particles must be transported over significant distances by convection or diffusion, and (4) the contaminants must be associated to a significant extent with the mobile particles (McCarthy & Zachara, 1989).

The objective of this report is to compile and discuss the available information necessary to evaluate the potential relevance of colloids for the assessment of radionuclide migration in Opalinus Clay. Four questions are addressed: (1) Which types of colloids might be expected in Opalinus Clay ground water? (2) Are dispersed particles expected to be stable regarding the geochemical composition of Opalinus Clay groundwater? (3) Are dispersed particles mobile under the given hydroligic conditions in Opalinus Clay? (4) Are colloids relevant for radionuclide migration in Opalinus Clay? This report, however, is not intended to give a comprehensive review on the colloid transport literature or to provide extensive transport calculations. Reviews on colloid transport in the environment were given by, e.g., Kretzschmar et al. (1999), McCarthy & Degueldre (1993), Ryan & Elimelech (1996), Swanton (1995), and van der Lee et al. (1994).

2   CHARACTERIZATION OF OPALINUS CLAY – AVAILABLE INFORMATION

2.1   Bulk Composition and Exchanger Coverage of Opalinus Clay

The bulk composition of Opalinus Clay, as observed in the Benken borehole, is given in Table 1. Dominant mineral phases are calcite, quartz, illite, mixed-layer illite/smectite, and kaolinite, which together account for roughly 85 % of the total mass. Organic carbon represents 0.6 % w/w. For the Opalinus Clay at the Mont Terri, which has a similar bulk composition, it was postulated that approximately 0.15 % of the organic carbon content were humic acids (Thury & Bossart, 1999), i.e., ~ 10 ppm of the total rock mass. Despite the small amounts, humic acids might be relevant for safety assessment because they may form stable complexes with radionuclides (Artinger et al., 1998; Hummel et al., 2000). The saturation of the cation exchange sites of the Opalinus Clay from the Benken borehole is given in Table 2. Approximately 50 % of the cation exchange capacity is saturated by Na^+, as expressed by the exchangeable sodium percentage (ESP).

Table 1:   Bulk composition of Opalinus Clay from the Benken borehole (Nagra, 2002a).

	Weight Fraction (%)
Calcite	16 ± 10
Dolomite/Ankerite	1 ± 0.4
Siderite	4 ± 2.4
Quartz	20 ± 5
Albite	1 ± 0.3
K-Feldspar	2 ± 1.0
Pyrite	1.1 ± 1.0
Sum Phyllosilicates	54 ± 10
Illite	18 ± 6
Illite/Smectite	14 ± 4
Chlorite	5 ± 2
Kaolinite	17 ± 6
C(org)	0.6 ± 0.3

2.2   Reference Pore Water Composition of Opalinus Clay

Reference pore water compositions for Opalinus Clay were calculated by Pearson (2002) based on its mineralogical composition, on the saturation of its cation exchange sites, and on results from laboratory leaching experiments. The pore water was assumed to be in equilibrium with kaolinite, calcite, dolomite, fluorite, pyrite, rhodochro-

site, siderite, and quartz. For the Cl, Br, and SO_4 concentrations and the partial pressure of CO_2, a range of input values was used to cover the range of measured values and parameter uncertainty. The compositions of the nominal reference groundwater and the reference groundwaters with the highest and lowest pH are given in Table 3 (from Pearson, 2002). The nominal groundwater was calculated from best estimates for the input values. The assumptions of low CO_2 pressure (Opalinus Clay in contact with air in the repository) and low anion concentrations (lowest concentrations measured in Benken borehole) yield the reference water with the highest pH and lowest ionic strength.

Table 2: Saturation of the cation exchange capacity (CEC) of the Opalinus Clay from the Benken borehole (Nagra, 2002a).

	Cation saturation ($mmol_c$/kg)
Na	54
K	8
Mg	13
Ca	29
CEC	106
ESP (%) [a]	51

[a] ESP = exchangeable sodium percentage

Table 3:   Calculated reference compositions of Opalinus Clay pore water in the Zürcher Weinland (Pearson, 2002).

	Nominal	High-pH	Low-pH
pH	7.24	8.18	6.80
Pe	- 2.83	- 4.02	- 2.29
log pCO_2 (atm)	- 2.2	- 3.5	- 1.5
Solutes (mmol/kg H_2O)			
Na	170	80	210
K	5.7	2.6	7.3
Mg	7.5	1.3	13
Ca	11	1.9	18
Fe	0.043	0.0080	0.077
Si	0.18	0.18	0.18
Total Solutes (ppm)	13900	5530	19200
Ionic Strength (mmol/L)	230	94	310
Normality (mmol$_c$/L)	210	89	280
SAR ((mol/m^3)$^{1/2}$)	40	45	38
Saturation Index [a]			
Goethite	1.84	2.89	1.24
Hematite	0.57	2.66	- 0.64
Magnetite	1.13	4.52	- 0.78

[a] saturation index = 0 for Kaolinite, Calcite, Dolomite, Fluorite, Pyrite, Rhodochrosite, Siderite and Quartz

The calculated Fe concentrations listed in Table 3 are roughly one order of magnitude higher than the measured concentrations in pore waters from Mont Terri. However, this may be due to iron (hydr)oxide precipitation during water sampling (Pearson, 2002). The calculated positive saturation indices for hematite, goethite, and magnetite indicate, that iron oxide precipitates may be expected in the Opalinus Clay environment. Oxide coatings on silicate surfaces, although not reflected in the bulk rock composition (Table 1), may strongly affect surface chemical and colloidal processes (Puls et al., 1993; Yariv & Cross, 1979).

Reference concentrations of total organic carbon (TOC) and dissolved organic carbon (DOC) for Opalinus Clay listed in Table 4 were estimated from Mont Terri pore water data. Nominal values represent the best estimate, whereas the low and high values indicate the range of uncertainty. In water samples, the TOC was determined as the

organic carbon content of unfiltered samples and the DOC as the organic carbon content of samples filtered through 0.45 µm membranes (Pearson, 2002). The colloid data provided in Table 4 were determined in Mont Terri pore water samples (Degueldre et al., 1998). Colloid concentrations were determined from particle countings of colloids larger than 500, 200, and 100 nm assuming a Pareto size distribution and a density of 2000 kg/m^3 of the colloid particles (Degueldre et al., 1998). The concentration of colloids from 1 to 10 nm is extrapolated.

Table 4:   Organic carbon and colloid concentration of Opalinus Clay pore waters, based on data from the Mont Terry (Degueldre et al., 1998; Pearson, 2002).

	nominal	low	high
Organic Carbon (mg/L) [a]			
TOC (unfiltered)	10	6	100
DOC (< 0.45 µm)	6	3	100
Colloids (mg/L) [b]			
100-1000 nm	0.6		
1-10 nm [c]	0.02		

[a] from Pearson (2002), nominal value represents best estimate, low and high values indicate range of uncertainty;

[b] from Degueldre et al. (1998)

[c] extrapolation from data at 100, 200 and 500 nm based on a power-law size distribution

The reference TOC and DOC values indicate that Opalinus Clay ground water should contain ~ 4 ppm of organic colloids larger than 450 nm. This result apparently contrasts with the measured colloid concentration. Organic colloids hence might not be properly accounted for in the particle counting. Regarding the composition of TOC and DOC, earlier studies concluded from extraction data, that humic substances might represent a significant fraction of the organic carbon in solution (Thury & Bossart, 1999). The presence of humic substances in solution appears to be likely considering that Opalinus Clay is postulated to contain ~ 10 ppm of humic acids. Contrasting conclusions on the composition of the DOC were drawn from a recent study on the effect of DOC from Opalinus Clay on the sorption behavior of Ni, Eu, and Th on an ion exchange resin (Glaus et al., 2001). The data suggest that only a small fraction of the organic matter consists of humic or fulvic acids, and that the largest part of the TOC consists probably of low molecular weight organic molecules or organic macromolecules with a low content in high-affinity ligand sites.

Regarding the experimentally determined colloid concentration, it should also be considered, that artifacts may arise during colloid sampling, e.g. calcite or iron oxide precipitation upon contamination with air (Degueldre et al., 2000; Düker & Ledin, 1998;

McCarthy & Degueldre, 1993). In the Opalinus Clay ground water, the measured concentration of colloids (~ 0.6 ppm) corresponds to 0.03 to 0.01 % of the estimated total mass of dissolved species (5500 - 19000 ppm, Table 3). This indicates the risk of artifacts in the determination of colloid concentrations. The experimental value should therefore be interpreted with caution.

2.3   Texture and Hydrological Parameters of Opalinus Clay

Textural parameters of the Opalinus Clay as found in the Benken borehole are listed in Table 5. These parameters represent best estimates based on a series of different determination methods. The pore diameter distribution is approximate and little is known about the spatial structure and connectivity of these pores (Nagra, 2002a).

An extensive series of field data indicate that fractures in Opalinus Clay do not represent preferential flow paths (Gautschi, 2001): Hydraulic tests in boreholes at depths below 300 m gave hydraulic conductivities $<10^{-12}$ m/s, even in the presence of joints and faults. The inspection of numerous tunnel sections in Opalinus Clay (total length 6600 m) showed only minor water inflows and only where the overburden was less than 200 m. These findings indicate that the very low hydraulic conductivity of Opalinus Clay results from matrix water flow, whereas fracture flow at present conditions is likely to be irrelevant (Gautschi, 2001; Mazurek, 2001). Reference values (RV, best estimates, defensible values) and alternative values (AV, pessimistic values) for the hydraulic conductivity and hydraulic gradient parameters are listed in Table 6. The Opalinus Clay layer extends 40 m above and below the repository. The reference values (RV) represent the most likely case for the matrix flow in the Opalinus Clay and the vertical hydraulic conductivity and gradient indicate a slow upward water flow from the Sandsteinkeuper below the Opalinus Clay to the Wedelsandstein above the Opalinus Clay (Marschall et al., 2001). While the hydraulic conductivity in the horizontal direction is assumed to be 5 times higher than in the vertical direction (Nagra, 2002a), the horizontal hydraulic gradient indicates that horizontal matrix water flow is negligible. The first set of alternative values (AV1) describes the case of 25 times higher pore water velocity in the upward direction. The second alternative parameter set (AV2) describes the case of downward water flow in the Opalinus Clay.

Table 5:   Textural parameters of Opalinus Clay based on data from the Benken borehole (Nagra, 2002a).

