

**Technical Report**

**TR-10-20**

**Sorption of prioritized elements on  
montmorillonite colloids and their  
potential to transport radionuclides**

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April 2010

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the author. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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## Summary

Due to colloids potential to bind radionuclides (RN) and even mobilise sorbed RN, colloid transport of RN should be taken into account when modeling radionuclide transport in the scenario of a leaking canister in a deep bedrock repository of spent nuclear fuel. Colloids are always present in natural waters and the concentrations are controlled by the groundwater chemistry where specifically the ionic strength is of major importance. In many deep bedrock groundwaters, the ionic strength is fairly high (above the Critical Coagulation Concentration) and therefore colloids are not likely to be stable. In these types of groundwaters colloid concentrations up to 100 µg/l could be expected, and clay colloids organic degradation products and bacteria and viruses represent can be found.

In a long time perspective cycles of glaciations can be expected in Sweden as in other Nordic countries. It can not be excluded that glacial melt water can intrude to repository depth with high flows. In this scenario the groundwater conditions may drastically change. In contact with dilute groundwater the bentonite barrier can start to propagate a bentonite gel and further release montmorillonite colloids into water bearing fractures. The concentration of colloids in vicinity of the bentonite barrier can then increase drastically. In contact with Grimsel groundwater types with [Na] and [Ca] of 0.001 and 0.0001 M respectively a montmorillonite concentration of a maximum of 20 mg/l is expected. Further, the groundwater chemistry of Grimsel seems to be representative for glacial meltwater when comparing with the water chemistry data on meltwaters from existing glaciers.

A key to be able to model colloid transport of radionuclides is the sorption strength and the sorption reversibility. To facilitate this, a compilation of literature  $K_d$ -values and an inventory of available sorption kinetic data has been composed for the prioritized elements Pu, Th, Am, Pb, Pa, Ra, Np, Cm, Ac, Tc, Cs, Nb, Ni, Pd, Se, Sn, Zr and U.  $K_d$ -values for colloids and radionuclides are scarce as well as sorption kinetics. Sorption values were not found for the elements Ra, Nb and Pd, yet sorption of the analogues Sr, Pu and Ni are instead representing these elements. Since sorption and desorption kinetic studies are scarce, recommendations on the reversibility have been based on the elements sorption mechanisms and from their  $K_d$ -values.

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# 1 Background

Colloids are particles with at least one dimension in the size range 1–1,000 nm /IUPAC 1997/. Because of their small size, Brownian motion can keep them in suspension over geological time scales. The importance of colloids in the environment is linked to their surface properties, whereas the bulk properties are of less importance. Their large specific area gives high surface charge density per unit mass, with a strong affinity for pollutants. Multivalent metal ion sorption occurs by way of electrostatic association and covalent bonding with surface sorption sites of opposite charge. Clays possess a net negative charge at all reasonable groundwater pH values as with positively charged edges in neutral pH, whereas organic degradation products usually only exhibit negative charge in neutral to alkaline pH ranges. Therefore these types of colloids have a tendency to bind ions, in particular positively charged metal ions in natural waters, and as a consequence metals are often bound to colloids. Depending upon particle density, smaller colloids remain in stable suspension for a very long time because Brownian motion prevails over gravitational forces. Stability against aggregation in combination with high sorption capacity gives colloids an important role in the transport of contaminants, particularly those with low solubility. A well known example is the colloid-facilitated Pu (plutonium) migration at the Nevada Test Site /Kersting et al. 1999/, where the Pu has been transported further from the source than predicted without taking the colloid phase into account. However, the Pu most certainly travelled as true colloids, but the enhancement of the migration of Co (cobalt), Cs (cesium) and Eu (europium) at the same site was attributed to their association to clay colloids. In a deep bedrock repository there are different classes of colloids that could be present. In groundwater, the erosion of rock minerals and alteration products, the precipitation of mineral oxides and the degradation of organic material form natural colloids. A special group of colloids includes viruses (2 to 80 nm) and bacteria (200 nm to several microns). The montmorillonite component of bentonite is of colloid size and can under certain conditions be a colloid source. The bentonite also contains a small amount of organic material, which under can release colloids in the contacted groundwater. True colloids formed by precipitation of RN (radionuclides) can be expected in close proximity to the fuel inside a failed canister. Metal ions with higher charge, such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Pu^{4+}$   $Th^{4+}$  etc, are strongly hydrolysed at the pH values prevailing in groundwater. The hydrolysis products contain several metal ions (polynuclear) and by aggregation they can form colloidal particles. In the case of  $Pu^{4+}$  the formation of colloids is practically irreversible. For colloids to contribute to contaminant transport, they have to be present in sufficiently high concentrations, be mobile and remain in stable suspension for longer periods of time.