Porosity (v/v)	12 %
Water Content (w/w)	5 %
Pore Diameter Distribution (v/v)	
r < 2 nm	20 %
2 nm < r < 50 nm	55 %
50 nm < r < 20'000 nm	25 %

Table 6:   Hydrological parameters of Opalinus Clay based on data from the Benken
            borehole (Nagra, 2002a).

	RV [a]	AV1 [b]	AV2 [b]
Conductivity K (m/s)			
vertical	2×10^{-14}	1×10^{-13}	1×10^{-13}
horizontal	1×10^{-13}	5×10^{-13}	5×10^{-13}
Hydraulic Gradient $\delta h/\delta x$ (m/m)			
vertical	1 upward	5 upward	0.5 downward
horizontal	0	0	0

[a] RV = reference values (best estimates, defensible values),
[b] AV = alternative values (pessimistic values)

3   COLLOIDS IN OPALINUS CLAY: INVENTORY, CHEMISTRY, AND MOBILITY

3.1   Inventory of Colloids in Opalinus Clay

Measurements of colloid concentrations in Opalinus Clay from two sampling sites at Mont Terri (Table 4) yield colloid concentrations of ~ 0.6 ppm (Degueldre et al., 1998). No information on their composition is available. The colloid concentration found in Opalinus Clay are similar to average values found in a series of granitic ground waters (Degueldre et al., 1996; Düker & Ledin, 1998; Vilks et al., 1993; Vilks et al., 1991). In these studies, colloids were found to consist of aluminosilicates, quartz, iron oxides, calcite, and organic carbon, reflecting the composition of the bulk rock or of fracture-linings.

Table 7:   Natural colloids in Opalinus Clay inferred from mineralogical composition of Opalinus Clay (Table 2), pore water speciation calculations (Table 3), and DOC/TOC data (Table 4).

Clay Minerals
Kaolinite
Illite
Mixed-layer Illite/Smectite
Quartz/Silica
Calcite
Iron Oxides (also as coatings)
Organic (also as coatings)

The chemical reactivity and the stability of colloids depend on their composition. Possible colloid size particles in Opalinus Clay groundwater are listed in Table 7. While clay mineral, quartz, and calcite colloids are inferred from the dominant minerals in the Opalinus Clay (Table 1), iron oxide colloids can be postulated considering the over-saturation of reference waters with respect to a series of iron oxides (Table 3). The high reference values for DOC and TOC (Table 4) indicate that organic colloids could also be relevant. Both iron oxides and organic carbon may be present as surface coatings on other colloids and on the bulk rock matrix. According to the points of zero charge (p.z.c.) or isoelectric points (i.e.p.) listed in Table 8, iron oxide or calcite colloids may be positively charged, whereas most other rock and colloid surfaces are nega-tively charged. Considering the rather high DOC values, however, it is likely that the reactive surfaces of colloids and the rock matrix are coated with organic substances and are therefore negatively charged.

Table 8:   Isoelectric points (i.e.p.) or points of zero charge (p.z.c.) of some mineral phases.

Precipitate or Mineral	pH		Source [a)]
amorphous Al(OH)$_3$	7.1 - 9.5	i.e.p. [b)]	1
amorphous Fe(OH)$_3$	8.5	p.z.c. [c)]	2
Goethite	7.8	p.z.c.	2
Hematite	8.5	p.z.c.	2
Magnetite	6.5	p.z.c.	2
Quartz	2.0	p.z.c.	2
amorphous SiO$_2$	1.8	i.e.p.	1
Calcite	9.5	i.e.p.	1
Feldspars	2 - 2.4	p.z.c.	2
Kaolinite	4.6	p.z.c.	2
Montmorillonite	2.5	p.z.c.	2
Albite	2.0	p.z.c.	2
Pyrite	1.4	i.e.p.	3

[a)] from: 1. Yariv & Cross (1979); 2. Stumm (1992); 3. Bébié et al. (1998).
[b)] i.e.p. = isoelectric point, pH at which electrophoretic mobility is zero.
[c)] p.z.c. = point of zero charge, pH at which the net surface charge is zero

Colloids might also be generated in the near field by the corrosion of steel canisters and waste glass, by the alteration of the bentonite backfill (Abrajano et al., 1990; Bates et al., 1992; Feng et al., 1994; Nagra, 1993), or by direct precipitation of radionuclides (Geckeis et al., 1998; Olofsson et al., 1982). However, the bentonite backfill of the spent fuel and high-level waste emplacement tunnels can be considered an effective filter for colloids (Nagra, 1993). Colloids originating from the near field are therefore not explicitly addressed in this report. However, if they were released into the far field, near field colloids would likely behave in analogy to natural colloids.

In the following paragraphs, the colloidal stability of potential types of colloids in the Opalinus Clay groundwater is discussed.

3.2   Nature and Properties of Colloids in Opalinus Clay

3.2.1   Clay Minerals (Illite, Smectite, Kaolinite)

Phyllosilicates (illite, smectite, kaolinite) account for more than 50 % of the total bulk rock mass (Table 1). As indicated by their p.z.c. or i.e.p. (Table 8), these clay minerals bear a net negative surface charge. The coagulation behavior of clay mineral was extensively studied with respect to soil dispersion as affected by sodicity. Important parameters in this context are the exchangeable sodium percentage (ESP = fraction of exchanger charge saturated with Na$^+$) and the sodium adsorption ratio of the solution phase (SAR = $c_{Na}/(c_{Ca}+c_{Mg})^{1/2}$, c: concentrations in mol/m^3) (Sposito, 1989). Respective

values for Opalinus Clay are listed in Tables 2 and 3. Increasing ESP and SAR indicate an increasing tendency of the clay minerals to disperse, and an increasing critical coagulation concentration (CCC) is required to keep the clay particles coagulated. As pointed out by Sposito (1989), "soil salinity tends to counteract the effect of exchangeable sodium on soil structure." This also applies to the Opalinus Clay, where the high ESP and SAR go along with a high salinity of the ground water. From the three reference waters (Table 3), the water with the lowest ionic strength has the highest pH value. Since high pH and low ionic strength both favor the stability of dispersed clay particles, an evaluation of colloid mobility based on the composition of the high-pH water is considered to be conservative.

The stability of clay colloids can be estimated from CCC values of respective reference clay minerals. The CCC value is defined by the transition between slow and fast coagulation kinetics. Below the CCC, the collision efficiency, i.e., the fraction of physical collisions that lead to aggregation, decreases with the electrolyte concentration. Above the CCC, fast transport-controlled coagulation is observed (Elimelech et al., 1995). Instead of extensive kinetic aggregation studies, batch coagulation tests were frequently used to estimate CCC values of colloidal clay particles. In such tests, the CCC is estimated as the electrolyte concentration, at which a certain percentage of the initial clay colloids has settled over a certain time period. Such operationally defined CCC values depend on the experimental conditions and generally decrease with increasing coagulation time (Hesterberg & Page, 1990b). The CCC values determined from batch tests are often lower than CCC values determined from kinetic aggregation studies, since substantial coagulation can also occur at coagulation rates below the fast coagulation rate. In a kinetic aggregation study with illite at pH 10 in KCl background, for instance, Novich & Ring (1984) determined a CCC of 0.20 M, whereas Hesterberg & Page (1990a) determined CCC values of 0.030 to 0.014 M in batch coagulation tests (2.2 to 17 h equilibration time). Considering the typical decrease of kinetic collision efficiencies with decreasing electrolyte concentration, collision efficiencies of 0.01 to 0.1 can also be expected at electrolyte concentrations of a factor ten below the kinetic CCC. Therefore, CCC values determined from batch tests allow at least qualitative estimates of the stability of colloids under specific conditions.

For kaolinite, montmorillonite, and illite, Goldberg & Forster (1990) report CCC values of ≤ 40 $mmol_c/L$ at a SAR of 60 $(mol/m^3)^{1/2}$ and for pH values from ~ 6 to ~ 9 (batch study, equilibration time 3h, CCC at 80 % removal, ~ 1000 ppm clay in suspension). Substantially higher CCC values than in mixed Na/Ca systems are measured in pure Na systems, where the strong coagulating effect of Ca is absent (Goldberg et al., 1991; Goldberg & Glaubig, 1987; Tarchitzky et al., 1993). Therefore, CCC values from pure Na systems are likely misleading when inferred to estimate clay colloid stability in Opalinus Clay pore water. Overall, the CCC values from Goldberg & Forster (1990) are in qualitative agreement with results from other coagulation studies with clay particles (Hesterberg & Page, 1990a; Keren et al., 1988; Kretzschmar et al., 1993; Oster et al., 1980; Tarchitzky et al., 1993) and clay size soil particles (Grolimund et al., 2001). Therefore, based on the CCC values from Goldberg & Forster (1990) and considering the ionic strength of the high-pH reference pore water, the stability of clay colloids is likely rather low in the Opalinus Clay ground waters.

Coatings of iron oxides are expected to reduce the negative charge of clay colloids and therefore can have a destabilizing effect on clay colloids (Goldberg & Glaubig, 1987; Kretzschmar et al., 1993).

Because of the high DOC of the reference Opalinus Clay ground waters (Table 4), it is likely that clay colloids are coated with organic substances. Such organic coatings increase the stability of clay colloids, either due to an increase in their negative charge or due to steric stabilization (Frenkel et al., 1992; Heil & Sposito, 1993; Jekel, 1986; Kretzschmar et al., 1997; Kretzschmar et al., 1998; Tarchitzky et al., 1993). However, in systems containing Ca this effect is much less pronounced than in pure Na systems (Tarchitzky et al., 1993). This is for instance reflected by the CCC values of soil clay fractions and model minerals reported by Goldberg & Forster (1990): In pure Na systems, the CCC values of organic carbon containing soil clay fractions are much higher than those of organic carbon free clay model compounds. At a SAR of 60 $(mol/m^3)^{1/2}$, however, the CCC of soil clay fractions never exceed 50 $mmol_c$/L and are therefore only slightly higher than the 40 $mmol_c$/L previously reported for model minerals. Thus, even though organic coatings might have a stabilizing effect on clay colloids in Opalinus Clay, the concentrations of Ca, Mg, and Na appear sufficiently high to induce clay colloid coagulation.