The compacted bentonite barrier is believed to act as a filter for colloids released from the waste package/Kurosawa and Ueta 2001/. Hence, in the case of a leaking canister and formation of true colloids, these will be efficiently filtered out in an intact bentonite barrier. Strongly sorbing radionuclides will also be immobilised in the compacted saturated bentonite.

With climate change, the hydrological conditions may change, with the potential to significantly affect groundwater chemistry. In Sweden, as in the other Nordic countries, glacial cycles can be expected, with the first predicted on the order of 10,000 years from now. The possibility of rapid glacial melt water intrusion down to repository depth cannot be excluded /SKB 2007a/, displacing the existing saline groundwater. If no mixing occurs the glacial water will flow in a front and press away the old saline groundwater. A very long time will be needed to increase the salinity back to higher concentrations by diffusive mixing of the dilute water with relict saline water in the rock matrix along with upconing from greater depth, and/or equilibration of the mineral surfaces with the passing water. Since montmorillonite colloids are known to be stable in dilute waters, bentonite-based barriers may start to erode, followed by bentonite colloid transport away from the barrier /Missana et al. 2003/. This erosion may lead to significant material loss, and endanger the functionality of the bentonite barrier.

Strongly sorbed RN, which under ordinary conditions can be considered to be practically immobile, might be transported rapidly to the biosphere by eroded colloids if these are stable. If the uptake of RN on colloidal particles is reversible, radionuclide transport by colloids will most probably be negligible due to the fracture surface available, which provides an enormous surface on which to sorb compared with the colloid surface. In addition, the composition of the inorganic colloids is similar

to that of the surface mineral, so the sorption strength is most probably very similar. If radionuclides adhere irreversibly, on the other hand, the situation will be different. In this case, radionuclides that will be transported mainly with the particles and, at worst, not be delayed by either sorption on fracture walls or by matrix diffusion in the rock. Irreversibility is problematic when results from shorter-term experiments are extrapolated to longer time scale. In short term experiments sorption might appear to be irreversible due to a faster rate of uptake than desorption. When studied over a longer period of time, desorption might eventually be seen thereby implying reversibility. The reversibility of RN can also change with varying groundwater conditions, in particular from RN sorbing by cationic exchange. Colloids have been observed to travel even faster than conservative tracers, e.g. in the Colloid and Radionuclide Retardation experiment at the Grimsel test site /Geckeis et al. 2004/. Early breakthrough for Am sorbed to bentonite colloids compared with the non-sorbing tracer <sup>131</sup>I is explained by hydrodynamic chromatography effects, i.e. the colloids taking the fast track through the middle of the fracture, whereas the tracers are transported in the whole flow profile, even close to the walls /Kurosawa et al. 2006/. The sorption properties of actinides, fission products and activation products on bentonite and minerals have been well studied. However, few data on desorption are available, and also very few on sorption/desorption to the colloidal fraction, particularly on longer time scales relevant for modeling of the transport processes in the geosphere. This information is essential for knowing whether or not sorption should be treated as a reversible process when modeling the effect of colloids on radionuclide transport. Changing the groundwater conditions in the experiments should also test the reversibility. If the  $K_d$ -values for bulk materials were normalized with regard to specific surface area rather than mass, comparison of  $K_d$ -values for the bulk material and colloid fraction would be more straightforward. However, in the literature the majority of sorption data relating to, for example, montmorillonite are normalized by mass. The aims of this desktop study were to:

- Present  $K_d$ -values for the sorption of Pu, Th, Am, Pb, Pa, Ra, Np, Cm, Ac, Tc, Cs, Nb, Ni, Pd, Se, Sn, Zr and U on /montmorillonite colloids.
- Present sorption and desorption rates for Pu, Th, Am, Pb, Pa, Ra, Np, Cm, Ac, Tc, Cs, Nb, Ni, Pd, Se, Sn, Zr and U on montmorillonite colloids. Where data are lacking, recommended sorption/desorption rates based on estimations from sorption data, where approximate rate constants can be derived from the  $K_d$ -values with the knowledge of sorption times and the solid to volume ratios used.
- Discuss the uncertainties in the literature data and in the recommended  $K_d$ -values for Pu, Th, Am, Pb, Pa, Ra, Np, Cm, Ac, Tc, Cs, Nb, Ni, Pd, Se, Sn, Zr and U on /montmorillonite colloids and their sorption kinetics.
- Summarize existing data on natural colloids at the Forsmark and Laxemar sites and examine how the concentrations of natural and bentonite colloids can vary with groundwater composition when salinity, pH and temperature are changed, for example due to climate change.
- Provide a value with uncertainty limits for the bentonite colloid concentration that can be expected outside the bentonite buffer in a situation with intruding dilute glacial melt water.

## 2 Colloid transport

### 2.1 Conditions to be fulfilled

For colloid transport in general and colloid-enhanced transport of RN in particular to be an important process necessary for inclusion in safety assessment modeling, a number of conditions have to be fulfilled:

- The colloids have to be present in concentrations high enough to compete for sorption of RN with fracture surfaces and fracture fillings and the affinity for binding RN has to be substantial. A special case is bentonite erosion where RN sorbed to montmorillonite colloids in the bentonite can migrate out from the barrier as it is eroded.
- The colloids have to be stable in the groundwater for a sufficiently long time to transport RN long distances.
- The colloids have to be mobile to have any impact on the transport rate of RN.
- The affinity for RN to the colloids has to be sufficiently strong to have an impact on the overall RN transport. A strong affinity could be considered as having a higher  $K_d$  for the colloid compared to the rock, and/or irreversible sorption over the time scale of interest.
- To have any impact on RN transport in water-bearing fractures, from the bentonite barrier, all of the above conditions have to be fulfilled.

It is difficult to establish proper quantitative criteria, based upon the above list of conditions, to determine whether colloid transport will be an important process or not. The affinity of elements to the colloids is a crucial parameter. Sorption is frequently represented by a  $K_d$ -value, which is simply the ratio of sorbed and dissolved solute. It is an empirical parameter that is specific to the system being studied and can be regarded as an equilibrium constant for the sorption process. For the sorption of metals on natural minerals the measured value of the  $K_d$  can be misleading since it implies an equilibrium state, which is rarely achievable on the timescales characterizing a typical sorption experiment. Modeling is necessary in order to vary the conditions and determine when colloid transport will have an impact on RN transport or not.

The colloid concentration is determined by the balance between the rate of production and consumption of colloids (i.e. removal from suspension) in the fracture water. For colloids to be present there must be a source of production. In natural waters there is a constant production of colloids by mineral weathering, mineral-oxide precipitation, degradation of organic material and the growth of bacteria and viruses. Since the montmorillonite in the bentonite in itself is colloidal, the bentonite barrier can be seen as an additional source of colloid production that could be infinite. However, the ability to produce and further release colloids is strongly linked to the groundwater conditions and will only be significant under specific conditions.

The consumption of colloids is linked to their stability in solution and to fracture and colloid interactions.

#### 2.1.1 Colloid stability – Removal of colloids from solution by aggregation followed by sedimentation

The stability of colloids is determined mainly by groundwater composition, where ionic strength and pH are the most dominant factors, in that order /García García et al. 2006, 2007/. Increasing ionic strength decreases the width of the electrical double layers around the colloids, leading to lower repulsion and even lower stability. An increase in pH gives a higher surface potential and higher repulsion, resulting in increased stability for montmorillonite colloids. Temperature and exposure to irradiation have been shown to influence bentonite colloidal stability /Holmboe et al. 2009/, with irradiated montmorillonite colloids having higher stability. Montmorillonite colloids appear to be more stable at higher temperatures than at room temperature at ionic strength of 0.001 M. This is counter intuitive, since collision theory states that increasing temperature results in more collisions between colloids, giving a higher frequency of aggregation and sedimentation. From an examination of DLVO theory, it is obvious that the temperature dependence is included in many terms, and the