3.2.2   Quartz and Amorphous Silica

Due to its low p.z.c. (Table 8), quartz colloids are negatively charged at Opalinus Clay reference pH values. For quartz colloids, a CCC of ~10 mM Ca^{2+} at pH 4.5-7.5 was reported from a kinetic aggregation study (Jekel, 1986). Higher coagulation rates were observed at pH values above 7.5. Increasing DOC concentrations led to an increasing stability of dispersed quartz colloids. This effect, though, was smaller at higher pH levels. From a batch coagulation study, on the other hand, Ledin et al. (1993) report a CCC of ~100 mM Na^+, which was found to be independent of the presence of fulvic acid (2 mg/L). The concentrations of Ca and Na in the high-pH reference water (~2 mM Ca, ~ 80 mM Na, pH 8.2, Table 3) are slightly below the above cited CCC for quartz colloids, and the DOC may exert a stabilizing influence. On the other hand, the presence of Ca and Na considerably lowers the CCC in the groundwater. Under conservative assumptions, the presence of quartz colloids in the Opalinus Clay ground water therefore cannot entirely be ruled out, but appears rather unlikely.

Higher CCC values than for quartz colloids are reported for amorphous silica colloids. In contrast to clay minerals, the colloidal stability of silica and hence its CCC, increases with decreasing pH (Iler, 1979; Swanton, 1995). It is postulated that the amount of adsorbed cations rather than their concentration in solution determines coagulation. Because adsorption of cations decreases with decreasing pH, higher cation concentrations in solution are required at lower pH to obtain the surface coverage required for coagulation (Iler, 1975; Milonjic, 1992). At the relevant pH levels around 7 to 8, rather high CCC values of > 1 M Na^+ or ~100 mM Ca^{2+} are reported for silica colloids. However, the solubility of amorphous silica is ~2 mM (~140 ppm) (Iler, 1979). The concentrations of Si measured in Mont Terri Opalinus Clay ground waters are ~ 0.18 mM (~ 5 ppm) (Degueldre et al., 1998), in agreement with the solubility product of quartz used in the calculation of the reference Opalinus Clay ground water compositions (Table 3). At these conditions, amorphous silica is hence unstable and expected to dissolve with time (Yariv & Cross, 1979), and no polymerization of monomeric silicic acid to form colloidal silica does occur (Iler, 1979). Silica colloids are therefore assumed to be irrelevant under Opalinus Clay ground water conditions.

3.2.3   Calcite

Calcite colloids are detected in granitic ground waters even below the calcite solubility limit (Vilks et al., 1993). Little is known, however, on the colloidal behavior of calcite. Recently, Rieger et al. (2000) found that in an initial phase of calcite precipitation, nanoparticles of ~ 50 nm are formed. These nanoparticles interact with additives such as polycarboxylate molecules, and build up the calcite crystal. In a study with natural calcite, Baghernejad & Dalrymple (1993) showed that natural calcite contained colloid size platelets, that were stable in suspension for at least 30 hours. They postulated that colloid size calcite particles could be mobilized and transported through soil pores and deposited as linings on pore walls. From the p.z.c. of calcite, it might be concluded that calcite bears a positive surface charge in the relevant pH range (Table 8), which would lead to fast deposition on negatively charged rock surfaces. However, calcite surface charge not only depends on protons, but also on the concentrations of Ca^{2+}, carbonate, and further potential determining ions (Stumm & Morgan, 1981). As in the case of clay minerals and quartz, organic coatings might also stabilize calcite colloids. Based on the available information, it is difficult to predict the stability and mobility of calcite colloids in Opalinus Clay pore water.

3.2.4   Iron Oxides

The presence of iron oxides may be postulated from the saturation indices of hematite, goethite, and magnetite in the reference ground waters (Table 3). The fact that measured Fe concentrations in Mont Terri pore water were ten times lower than the calculated concentrations may be due to iron oxide precipitation in groundwater samples in contact with air (Pearson, 2002). From the p.z.c. of iron oxides (Table 8), it can be postulated that they bear little if any negative charge. They therefore rapidly coagulate or deposit as coatings on negatively charged clay mineral, quartz, or organic colloids. This reasoning was invoked by Vilks et al. (1993) to explain the finding that iron colloids were more dominant in the size range above 10 nm than between 1-10 nm. Organic coatings can lead to the stabilization of iron oxide colloids (Kretzschmar & Sticher, 1997; Tipping & Higgins, 1982). Other results indicate, that up to a certain concentration DOC neutralizes the positive charge of hematite colloids, leading to colloid destabilization, but that higher DOC levels lead again to the stabilization of the negatively charged colloids (O'Melia & Tiller, 1993).

Since iron oxide coatings infer positive charge to colloid and rock surfaces, they might overall have a destabilizing effect on other negatively charged natural colloids. Organic coatings causing steric or electrostatic stabilization of colloids, on the other hand, could compensate for this effect.

3.2.5   Organic Carbon

Regarding the organic carbon in Opalinus Clay ground water, it is not yet fully resolved whether humic substances are a relevant fraction or whether it is mainly composed of low molecular weight molecules or macromolecules with a low number of high-affinity metal binding sites. Also, TOC/DOC data from Mont Terri Opalinus Clay ground water are not in agreement with colloid concentrations measured by particle counting.

Clearly, additional research is necessary to clarify the composition and complexation properties of Opalinus Clay organic matter and DOC.

Assuming that part of the DOC consists of humic acids, the main concern would arise from the complexation of radionuclides by these colloidal macromolecules. In batch coagulation studies with humic materials, Ong & Bisque (1968) and Temminghoff et al. (1998) found the CCC to decrease from monovalent to divalent to trivalent cations, in agreement with the Schulze-Hardy rule. For Ca^{2+}, CCC values ranged from ~ 3 mM (pH 4 and 6, 20h) to ~7 mM (pH 7, 4 h). These compare qualitatively to results from Tipping & Ohnstad (1984). For Na^+, Ong & Bisque (1968) report a CCC of 600 mM (pH 7, 4h). Considering the time-scales of these batch experiments, and the combined coagulating effect of Ca, Mg, and Na ions, these findings suggest that humic acid would readily coagulate in Opalinus Clay ground water.

Rapid coagulation of humic acid would be consistent with the assumption that the DOC mainly consists of small organic molecules. In this case, its relevance with respect to colloid behavior would result from the stabilization of inorganic colloids by organic surface coatings, which increase the negative surface charge of inorganic colloids and of the rock matrix (O'Melia & Tiller, 1993). However, this effect is expected to be rather small at in Opalinus Clay ground water because of the rather high concentration levels of Ca, Mg, and Na. Alternatively, if the DOC would mainly consist of small fulvic acid molecules, these may form stable complexes with radionuclides. McCarthy and coworkers, for instance, found that DOC with a nominal diameter of less than 1 nm (< 3000 Dalton) facilitated the transport of actinides in a Ca-rich groundwater (McCarthy et al., 1998a; McCarthy et al., 1998b).

In the Boom Clay (Belgium), DOC was found to be rather mobile (Dierckx et al., 2000; Put et al., 1998). In laboratory transport experiments, a higher mobility was observed for the smaller size fraction of DOC, which was attributed to increasing filtration of organic molecules with increasing molecule size. However, Boom Clay contains a much larger fraction of organic matter (up to 5 %) than the Opalinus Clay (~1 %). About 0.05 % of the organic matter in Boom Clay are considered mobile (Put et al., 1998). In contrast to the Opalinus Clay, the Boom Clay is a plastic clay formation with a water content of up to 42 % (v/v). Finally, Boom Clay ground water has a rather high pH (8.4) and a much lower ionic strength (<0.020 M) than the Opalinus Clay ground water (cf. Table 3), two factors that both favor colloid stability and mobility. Therefore, findings on the mobility of DOC in Boom Clay are not applicable to Opalinus Clay.

3.2.6 Colloidal Stability of Colloids in Opalinus Clay Groundwater

The information on clay mineral, quartz, and organic colloids compiled in the precedent paragraphs indicates that these particles would aggregate and therefore be unstable under Opalinus Clay ground water geochemical conditions. Amorphous silica colloids are not expected as the silica concentration in solution is below the solubility limit. Iron oxide and calcite colloids are likely neutral or positively charged and therefore highly immobile. Coatings of iron oxides on other colloidal particles might decrease their colloidal stability by lowering their generally negative surface charge. Organic coatings, on the other hand, lead to an electrostatic and steric stabilization of inorganic colloids. However, based on the available information, this effect is likely irrelevant in the presence of sufficiently high Ca, Mg, and Na concentration levels. These considerations indicate that individual types of colloids are rather unstable in Opalinus Clay

ground water. The heteroaggregation of different types of colloids and different types of surfaces represents an additional factor, that likely decreases colloid stability in the natural environment as compared to model studies with single components (Findlay et al., 1996; Ryan & Elimelech, 1996).

An alternative approach to assess the stability of ground water colloids based on field observations was presented by Degueldre et al. (2000), who related the concentrations of colloids measured in ground water samples to ground water properties. Colloid concentrations were shown to decrease with increasing hardness (Ca+Mg) and salinity (Na+K) of the ground waters. These trends correspond with collision efficiencies of montmorillonite measured in laboratory systems. Concentrations of alkaline elements (Na+K) below 10 mM and of alkaline earth elements (Ca+Mg) below 0.1 mM were found to lead to increasing colloid stability. These trends reflect the previously reported observations for different types of model colloids. A low colloidal stability of Opalinus Clay ground water colloids can also be postulated from collision efficiencies of aquatic colloids in lakes compiled by O'Melia (1990): At DOC levels between 1 to 4 ppm and Ca concentrations between 0.5 and 2 mM, conditions comparable to Opalinus Clay ground water, collision efficiencies between 0.036 and 0.091 were determined.

Overall, both the behavior of individual types of colloids as well as results from field studies indicate a low stability of colloids under present conditions in Opalinus Clay ground water. This is in agreement with the measured colloid concentrations in Mont Terri ground water. An increased mobility of colloids might only be expected if the geochemical conditions changed dramatically, e.g. if a ground water of lower ionic strength were to intrude into Opalinus Clay (Faure et al., 1996; Grolimund et al., 1996).

3.3   Mobility of Colloids in Opalinus Clay

3.3.1   General Considerations

A series of data indicate that fractures in Opalinus Clay do not represent preferential flow paths at present conditions and that the very low hydraulic conductivity of Opalinus Clay results from matrix water flow. Opalinus Clay is a mesoporous medium, as can be seen from its pore diameter distribution (Table 5). Approximately 75 % of all pores have diameters below 50 nm. Such pores apparently only allow the smallest colloids to pass. On the other hand, pores of diameters from 50 up to 20000 nm might contribute ~25 % of the pore volume. In such pores, also larger colloids could be mobile. However, little is known about the spatial structure and connectivity of these pores (Nagra, 2002a).

Based on the very low conductivity of Opalinus Clay (Table 6), it was suggested that solute transport occurs mainly by diffusion rather than advection (Gautschi, 2001; Soler, 1999). However, with increasing size, colloids exhibit much lower diffusion coefficients than ionic or small molecular solutes, and colloid transport by diffusion may therefore also be limited.

In the following paragraphs, some simple model calculations on the diffusion, advection, and filtration of colloids in Opalinus Clay are discussed.

3.3.2   Colloid Diffusion in the Opalinus Clay

Colloid diffusion through the Opalinus Clay was evaluated by some simple diffusion calculations. As indicated by the horizontal hydraulic gradient (Table 6), horizontal advection in Opalinus Clay is irrelevant. Diffusion is hence the dominant horizontal colloid transport process.
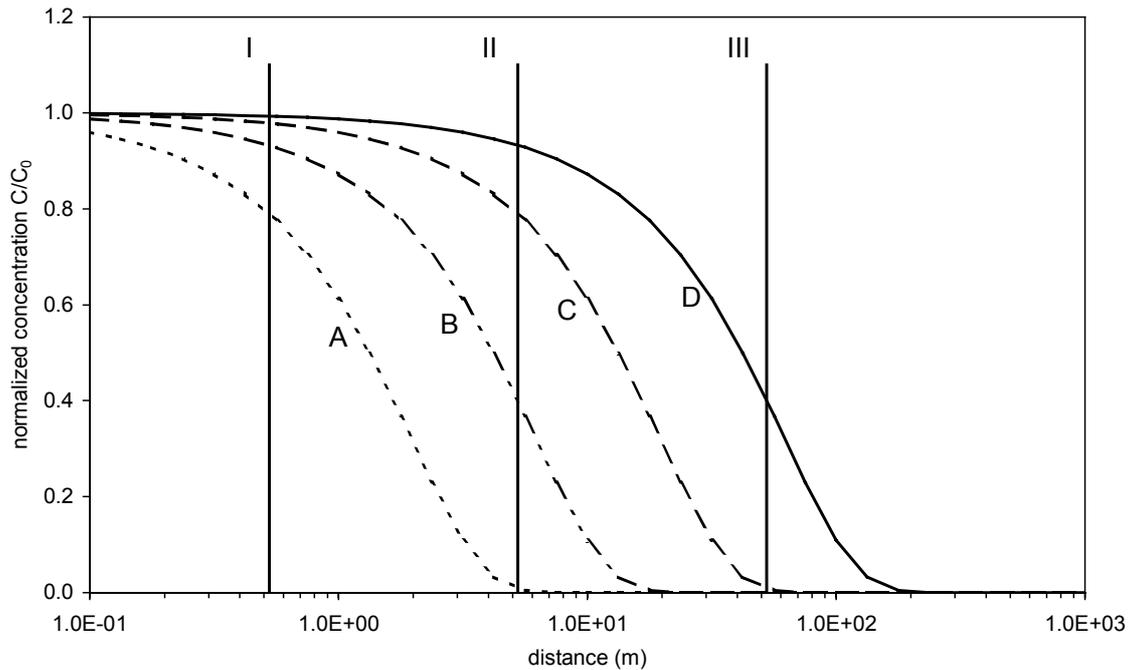

Figure 1:   Unretarded diffusion and advection of colloids in Opalinus Clay from a constant source at x = 0. Curves A, B, C, and D represent concentration profiles for colloids of 1 nm of diameter after 0.01, 0.1, 1, and 10 Ma, or concentration profiles after 10 Ma for colloids of diameters of 1000, 100, 10, and 1 nm, respectively. Vertical lines I, II, and III represent the position of the breakthrough fronts resulting from unretarded colloid advection at reference hydraulic conditions (RV, Table 6) after 0.1, 1, and 10 Ma.

The bulk diffusion coefficient D_0 of a spherical particle is given by:

$$D_0 = \frac{kT}{3\pi\mu d_p} \tag{1}$$

where k denotes the Boltzmann constant (1.38×10^{-38} m^2 kg s^{-2}), T the temperature in K, μ the viscosity (1×10^{-3} kg m^{-1} s^{-1} for water at 293 K), and d_p the particle diameter (in m), respectively. Based on this bulk diffusion coefficient and the porosity of the matrix Φ, the effective diffusion coefficient D_e of a particle in a porous medium can be estimated as:

$$D_e = \phi^{-m} D_0 \tag{2}$$

where m is an empirical parameter (cementation exponent), which for compacted sediments is ~ 2 (Soler, 1999). For the simple case of 1-dimensional diffusion from a constant source of colloids at $x = 0$ and for $t>0$ in one direction ($x>0$), the concentration C normalized to the source concentration C_0 at time t and position x is given by (Crank, 1979):

$$\frac{C}{C_0} = \text{erfc}\left(\frac{x}{2\sqrt{D_e t}}\right) \tag{3}$$

Some model calculations based on Eq. 3 are presented in Figure 1. Curves A, B, C, and D represent the concentration profiles of 1 nm colloids after 0.01, 0.1, 1, and 10 million years. Since the concentration profile is a function of the ratio of time over colloid diameter (see Eq. 1 and 3), the curves A, B, C, and D also represent the concentration profiles after 10 Ma for colloids of 1000, 100, 10, and 1 nm diameter, respectively. Considering the horizontal extension of the Opalinus Clay formation, diffusion of colloids in horizontal direction is obviously irrelevant. In the vertical direction, considering a layer of 40 m of Opalinus Clay above and below the repository, the results show that only colloids smaller than ~10 nm and over time scales of at least ~1 Ma could diffuse over relevant distances (>10 m). These diffusion calculations are based on the assumptions that there is a constant source of colloids at $x = 0$ for all times $t>0$ and that colloids are not immobilized by straining, aggregation, or deposition. The calculations are therefore considered to be highly conservative.

3.3.3   Advective Colloid Transport

As indicated by the reference values for the hydraulic conductivity and gradient (Table 6), a slow upward water flow may be expected in the Opalinus Clay near Benken. Based on the hydraulic conductivity K (in m/s), the hydraulic gradient $\delta h/\delta x$ (in m/m), and the porosity ϕ, the Darcy velocity v_d is given as

$$v_d = K\, \partial h / \partial x \tag{4}$$

and the pore water velocity v_p as

$$v_p = \frac{v_d}{\phi} \tag{5}$$

Considering an Opalinus Clay layer of 40 m above the repository, it would take 7.6 Ma for unretarded colloids to reach the upper Opalinus Clay boundary at reference hydraulic conductivity and gradient (RV, Table 6). In the first alternative case of a 25 times higher pore water velocity (Table 6, AV1), unretarded colloids would reach the upper Opalinus Clay boundary after roughly 0.3 Ma. In the second alternative case of downward matrix flow (Table 6, AV2), unretarded colloids would take 3.0 Ma to reach the lower Opalinus Clay boundary.
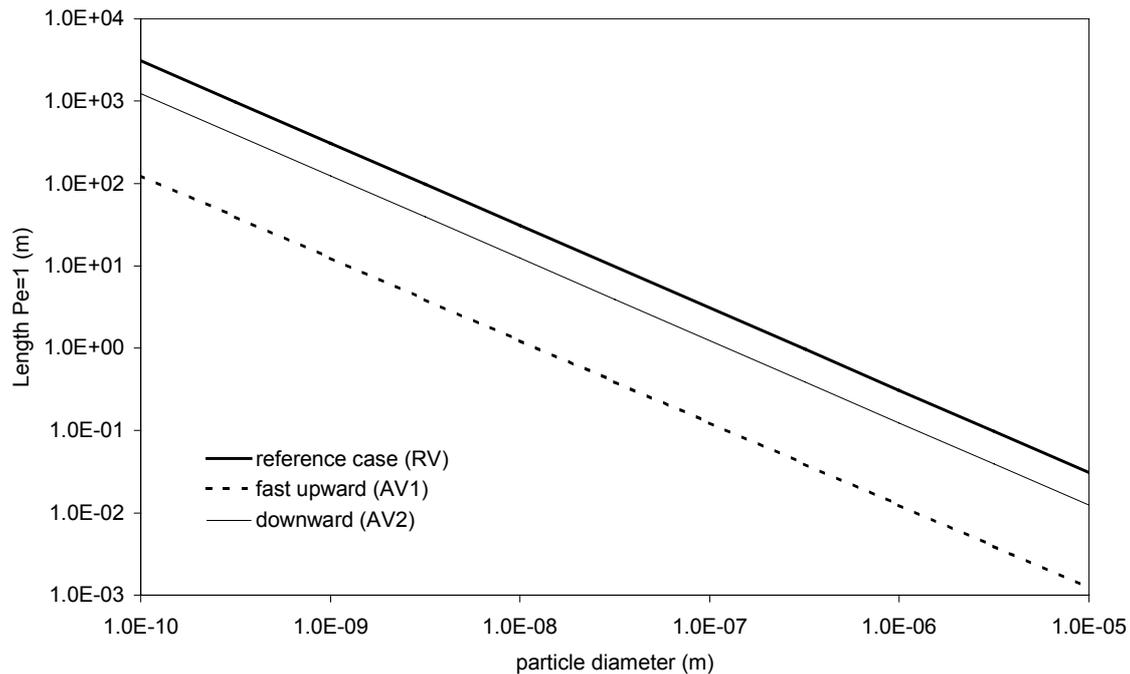
Figure 2:   Lengths at which Pe = 1, i.e. above which advection dominates vertical transport. In the reference case and in the case of downward water flow, and over distances larger than 10 m, only the movement of ionic species and of colloids smaller than ~10 nm is diffusion controlled, whereas the movement of larger colloidal particles is advection controlled. At a 25 times higher upward water flow and over distances larger than ~10 m, movement of all colloidal size particles would be controlled by advection.

For the reference case (RV), the vertical lines I, II, and III in Figure 1 indicate the position of the step input of colloids after 0.1, 1, and 10 Ma, respectively. Comparing these positions with the diffusion profiles of colloids of different sizes at different times, it is obvious that for larger colloids, advection might be the dominant transport process in the hypothetical absence of filtration. The Péclet number

$$Pe = \frac{v_d L}{D_e} \tag{6}$$

indicates the contributions of advection and diffusion to particle movement, L denoting the distance under consideration. At Pe>1, advection dominates transport, at Pe< 1, transport is diffusion controlled. By calculating the length L, for which Pe = 1, one obtains an estimate of the distance, below which diffusion is the dominant transport process (Soler, 1999). Respective lengths as a function of particle diameter (affecting D_e) for the reference and alternative cases of matrix water flow (v_d) are shown in Figure 2. At the reference vertical conductivity and over a distance of ~ 40 m, upward movement of particles larger than ~10 nm is dominated by advection, whereas diffusion would be dominant for smaller particles. At a 25 times higher upward pore water velocity colloids of sizes >1 nm would predominantly be transported by advection. In

the case of downward matrix flow, similarly to the reference case, the movement of particles larger than ~10 nm would be dominated by advection.