outcome is therefore not immediately transparent. Due to different properties, the dependence is colloid-specific. The critical coagulation concentration (CCC) is a measure of colloid stability that is often used to estimate the potential of a given groundwater to carry significant amounts of colloids. A total cation concentration value that is greater than or equal to the CCC represents unfavorable conditions for colloid stability, i.e. the aggregation is diffusion-controlled and sedimentation appears to be an instantaneous process. CCC values in the magnitude of 0.01–0.1 M Na<sup>+</sup> for Na-montmorillonite and 0.0001–0.001 M Ca<sup>2+</sup> for Ca-montmorillonite have been reported /García García et al. 2007/. Groundwater colloids are particularly unstable in the presence of divalent ions such as Ca<sup>2+</sup> and Mg<sup>2+</sup>. /Degueldre et al. 1996/. The CCC values in the literature confirm the general finding that natural colloid concentrations are in the range of µg/L in e.g. Äspö groundwater, which is saline /Laaksoharju and Wold 2005/. The low measured natural colloid concentrations certify the existence of unfavorable conditions for colloidal stability.

Until recently it was believed that as long as the groundwater composition is such that the ionic strength is high, with a high content of divalent ions such as Ca<sup>2+</sup> or Mg<sup>2+</sup>, it is unlikely that colloidal transport will be significant since the colloids are simply not stable. For example, in colloid migration tests in a fracture with an aperture of mm-size, injected bentonite colloids readily aggregated and fell out of solution in synthetic Äspö groundwater /Vilks et al. 2008/. The claim regarding high ionic strength and low colloid transport is most probably correct as regards natural colloids in groundwater. However, if the bentonite barrier is the colloid source the relationship is far more complex.

The SKB Bentonite Erosion project lead by Professor Ivars Neretnieks, investigated the ability of the bentonite buffer to generate a gel and progress further through the sol state, releasing montmorillonite colloids. The work has shown that there is a complex connection between the bentonite type (Ca or Na) and the groundwater composition, especially in terms of the ions Ca and Na. As long as the bentonite stays with 90% Ca and 10% Na in the exchange positions, it will remain stable and not form a sol that starts to release colloids. However, if ionic exchange increases the Na content of the clay, the bentonite will have a tendency to form a sol from which colloids can be released /Birgersson et al. 2009/. This means that phase diagrams for sol formation for bentonite are specific for different types of montmorillonite. If the bentonite is set, the question is what type of groundwater composition can be expected in the early and long-term lifetime of the repository.

### **2.1.2 Interactions between fracture and colloid – Removal of colloids from solution by physical filtration or attachment to fracture surfaces**

If the colloids are present in sufficiently high concentrations and remain stable for a long time, they can be transported with or without sorbed RN out from the bentonite barrier. The transport and the retention in the water-bearing fractures are then determined by:

- Flow velocity.
- Aperture distribution.
- Whether fracture-filling minerals are present in the fractures.
- Fracture surface characteristics such as roughness and mineralogy and mineral distribution.
- Colloid characteristics such as size distribution, surface charge density, density and structure.

At higher flow velocities and in larger apertures, interactions between colloids and the fracture will be insignificant. However, decreasing the flow and the aperture width will increase the chance of interactions. The presence of fracture-filling minerals will give the colloids a longer transport pathway and may also trap colloids, removing parts of the initial colloid size distribution. In colloid transport in fractures, the retention is explained by colloids being trapped in cavities due to roughness on the surface and to electrostatic interactions between the mineral and the colloid surfaces. However, in most natural waters colloid interactions and deposition are inhibited by the repulsive forces between the overall negatively charged mineral and colloid surfaces /Johnson et al. 1996/.

Even in unfavorable conditions for sorption, deposition of colloids on surfaces has been observed, with considerably higher magnitude than can be predicted theoretically. The explanation for this unexpectedly high deposition can be cavities, dislocations and geochemical impurities /Ryan and



Elimelech 1996/. At neutral pH most minerals carry a negative charge, although there are examples of oxides of iron, aluminium and manganese that are positively charged in the neutral pH range. The impact of such positive islands in an otherwise negatively charged surface has been tested in transport experiments on silica colloids with a mean diameter of 300 nm in columns packed with clean sand and grains coated with 0–16% iron oxyhydroxide. The porosity was found to be around 39% and the flow velocity  $1.02 \cdot 10^{-4}$  m/s /Johnson et al. 1996/. The experiment clearly showed the influence of the positive mineral surfaces, with retardation of the colloids significantly increasing with increasing amount of coated particles. Furthermore, the authors concluded that their results demonstrated that the rate of deposition is controlled by the positively charged surfaces and that the overall deposition can be explained by deposition on these favorable sites.