The above advection calculations did not account for longitudinal and lateral dispersion processes during advective colloid transport. Lateral dispersion during vertical colloid transport would lead to some horizontal spreading of colloids. Longitudinal dispersion would result in a broadening of the migration front and an earlier arrival of first colloids at the Opalinus Clay boundary. These effects would contribute to the apparent colloid diffusion. However, it is assumed that the apparent diffusion in Opalinus Clay is mainly due to molecular diffusion and that dispersion is negligible (Nagra, 2002b).

Based on these simple calculations of colloid diffusion and advection in Opalinus Clay, some first conclusions can be drawn. In the horizontal direction, no advection occurs and diffusion of colloids is limited compared to the horizontal extension of the Opalinus Clay. In the vertical direction, only colloids smaller than ~10 nm can diffuse over relevant distances (>10 m) and only over time scales of more than 1 Ma. Results for colloid advection in the vertical direction depend on the assumptions on vertical hydraulic conductivity and hydraulic gradient. Only in the alternative (pessimistic) case of upward water flow at an increased conductivity and higher hydraulic gradient (AV1) might unretarded colloids reach the Opalinus Clay boundary before 1 Ma. All these calculations notably do not account for particle attachment to the rock matrix and are therefore highly conservative with respect to colloid mobility.

3.3.4   Colloid Filtration

Filtration theory has been developed to quantitatively describe the removal of colloids during saturated flow through granular porous media. The description and evaluation of the performance of clean-bed filters for water and wastewater treatment is a wide-spread application of filtration model concepts (Elimelech et al., 1995). Filtration theory was also used to describe the movement of bacteria in column and field experiments (Harter et al., 2000; Harvey & Garabedian, 1991; Martin et al., 1992). Recently, Huber et al. (2000) applied filtration theory to column experiments with natural porous media (gravel and sand) and latex colloids. Gribi et al. (1998) used colloid filtration theory to estimate filter coefficients for Wellenberg marl.

To estimate the colloid travel distances in Opalinus Clay, an approach using Yao's expression for the single collector efficiency and Happel's sphere-in-cell model as described in Elimelech et al. (1995) is followed. According to Yao et al. (1971), collisions of particles with collector grains are due to diffusion, interception, and particle settling. The maximum efficiency of a single collector unit, η_0, is given by

$$\eta_0 = \eta_D + \eta_I + \eta_G \tag{7}$$

where η_D, η_I, and η_G denominate the contributions from particle diffusion, particle interception, and particle settling, respectively. These efficiencies for a spherical collector in a porous medium are given by

$$\eta_D = 4A_S^{1/3} \left(\frac{D_0}{v_d d_c} \right)^{2/3} \tag{8}$$

$$\eta_I = \frac{3}{2} A_S \left(\frac{d_p}{d_c} \right)^2 \tag{9}$$

$$\eta_G = \frac{(\rho_p - \rho) g d_p^2}{18 \mu v_d} \tag{10}$$

where d_c denotes the collector grain radius. Based on Happel's sphere-in-cell model, the porosity dependent parameter A_S is defined as

$$A_S = 2(1 - p^5)/(2 - 3p + 3p^5 - 2p^6) \tag{11}$$

where $p = (1-\phi)^{1/3}$. For an Opalinus Clay porosity of 12 %, A_S equals 563.

The filter coefficient λ of a filter-bed is given by

$$\lambda = \frac{3}{2} \frac{(1-\phi)}{d_c} \eta_0 \alpha \tag{12}$$

Table 9: Reference and worst case parameters for filtration calculations.

	Reference	Worst Case
Colloids		
density (kg/m^3)	2500	1001
attachment efficiency	0.01	0.0001
Collector		
diameter (mm)	0.5	5
porosity	12 %	60 %
hydraulic conductivity (m/s)	2×10^{-14}	2×10^{-13}
hydraulic gradient (m/m)	1	10

T = 293 K, μ = 1 x 10^{-3} kg m^{-1} s^{-1}

In Eq. 12, the attachment efficiency α as the chemistry dependent parameter is introduced into the filtration model, indicating the fraction of collisions that effectively lead to particle deposition. Particle attachment efficiencies may be inferred from collision efficiencies of the respective particles (Grolimund et al., 2001). The colloid concentration profile in the filter bed is equal to

$$\frac{C}{C_0} = e^{-\lambda x} \tag{13}$$

Eq. 13 can be reformulated to calculate a particle travel distance L at which, for instance, 99.99 % of all entering colloidal particles are removed from the solution (i.e. where $C_L/C_0 = 0.0001$)

$$L = -\frac{\ln(C_L/C_0)}{\lambda} \tag{14}$$

Respective travel distance calculations for 99.99 % particle removal as a function of particle diameter are shown in Figure 3. Model parameters are listed in Table 9. The reference calculation was based on Opalinus Clay reference values for porosity, hydraulic conductivity, and hydraulic gradient (Tables 5 and 6). Considering the clayey composition of the Opalinus Clay, the collector diameter was estimated as 0.5 mm (i.e. 500μm), equal to the reference value for the argillaceous Wellenberg marl used by Gribi et al. (1998). Compared with values of 0.25 mm for a gravel aquifer and 0.10 mm for a sand aquifer used to describe laboratory column experiments (Huber et al., 2000) or with a value of 0.6 mm used to describe bacteria filtration in a sandy aquifer (Harvey & Garabedian, 1991), this value appears conservative. Also an attachment efficiency of 0.01 is rather conservative, considering the stability of colloids in Opalinus Clay as discussed in the previous section. For comparison, O'Melia (1990) lists collision efficiencies for aquatic colloids in lakes between 0.036 and 0.091 at DOC levels from 1 to 4 ppm and Ca concentrations between 0.5 and 2 mM. The particle density was adjusted to an average value for natural colloids and corresponds to the value applied by Gribi et al. (1998). The travel distances obtained with reference values are always below 10^{-6} m, which means that all colloids released into Opalinus Clay would almost immediately be removed from the solution by filtration. Travel distances of particles larger than ~ 60 nm decrease with increasing particle diameter due to gravitational settling, as reflected by the gravitational single collector efficiency (Eq. 10). The decreasing particle travel distance with decreasing particle size for colloids smaller than ~ 60 nm results from increasing particle removal due to increasingly rapid colloid diffusion to matrix surfaces (Eq. 8). Particle deposition due to interception is irrelevant in all presented model calculations. While the simple diffusion estimates indicate that small colloids might be mobile in Opalinus Clay, filtration calculations imply that with decreasing size, colloids again become increasingly immobile due to diffusion induced deposition.

In further model calculations, parameters were step-wise changed to worst-case assumptions to investigate their effect on the travel distance. Increasing the collector diameter and the porosity affect the travel distances of colloids of all sizes due to their effect on the filter coefficient (Eq. 12). The mobility of small colloids is further increased because also the diffusion dependent single collector efficiency (Eq. 8) decreases with increasing collector diameter and increasing porosity (via Happel's parameter, Eq. 11). A 100 times higher hydraulic conductivity and Darcy velocity lead to a hundred times longer travel distance of large colloids, since the gravitational single collector efficiency is decreased proportionally (Eq. 10). The travel distance of small colloids, which depends on the diffusive single collector efficiency (Eq. 8), increases only by a factor of $100^{2/3}$~20. After changing all matrix and flow related parameters, i.e. collector diameter, porosity, and conductivity, to worst case values (Table 9), the colloid travel distance for 99.99 % particle removal is still less than 1 cm.
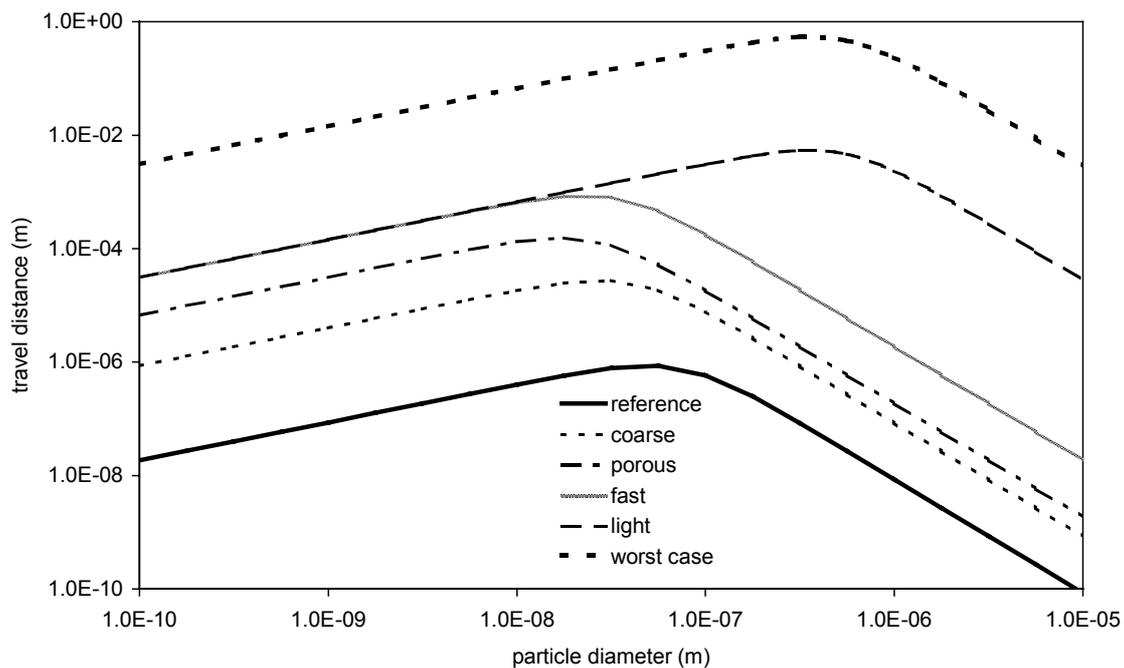
Figure 3:   Travel distances (for 99.99 % particle removal) calculated by filtration theory. Reference model parameters yield travel distances below 10^{-6} m. Parameters are step-wise changed to worst-case conditions. However, even under worst-case assumptions, calculated travel distances are still less than 1 m. Calculations: *reference*: reference model parameters; *coarse*: larger collector grains; *porous*: higher porosity; *fast*: higher conductivity; *light*: low colloid density; *worst case*: lower attachment efficiency; all parameters given in Table 9.

The density of colloids strongly varies with their composition, and especially very small organic colloids with a hydration layer might have densities close to the density of water. A next calculation was therefore carried out assuming an extremely low particle density for colloids (Table 9). According to filtration theory, the particle density only affects the gravitational removal of large colloids (Eq. 10), but not the removal of small colloids by diffusion (Eq. 8). An increased travel distance of extremely light particles is therefore not expected.

Finally, decreasing the attachment efficiency by a factor of 100 to a value of 10^{-4} equally affects colloids of all sizes. However, even under these worst-case conditions, the maximum travel distance of colloids through Opalinus Clay for 99.99 % particle removal is still less than 1 m.

Opalinus Clay does not represent an ideal granular clean-bed filter with spherical collector grains, and results from the filtration calculations should therefore be considered as qualitative estimates. However, they allow to estimate the approximate scales of travel distances and to evaluate the relevant factors for particle attachment. Because filtration was assumed to be irreversible and colloid detachment was neglected, calculated travel distances for 99.99 % particle removal may be too short. However, release rates parallel the colloidal stability of particles in solution and are therefore expected to be low in the Opalinus Clay groundwater. Filtration calculations

also do not explicitly account for physical straining of colloids. Considering the size range of colloids (diameters from 1 to 1000 nm) and the approximate pore diameter distribution (Table 5, 75 % of pores with diameters < 50 nm), physical straining likely reduces the mobility of colloids in Opalinus Clay. In the filtration calculations, the particle attachment efficiency was assumed to be constant over time and with filter loading. However, over time it might also increase due to filter ripening or decrease due to the blocking of favorable deposition sites (Elimelech et al., 1995; Kretzschmar et al., 1995; Ryan & Elimelech, 1996). These effects depend on particle-surface and particle-particle interactions.

3.3.5   Other Model Approaches to Colloid Transport

The transport of colloids, and hence their potential effect on radionuclide transport, critically depends on colloid interactions with rock surfaces (Smith & Degueldre, 1993). In the diffusion and advection calculations, attachment of colloids was neglected, an assumption frequently made in the assessment of colloid-facilitated radionuclide transport (Baek & Pitt, 1996; Contardi et al., 2001; Gribi et al., 1998; Nagra, 1993; Schüßler et al., 2001; Smith, 1993). In other studies, colloid-matrix interactions are described with a distribution coefficient (Grindrod, 1993; Smith & Degueldre, 1993) or as a dynamic equilibrium between colloid attachment and detachment (Lührmann et al., 1998). A more detailed model approach apparently would have to account for the kinetics of both particle attachment and detachment. However, while particle attachment rates can be estimated from filtration theory, no corresponding theory on particle detachment is currently available (Kretzschmar et al., 1999; Smith & Degueldre, 1993).

3.3.6   Colloid Mobility in Opalinus Clay

Simple diffusion calculations have shown that only small colloids could diffuse over significant distances. Advective transport of colloids to the boundary of the Opalinus Clay layer within less than 1 Ma is only expected in the alternative case of increased upward water flow. Filtration calculations yield very low travel distances less than 1 m for colloids of all sizes even under worst-case assumptions. They indicate that small colloids could be effectively retained by diffusion to collector grains, while gravitational settling would limit the movement of larger colloids. Overall, the calculations indicate a low mobility of colloids in Opalinus Clay under current matrix flow conditions. An increased fracture flow, however, might cause an increase in mechanical colloid generation by abrasion of fracture surfaces and in colloid mobility due to advective transport.

3.4   Effect of Colloids on the Mobility of Radionuclides

The relevance of colloids for radionuclide migration finally also depends on the sorption behavior of radionuclides on colloids and on rock surfaces. For the assessment of colloid-facilitated radionuclide transport, model concepts based on reversible or irreversible, kinetic or equilibrium sorption of radionuclides on colloids were developed (Baek & Pitt, 1996; Contardi et al., 2001; Gribi et al., 1998; Grindrod, 1993; Lührmann et al., 1998; Schüßler et al., 2001; Smith, 1993; Smith & Degueldre, 1993). Such model calculations are beyond the scope of this report, but some general considerations on colloid-facilitated radionuclide transport are briefly discussed.

In Opalinus Clay, 1 liter of ground water is in contact with approximately 20 kg of rock matrix and approximately 1 mg of colloids (see Tables 4 and 5). The rock matrix to colloid weight ratio is therefore about 20'000'000. Colloids are expected to reflect the rock matrix composition, and therefore, their sorption properties are assumed to compare to those of the rock matrix. In some studies, K_d values for radionuclide sorption on colloids were obtained by scaling K_d values for radionuclide sorption on the rock matrix by a factor of 100 to 1000 to account for the higher specific surface area of colloids (Contardi et al., 2001; Gribi et al., 1998). For Opalinus Clay, a scaling factor of 1 is considered as a best estimate and a scaling factor of 10 as conservative (Wersin et al., 2002). Hence, it can be estimated that the contribution from the immobile rock surface to radionuclide adsorption is approximately 2'000'000 to 20'000'000 times larger than the contribution from colloid surfaces. Furthermore, this colloid surface is likely to have a limited mobility. The same calculation can also be carried out for organic carbon exclusively, considering that the rock matrix contains 0.6 % organic carbon (Table 1) and the total organic carbon concentration in solution is 10 ppm (Table 4). The weight ratio of organic carbon in the matrix and in solution is then ~12'000, i.e. a much higher fraction of the organic carbon than of the total rock matrix is in solution. This indicates that even in the case of a lower nuclide sorption affinity to organic surfaces than to inorganic surfaces, the organic phase might still be the dominant carrier for nuclides in solution.

As discussed earlier with respect to the colloidal stability of different types of colloids in Opalinus Clay ground water, oxide and organic coatings might alter the colloidal properties of colloids. Equally, such coatings might also change the sorption properties of colloids as compared to respective pure phases.

Assuming reversible adsorption, the fraction of a radionuclide in solution, which is colloid-bound, can be estimated as

$$f_C = \frac{K_C C_C}{1 + K_C C_C} \tag{15}$$

where C_C (in kg/m^3) is the colloid concentration and K_C the radionuclide distribution coefficient for sorption to colloids (in m^3/kg). In Figure 5, colloid-bound fractions of a radionuclide as a function of the distribution coefficient are shown for 3 different colloid concentration levels. According to Wersin et al. (2002), a colloid concentration of 1 mg/L is considered conservative. While a K_C of 10'000 m^3/kg was used as a highly conservative assumption for ion sorption to colloids in the Kristallin safety assessment report (Nagra, 1993), a K_C of ~ 500 m^3/kg is a conservative estimate for metal adsorp-

tion on Opalinus Clay (Bradbury & Baeyens, 2002). At this K_C and at a colloid concentration of 1 ppm, the fraction of colloid bound radionuclides would not exceed 30 %. Furthermore, the relevance of the colloid-bound fraction for radionuclide mobility entirely depends on the mobility of the colloidal phase. The concept of colloid-facilitated transport is founded on the idea of an unretarded advective transport of strongly sorbing nuclides associated with colloids. This concept, however, may not apply under conditions, where radionuclide migration is diffusion-controlled as assumed for the Opalinus Clay near Benken (Gautschi, 2001). Because the diffusion coefficients of colloids are much smaller than those of free ions, radionuclides bound to colloids would diffuse much slower than free radionuclides. The overall effect on radionuclide transport also critically depends on the reversibility and kinetics of colloid and radionuclide sorption. If radionuclides were irreversibly sorbed to colloids, an assumption usually considered conservative in the context of colloid-facilitated radionuclide transport, it might be speculated that colloids could even slow down radionuclide migration, since they diffuse more slowly than ions and are filtrated from solution (Grindrod, 1993). In this case, a large f_C would indicate substantial radionuclide immobilization by colloid filtration. Even though being hypothetical, this demonstrates that the conservatism of model assumptions on radionuclide and colloid sorption may differ between diffusion-controlled and advection-dominated systems.
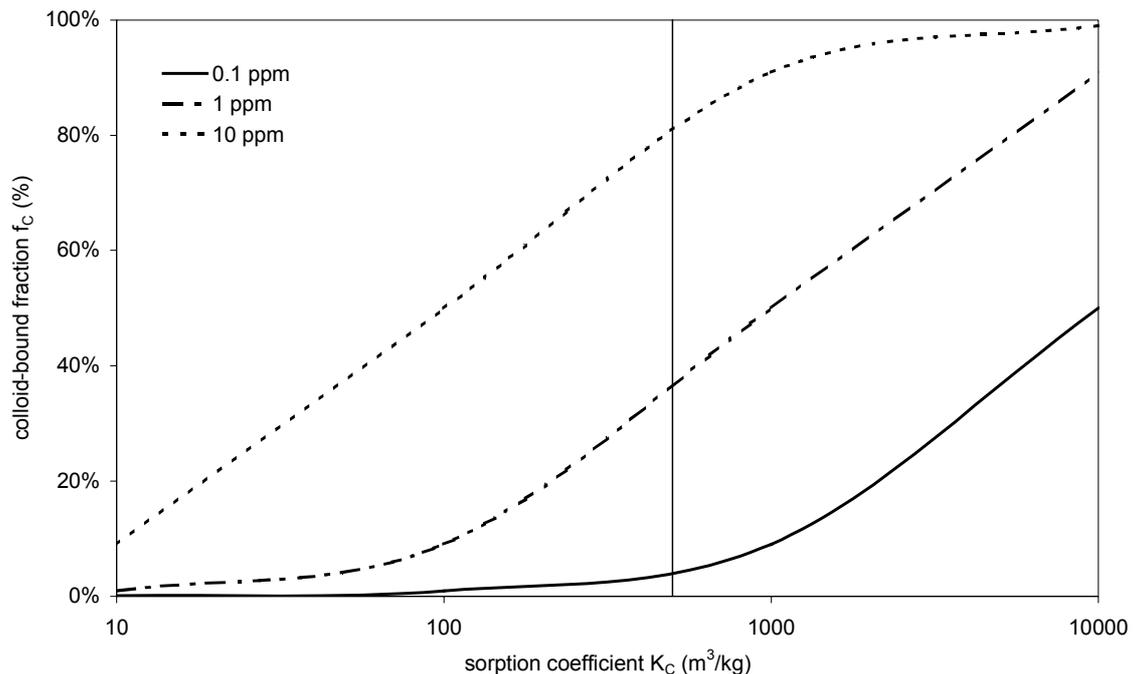

Figure 4:   Colloid-bound fraction of a radionuclide in solution, calculated as a function of the radionuclide sorption coefficient for different colloid concentrations in solution according to Eq. 15. A K_C value of 500 m^3/kg (marked by vertical line) and a colloid concentration of 1 ppm represent conservative assumptions.