The interaction of latex colloids (mean size 25 nm) with mineral surfaces and Grimsel granodiorite, as well as with several single minerals, in static conditions has been studied in the pH range 2–10, where the colloids were analyzed by fluorescence microscopy and the adsorbing mineral phases was detected with SEM/EDX /Filby et al. 2008/. The sorption of colloids on single minerals was found to take place below the pH for point of zero charge, for the different individual minerals in granodiorite. In neutral conditions, pH 6–8, no sorption/attachment of the latex colloids could be detected. For the interactions of colloids with the granodiorite surface, in lower pH:s, attachment of colloids could be detected on surface areas with a distinct morphology including holes, cavities or micro-fissures. Montmorillonite colloids can adhere to mineral surfaces even in unfavorable conditions with a higher sorption to less charged minerals in the overall negatively charged matrix /García García 2010/.

In colloid transport, characteristics such as size distribution, surface charge density, density and structure will affect the interactions between colloids and the fracture. In a transport experiment through a fracture of relatively small aperture (183  $\mu\text{m}$ ) in chalk stone with 1  $\mu\text{m}$  latex microspheres and 1.34  $\mu\text{m}$  montmorillonite colloids, it was clear that the montmorillonite colloids experienced higher retention in the fracture than the latex colloids /Zvikelsky et al. 2008/. The theory is that even if on a macroscopic level the artificial and natural colloids appear to be the same, the montmorillonite colloids have a density almost twice that of the latex, the size distribution for the montmorillonite is broad and that for the latex is sharp, the charge is evenly distributed on the latex but variable on montmorillonite and the latex colloid shape is uniform and spherical, whereas montmorillonite colloids may have a more heterogeneous structure.

In the SKB Colloid Dipole and Transport projects in collaboration with Nuclear Waste Management Organisation (NWMO) /Vilks et al. 2008/, a set of experiments was performed on latex and bentonite colloid transport in a clean granite fracture with a mean aperture of 2.45 mm. The experiments studied bentonite colloid transport in a well-characterized fracture to obtain information on the impact of: flow velocity, travel path, colloid size distribution, monodispersity/polydispersity, colloid structure and water chemistry. The experiments were first performed using bentonite and 100 nm latex colloids under conditions of different flow rates in order to identify the flow rates that favour bentonite colloid transport. The tracer experiments were later expanded to include experiments with different colloid sizes and longer transport distances. The main objectives of the experiments were to improve the understanding of retention processes that affect colloid mobility, and to provide additional information that cannot be obtained in field-scale tests concerning transport of bentonite and latex sphere colloids.

The data were further modeled to identify retention processes that affect colloid transport and to estimate the retention parameters /Cheng and Cvetkovic 2009/. Colloid attachment/detachment on fracture surfaces is described by first-order, linear and reversible kinetics in this modeling. Physical filtration and sedimentation are characterized by an irreversible first order mass removal rate. The modeling clearly indicates that the retention in the system in the time frame of the experiments can be divided into permanent mass loss, which is interpreted as irreversible physical filtration, and detachment/attachment, which represents sorption and reversible physical filtration. The colloids in general had lower recovery rates in the test than conservative tracers, implying higher retention for the colloids. The recovery of smaller colloids (10–20 nm) was slightly lower than the recovery of medium-sized colloids (100–200 nm), while the lowest recovery rates were found for the largest colloids (0.5–1  $\mu\text{m}$ ). Similar trends have been observed in experiments in other rock types /Zvekelsky et al. 2008/. The explanation for the lower recovery rates for the smaller colloids than for the medium-sized is that the former travel in the whole flow field, even close to the fracture walls. Any colloids

coming close to the fracture walls start to interact with the surface. The medium-sized colloids travel in the middle of the fracture. The largest colloids were presumed to have higher retention parameters, in particular high mass removal rates. The possible mechanisms for mass removal could be that the large colloids are relatively less stable and can undergo the process of irreversible filtration/sedimentation. The tendency for lower recoveries of small colloids have also been seen in transport experiments through fracture filling minerals /García García 2010/ where the higher retention of smaller latex colloids can, at least partly be explained by less negatively charged surfaces giving higher sorption to mineral surfaces than the larger latex colloids.