4   CONCLUSIONS

In this report, the behavior of colloids in Opalinus Clay was discussed based on literature data on colloid stability and some simple transport calculations. The composition of colloids in Opalinus Clay ground water likely reflects the bulk Opalinus Clay composition and the composition of rock surface coatings. Based on literature data on the colloidal stability of model compounds and on field data, it can be concluded that even in the Opalinus Clay reference water with highest pH and lowest ionic strength, colloids are likely to be unstable and to readily coagulate or attach to surfaces.

The mesoporous structure of Opalinus Clay suggests that the mobility of large colloids in Opalinus Clay is limited. Diffusion calculations indicate that only small colloids (< 10 nm) could diffuse over significant distances. Colloid advection is only relevant in the pessimistic alternative case of increased upward matrix water flow. Filtration calculations suggest that colloids are effectively be filtered, since they rapidly diffuse to collector grains or settle by gravity. Even under worst-case conditions, calculated travel distances for 99.99 % particle removal were less than 1 m.

The fraction of organic carbon in solution is higher than the fraction of inorganic material in solution and inorganic surfaces might be coated with organic molecules. Therefore, organic matter likely represents a key factor with respect to the mobility of radionuclides in Opalinus Clay. At present, however, its composition both in the rock matrix and in the solution phase has not yet been unequivocally determined. With respect to radionuclide transport modeling, it should be considered that the conservatism of sorption model assumptions may differ between diffusion- and advection controlled systems.

For colloid facilitated contaminant transport to be an important mechanism, colloids have to be present in relevant concentrations, they have to be chemically and colloidally stable, they have to be transported, and contaminants have to be associated with them to a significant extent (McCarthy & Zachara, 1989). In Opalinus Clay, colloids are present and radionuclides might be associated with them. However, because of the high ionic strength of the Opalinus Clay ground water, colloids are expected to have a low colloidal stability. Due to the low permeability of Opalinus Clay and its mesoporous structure, colloids are also expected to be immobile. At present hydrological and geochemical conditions, colloid-facilitated radionuclide transport in Opalinus Clay is therefore unlikely to be a relevant transport mechanism. Chemical or mechanical perturbations, however, might lead to an increase of colloid generation and mobility. If such perturbations were to be expected, the implications for colloid-facilitated radionuclide transport would have to be evaluated separately.

REFERENCES

Abrajano, T.A., Bates, J.K., Woodland, A.B., Bradley, J.P., Bourcier, W.L. (1990): Secondary phase formation during nuclear waste-glass dissolution. Clays and Clay Minerals 5: 537-548.

Artinger, R., Kienzler, B., Schüßler, W., Kim, J.I. (1998): Effects of humic substances on the [241]Am migration in a sandy aquifer: column experiments with Gorleben groundwater/sediment systems. Journal of Contaminant Hydrology 35: 261-275.

Baek, I., Pitt, W.W. (1996): Colloid-facilitated radionuclide transport in fractured porous rock. Waste Management 16: 313-325.

Baghernejad, M., Dalrymple, J.B. (1993): Colloidal suspensions of calcium carbonate in soils and their likely significance in the formation of calcic horizons. Geoderma 58: 17-41.

Bates, J.K., Bradley, J.P., Teesov, A., Bradley, C.R., Buchholtz ten Brink, M. (1992): Colloid formation during waste form reaction: Implications for nuclear waste disposal. Science 256: 649-651.

Bébié, J., Schoonen, M.A.A., Fuhrmann, M., Strongin, D.R. (1998): Surface charge development on transition metal sulfides: An electrokinetic study. Geochimica et Cosmochimica Acta 62: 633-642.

Bonin, B. (1998): Deep geological disposal in argillaceous formations: Studies at the Tournemire test site. Journal of Contaminant Hydrology 35: 315-330.

Bradbury, M. H., Baeyens, B. (2002): Far-field sorption data base for performance assessment of a high-level waste repository in an undisturbed Opalinus Clay host rock. Nagra Technical Report NTB 02-19, Nagra, Wettingen, Switzerland.

Contardi, J.S., Turner, D.R., Ahn, T.M. (2001): Modeling colloid transport for performance assessment. Journal of Contaminant Hydrology 47: 323-333.

Crank, J. (1979): The Mathematics of Diffusion. Oxford University Press, Oxford.

Degueldre, C., Pfeiffer, H.R., Alexander, W., Wernli, B., Bruetsch, R. (1996): Colloid properties in granitic groundwater systems. I: Sampling and characterisation. Applied Geochemistry 11: 677-695.

Degueldre, C., Scholtis, A., Thomas, B. (1998): Opalinus Clay Groundwaters and Colloids. A Sampling and Analysis Exercise at Mt. Terri (June/July 1997), Analytical Results. Technical Note TN 97-20A, Swiss National Hydrological and Geological Survey, Berne, Switzerland.

Degueldre, C., Triay, I., Kim, J.I., Vilks, P., Laaksoharju, M., Miekeley, N. (2000): Groundwater colloid properties: a global approach. Applied Geochemistry 15: 1043-1051.

Dierckx, A., Put, M., de Canniere, P., Wang, L., Maes, N., Aertsens, M., Maes, A., Vancluysen, J., Verdickt, W., Gielen, R., Christiaens, M., Warwick, P., Hall, A., van der Lee, J. (2000): Transport of radionuclides due to complexation with organic matter in clay formations (Trancom-Clay). Report No. EUR 19135, Office for Official Publications of the European Communities, Luxembourg.

Düker, A., Ledin, A. (1998): Properties of the particulate phase in deep saline groundwater in Laxemar, Sweden. Water Research 32: 186-192.

Elimelech, M., Gregory, J., Jia, X., Williams, R. (1995): Particle Deposition and Aggregation. Butterworth-Heinemann Ltd, Oxford.

Faure, M.H., Sardin, M., Vitorge, P. (1996): Transport of clay particles and radioelements in a salinity gradient: experiments and simulations. Journal of Contaminant Hydrology 21: 255-267.

Feng, X., Buck, E.C., Mertz, C., Bates, J.K., Cunnane, J.C., Chaiko, D.J. (1994): Characteristics of colloids generated during the corrosion of nuclear waste glasses in groundwater. Radiochimica Acta 66/67: 197-205.

Findlay, A.D., Thompson, D.W., Tipping, E. (1996): The aggregation of silica and hematite particles dispersed in natural water samples. Colloids and Surfaces A: Physicochemical and Engineering Aspects 118: 97-105.

Frenkel, H., Fey, M.V., Levy, G.J. (1992): Organic and inorganic anion effects on reference and soil clay critical flocculation concentration. Soil Science Society of America Journal 56: 1762-1766.

Gautschi, A. (2001): Hydrogeology of a fractured shale (Opalinus Clay): Implications for deep geological disposal of radioactive wastes. Hydrogeology Journal 9: 97-107.

Geckeis, H., Grambow, B., Loida, A., Luckscheiter, B., Smailos, E., Quinones, J. (1998): Formation and stability of colloids under simulated near field conditions. Radiochimica Acta 82: 123-128.

Glaus, M.A., Baeyens, B., Lauber, M., Rabung, T., van Loon, L.R. (2001): Water-extractable Organic Matter from Opalinus Clay: Effect on Sorption and Speciation of Ni(II), Eu(III), and Th(IV). Nagra Technical Report NTB 01-07, Nagra, Wettingen, Switzerland.

Goldberg, S., Forster, H.S. (1990): Flocculation of reference clays and arid-zone soil clays. Soil Science Society of America Journal 54: 714-718.

Goldberg, S., Forster, H.S., Heick, E.L. (1991): Flocculation of illite/kaolinite and illite/montmorillonite mixtures as affected by sodium adsorption ratio and pH. Clays and Clay Minerals 39: 375-380.

Goldberg, S., Glaubig, R.A. (1987): Effect of saturating cation, pH, and aluminum and iron oxide on the flocculation of kaolinite and montmorillonite. Clays and Clay Minerals 35: 220-227.

Gribi, P., Hugi, M., Schneider, J., Smith, P.A., Zuidema, P. (1998): SMA/WLB: Einfluss von Nahfeldkolloiden auf den Nuklidtransport. Nagra Internal Report, Nagra, Wettingen, Switzerland.

Grindrod, P. (1993): The impact of colloids on the migration and dispersal of radionuclides within fractured rock. Journal of Contaminant Hydrology 13: 1993.

Grolimund, D., Borkovec, M., Barmettler, K., Sticher, H. (1996): Colloid-facilitated transport of strongly sorbing contaminants in natural porous media: a laboratory column study. Environmental Science and Technology 30: 3118-3123.

Grolimund, D., Elimelech, M., Borkovec, M. (2001): Aggregation and deposition kinetics of mobile colloidal particles in natural porous media. Colloids and Surfaces A: Physicochemical and Engineering Aspects 19: 179-188.

Harter, T., Wagner, S., Atwill, E.R. (2000): Colloid transport and filtration of Cryptosporium partvum in sandy soils and aquifer sediments. Environmental Science and Technology 34: 62-70.

Harvey, R.W., Garabedian, S.P. (1991): Use of colloid filtration theory in modeling movement of bacteria through a contaminated sandy aquifer. Environmental Science and Technology 25: 178-185.

Heil, D., Sposito, G. (1993): Organic matter role in illitic soil colloids flocculation: I. Counter ions and pH. Soil Science Society of America Journal 57: 1241-1246.

Hesterberg, D., Page, A.L. (1990a): Critical coagulation concentrations of sodium and potassium illite as affected by pH. Soil Science Society of America Journal 54: 735-739.

Hesterberg, D., Page, A.L. (1990b): Flocculation series test yielding time-invariant critical coagulation concentrations of sodium illite. Soil Science Society of America Journal 54: 729-735.

Honeyman, B.D. (1999): Colloidal culprits in contamination. Nature 397: 23-24.

Huber, N., Baumann, T., Niessner, R. (2000): Assessment of colloid filtration in natural porous media by filtration theory. Environmental Science and Technology 34: 3774-3779.

Hummel, W., Glaus, M.A., van Loon, L.R. (2000): Trace metal-humate interactions. II. The "conservative roof" model and its application. Applied Geochemistry 15: 975-1001.

Iler, R.K. (1975): Coagulation of colloidal silica by calcium ions, mechanism and effect of particle size. Journal of Colloid and Interface Science 53: 476-488.

Iler, R.K. (1979): The Chemistry of Silica. John Wiley and Sons, New York.

Jekel, M.R. (1986): The stabilization of dispersed mineral particles by adsorption of humic substances. Water Research 20: 1543-1554.

Keren, R., Shainberg, I., Klein, E. (1988): Settling and flocculation value of sodium-montmorillonite particles in aqueous media. Soil Science Society of America Journal 52: 76-80.

Kretzschmar, R., Borkovec, M., Grolimund, D., Elimelech, M. (1999): Mobile subsurface colloids and their role in contaminant transport. Advances in Agronomy 66: 121-193.

Kretzschmar, R., Hesterberg, D., Sticher, H. (1997): Effects of adsorbed humic acid on surface charge and flocculation of kaolinite. Soil Science Society of America Journal 61: 101-108.

Kretzschmar, R., Holthoff, H., Sticher, H. (1998): Influence of pH and humic acid on coagulation kinetics of kaolinite: A dynamic light scattering study. Journal of Colloid and Interface Science 202: 95-103.

Kretzschmar, R., Robarge, W., Weed, S.B. (1993): Flocculation of kaolinitic soil clays: Effects of humic substances and iron oxides. Soil Science Society of America Journal 57: 1277-1283.

Kretzschmar, R., Robarge, W.P., Amoozegar, A. (1995): Influence of natural organic matter on colloid transport through saprolite. Water Resources Research 31: 435-445.

Kretzschmar, R., Sticher, H. (1997): Transport of humic-coated iron oxide colloids in a sandy soil: influence of Ca^{2+} and trace metals. Environmental Science and Technology 31: 3497-3504.

Ledin, A., Karlsson, S., Allard, B. (1993): Effects of pH, ionic strength and a fulvic acid on size distribution and surface charge of colloidal quartz and hematite. Applied Geochemistry 8: 409-414.

Lührmann, L., Noseck, U., Tix, C. (1998): Model of contaminant transport in porous media in the presence of colloids applied to actinide migration in column experiments. Water Resources Research 34: 421-426.

Marschall, P., Croise, J., Schlickenrieder, L., Schwarz, R. (2001): Hydrological Borehole Synthesis Benken: Final K- and Head-Profiles (Packer Tests). Nagra Internal Report, Nagra, Wettingen, Switzerland.

Martin, R.E., Bouwer, E.J., Hanna, L.M. (1992): Application of clean-bed filtration theory to bacterial deposition in porous media. Environmental Science and Technology 26: 1053-1058.

Mazurek, M. (2001): Sproedstrukturen und potentielle Migrationspfade im Opalinuston und seinen Rahmengesteinen. Nagra Internal Report, Nagra, Wettingen, Switzerland.

McCarthy, J.F., Czerwinski, K.R., Sanford, W.E., Jardine, P.M., Marsh, J.D. (1998a): Mobilization of transuranic radionuclides from disposal trenches by natural organic matter. Journal of Contaminant Hydrology 30: 49-77.

McCarthy, J.F., Degueldre, C. (1993): Sampling and characterization of colloids and particles in groundwater for studying their role in contaminant transport; in Buffle, J. ,van Leeuwen, H.P. (eds.) Environmental Particles. Lewis Publishers, Boca Raton.

McCarthy, J.F., Sanford, W.E., Stafford, P.L. (1998b): Lanthanide field tracers demonstrate enhandced transport of transuranic radionuclides by natural organic matter. Environmental Science and Technology 32: 3901-3906.

McCarthy, J.F., Zachara, J.M. (1989): Subsurface transport of contaminants. Environmental Science and Technology 23: 496-502.

Milonjic, S.K. (1992): A relation between the amounts of sorbed alkali cations and the stability of colloidal silica. Colloids and Surfaces 63: 113-119.

Nagra (1993): Kristallin-I, Safety Assessment Report. Nagra Technical Report NTB 93-22, Nagra, Wettingen, Switzerland.

Nagra (2002a): Projekt Opalinuston: Synthese der geowissenschaftlichen Untersuchungsergebnisse. Entsorgungsnachweis für abgebrannte Brennelemente, hochaktive sowie langlebige mittelaktive Abfälle. Nagra Technical Report NTB 02-03, Nagra, Wettingen, Switzerland.

Nagra (2002b): Project Opalinus Clay: Safety Report: Models, codes and data for safety assessment. Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste (Entsorgungsnachweis). Nagra Technical Report NTB 02-06, Nagra, Wettingen, Switzerland.

Novich, B.E., Ring, T.A. (1984): Colloid stability of clays using photon correlation spectroscopy. Clays and Clay Minerals 32: 400-406.

Olofsson, U., Allard, B., Torstenfelt, B., Andersson, K. (1982): Properties and mobilities of actinide colloids in geologic systems; in Lutze, W. (ed.) Scientific Basis for Radioactive Waste Management. Elsevier, New York.

O'Melia, C.R. (1990): Kinetics of colloid chemical processes in aquatic systems; in Stumm, W. (ed.) Aquatic Chemical Kinetics. John Wiley and Sons, New York.

O'Melia, C.R., Tiller, C.L. (1993): Physicochemical Aggregation and Deposition in Aquatic Environments; in Buffle, J. ,van Leeuwen, H.P. (eds.) Environmental Particles. Lewis Publishers, Boca Raton.

Ong, H.L., Bisque, R.E. (1968): Coagulation of humic colloids by metal ions. Soil Science 106: 220-224.

Oster, J.D., Shainberg, I., Wood, J.D. (1980): Flocculation value and gel structure of sodium/calcium montmorillonite and illite suspensions. Soil Science Society of America Journal 44: 955-959.

Pearson, F.J. (2002): Reference Water Chemistry. Nagra Internal Report, Nagra, Wettingen, Switzerland.

Puls, R.W., Paul, C.J., Clark, D.A. (1993): Surface chemical effects on colloid stability and transport through natural porous media. Colloids and Surfaces A: Physicochemical and Engineering Aspects 73: 287-300.

Put, M.J., Dierckx, A., Aertsens, M., De Canniere, P. (1998): Mobility of the dissolved organic matter through Boom clay cores. Radiochimica Acta 82: 375-378.

Rieger, J., Thieme, J., Schmidt, C. (2000): Study of precipitation reactions by X-ray microscopy: CaCO3 precipitation and the effect of polycarboxylates. Langmuir 16: 8300-8305.

Ryan, J.N., Elimelech, M. (1996): Colloid mobilization and transport in groundwater. Colloids and Surfaces A: Physicochemical and Engineering Aspects 107: 1-56.

Schüßler, W., Artinger, R., Kim, J.I., Bryan, N.D., Griffin, D. (2001): Numerical modeling of humic colloid borne americium (III) migration in column experiments using the transport/specation code K1D and the KICAM model. Journal of Contaminant Hydrology 47: 311-322.

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

Smith, P.A., Degueldre, C. (1993): Colloid-facilitated transport of radionuclides through fractured media. Journal of Contaminant Hydrology 13: 143-166.

Soler, J.M. (1999): Coupled Transport Phenomena in the Opalinus Clay: Implications for Radionuclide Transport. Nagra Technical Report NTB 99-09, Nagra, Wettingen, Switzerland.

Sposito, G. (1989): The Chemistry of Soils. Oxford University Press, New York.

Stumm, W. (1992): Chemistry of the Solid-Water Interface. John Wiley and Sons, New York.

Stumm, W., Morgan, J.J. (1981): Aquatic Chemistry. John Wiley and Sons, New York.

Swanton, S.W. (1995): Modelling colloid transport in groundwater; the prediction of colloid stability and retention behaviour. Advances in Colloid and Interface Science 54: 129-208.

Tarchitzky, J., Chen, Y., Banin, A. (1993): Humic substances and pH effects on sodium- and calcium-montmorillonite flocculation and dispersion. Soil Science Society of America Journal 57: 367-372.

Temminghoff, E.J.M., van der Zee, S.E.A.T.M., de Haan, F.A.M. (1998): Effect of dissolved organic matter on the mobility of copper in a contaminated sandy soil. European Journal of Soil Science 49: 617-628.

Thury, M., Bossart, P. (1999): Mont Terri Rock Laboratory - Results of the Hydrogeochemical, Geochemical and Geotechnical Experiments Performed in 1996 and 1997. Report No. 23, Swiss National Hydrological and Geological Survey, Berne.

Tipping, E., Higgins, D.C. (1982): The effect of adsorbed humic substances on the colloid stability of haematite particles. Colloids and Surfaces 5: 85-92.

Tipping, E., Ohnstad, M. (1984): Aggregation of aquatic humic substances. Chemical Geology 44: 349-357.

van der Lee, J., Ledoux, E., de Marsily, G., de Cayeux, M.D., van de Weerd, H., Dodds, J., Rodier, E., Sardin, M., Hernandez, A. (1994): A bibliographical review of colloid transport through the geosphere. Report No. EUR 15481 EN, European Commission, Luxembourg.

Vilks, P., Cramer, J.j., Bachinski, D.B., Doern, D.C., Miller, H.G. (1993): Studies of colloids and suspended particles, Cigar Lake uranium deposit, Saskatchewan, Canada. Applied Geochemistry 8: 605-616.

Vilks, P., Miller, H.G., Doern, D.C. (1991): Natural colloids and suspended particles in the Whiteshell Research Area, Manitoba, Canada, and their potential effect on radiocolloid formation. Applied Geochemistry 6: 565-574.

Wersin, P., Schwyn, B., Schneider, J. (2002): Input data to model colloid-facilitated radionuclide transport in the Opalinus Clay safety assessment. Nagra Internal Report, Nagra, Wettingen, Switzerland.

Yao, K.-M., Habibian, M.T., O'Melia, C.R. (1971): Water and waste water filtration: Concepts and applications. Environmental Science and Technology 5: 1105-1112.

Yariv, S., Cross, H. (1979): Geochemistry of Colloid Systems. Springer, Berlin.