### **2.1.3 Measurements of colloids in natural waters**

Measuring the background colloid concentrations is problematic, since measurement itself may disturb the overall conditions. Different sampling and analytical techniques are used and naturally the question arises as to whether the results are comparable. In filtering techniques that are commonly used, water is flushed through filters coupled in series. To get reliable results, it is very important to flush sufficiently high volumes through the filters to produce large numbers of colloids on the filters and give accurate counts. On the other hand, there is a risk that the filters can become clogged and it is therefore important not to flush too large volumes through the filters. Laser Induced Breakdown Detection (LIBD) is a very sensitive technique which, if used on site, probably gives the most reliable concentrations /Plaschke et al. 2001/. When water is sampled on sites at the ambient pressure and then analyzed with LIBD in the laboratory, the situation is far more problematic. The pressure drop before the analysis may induce colloid formation. Single Particle Counting (SPC) is another technique that is commonly used and is quite a robust technique to use in the field. However, sampling at the site and analysis in the laboratory give rise to the same uncertainties as when using LIBD, namely the risk of intrusion of oxygen and colloid formation. Not only are there concerns for colloid stability, redox changes, and potential precipitation caused by pressure release, but the very presence of the borehole used for sampling is intrusive. Boreholes need adequate flushing, yet too much flushing might reduce colloid concentrations to below natural levels due to colloid filtration from flowing water. Tangential flow ultrafiltration is also a method that is suitable for concentrating colloids in natural water.

## 3 Colloids at the Laxemar and Forsmark sites

### 3.1 Background colloid concentrations

At the Laxemar and Forsmark sites, colloid concentrations in water samples from boreholes at varying depth have been analyzed with different methods. Filtration of the groundwater through a series of connected filters (0.4, 0.2 and 0.05  $\mu\text{m}$ ) has been used or sometimes a 2.0  $\mu\text{m}$  filter connected before the 0.4  $\mu\text{m}$  filter in a system under pressurized argon to avoid precipitation. The elements in the colloids collected on the filters were analyzed with ICP after dissolution in acid. The metal concentrations were converted into  $\mu\text{g/L}$  values by taking the water flow through the filters and the filtration time into account. Fractionation using a cut-off membrane filter with filter pore sizes of 1,000 and 5,000 D has also been used, with complementary LIBD analysis, as well as microfiltration followed by scanning electron microscopy and energy dispersive spectroscopy (SEM/EDS) /Hallbeck and Pedersen 2008a, b/.

The boreholes sampled at both Laxemar and Forsmark were chosen to give a good representation of the volume to be used for a future nuclear waste repository. The colloid concentrations are therefore not necessarily representative of the span of groundwater chemistry found at the sites, but rather of the groundwater found in the proposed volume for the repositories. The colloid concentrations with depth at Forsmark and Laxemar are not significantly different in the groundwater samples. Most of the samples analyzed at both sites contain less than 60  $\mu\text{g/L}$ . Three samples, from the boreholes KFM01A KFM03A, KFM10A in Forsmark, exceeded that concentration, with KFM01A containing most colloids (164  $\mu\text{g/L}$  determined using the filtration method). In the Laxemar samples the concentrations were less than 40  $\mu\text{g/L}$  except in two samples, KLX08  $\sim$ 44  $\mu\text{g/L}$  and KLX17A, where values  $\sim$ 90  $\mu\text{g/L}$  were analyzed in filter series or with the fractionation method. The concentrations obtained with the three methods are not completely comparable, but the maximum concentration, taking all methods into account, can be set to less than 200  $\mu\text{g/L}$ . A method for avoiding as much of the artifacts as possible was implemented at two bore holes in Forsmark and Laxemar by Nilsson and coworkers /Nilsson et al. 2008/. Groundwater samples were collected at-line by submicro-filtration at the well head under in situ conditions. Artifacts induced by pH change due to  $\text{CO}_2$  exchange, forming carbonate particles, or intrusion of  $\text{O}_2$  giving oxyhydroxide colloids could thereby be avoided.

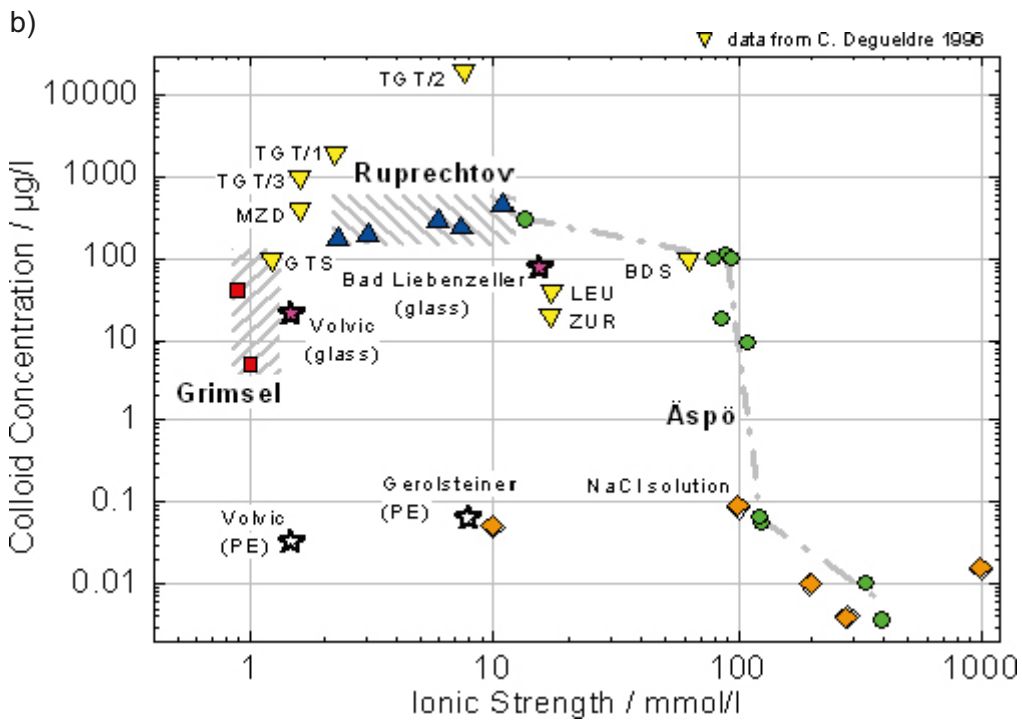
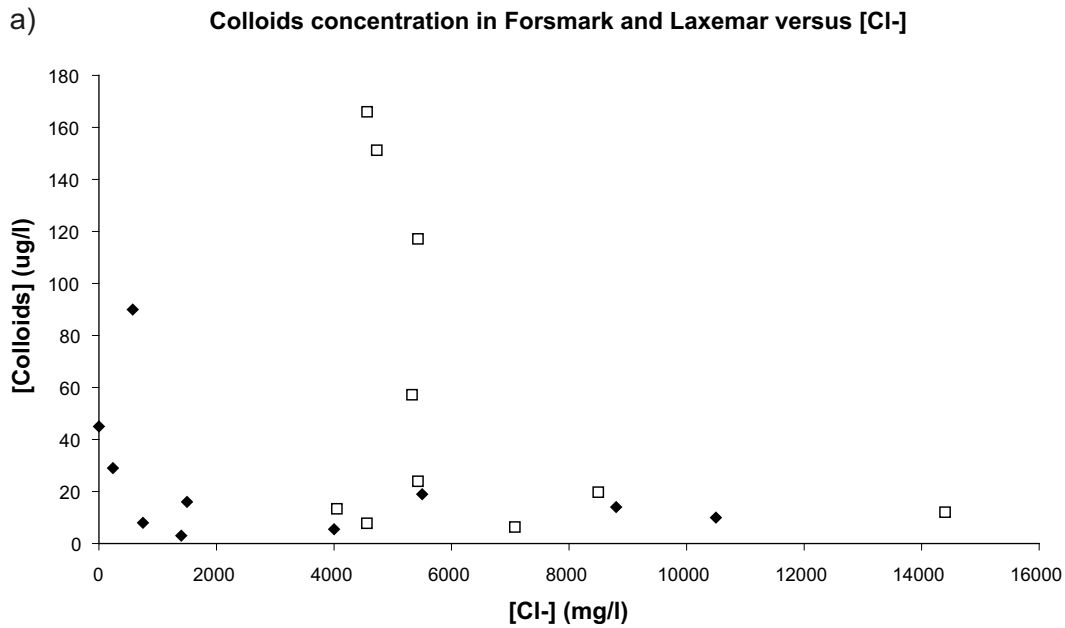
### 3.2 Colloid stability – Groundwater conditions

In a system in equilibrium, the strongest controlling factor in the groundwater is the ionic strength, even if the temperature and pH also affect the system. Therefore, it is important to determine the relationship between salinity and colloid concentration for the two sites.

In the groundwater samples analyzed for colloids, the  $\text{Cl}^-$  concentration ranged from 0.06–0.36 M at Laxemar and 0.18–0.42 M at Forsmark, which even at the lowest concentrations exceeded the CCC values (if assuming that  $\text{Cl}^-$  is proportional to monovalent cations) for clay colloids /Degueldre et al. 2000/.

Conditions for colloid stability were not fulfilled in the boreholes sampled at either of the sites in the present conditions. The concentrations in the boreholes sampled at Laxemar and Forsmark follow the general trend for natural colloid concentrations, not only in Sweden but also at international sites.

The uncertainty in the data in Figure 3-1 can mainly be attributed to the use of different analytical techniques, while the overall trend is consistent. Note that the colloid concentrations are not given for different size classes. Since larger colloids have a much higher mass than small ones, consequently the concentration of particles/ml can vary a lot even though the mass/ml stays the same. The Grimsel groundwater samples analyzed contained lower amounts of colloids than would be predicted by the general trend. The turnover of the water in the bedrock is fast, while the water that infiltrates is rainwater and does not bring many colloids into the bedrock. The fractures in the bedrock are also quite fine, which prevents colloid transport. According to /Degueldre et al. 2001/, the groundwater colloids in a granitic system are mainly phyllosilicates and silica originating. As long as the



**Figure 3-1.** a) Colloid concentrations from sampled groundwaters from Forsmark and Laxemar boreholes as a function of the chloride concentration. b) Correlation between background colloid concentration and ionic strength of the groundwater at different sites.

hydrochemical conditions remain constant, the background concentrations will not change and are further controlled by [Ca] and [Na] in the water. In groundwater with [Ca] > 10<sup>-4</sup> M and [Na] > 10<sup>-2</sup>, the colloid concentration will never exceed 100 µg/L. This is in accordance with reported CCC values /García García et al. 2007/. However, three sampled boreholes at Forsmark contain higher concentrations than 100 µg/L but less than 200 µg/L. Nevertheless, the uncertainties in these analyzes in low concentrations are very high.

### 3.3 Colloid characteristics

Various element analyzes have been performed on the colloids sampled at Laxemar and Forsmark. According to the filtration and fractionation method, the colloids at both sites are iron and sulphur. The LIBD and EDX analyzes indicate that the colloids are mainly composed of aluminium, silica and iron. Most of the colloids were collected on the 50 and 200 nm filters, which suggest that the colloids are not microbes, since they are preferentially in the  $\mu\text{m}$  size window. When the colloid concentration is very low in the groundwater it is hard to collect enough samples to perform a credible analysis and characterization. The concentrations are here so low that artifacts and contamination can contribute significantly and affect the results making it in principle impossible to analyze the colloids in terms of surface properties or structure. The composition of the Laxemar and Forsmark colloids is not significantly different, judging from the characterizations performed.

### 3.4 Conditions for colloid transport at present

In order to compare the conditions for colloid transport at the sites, different criteria have to be evaluated at establishment of the repositories, and then in terms of factors that could change conditions at the sites.

- The background colloid concentrations: These are less than 200  $\mu\text{g/L}$  at both sites.
- Colloid stability – Groundwater conditions: The salinity in the groundwater in sample boreholes is far higher than the critical coagulation concentration (CCC) and therefore the stability of colloids in the groundwater is very low at present at both sites. In a scenario with intrusion of glacial meltwater the groundwater chemistry can change drastically at both sites.
- Colloid characteristics: From the analyzes of samples from the boreholes at Laxemar and Forsmark it is not possible to determine the exact type of colloids present and colloid characteristics such as surface charge density, size distributions and structure.
- Colloid transport: In order to have any colloid transport and further colloid transport of RN, there has to be water-conducting fractures in direct contact with the bentonite barrier surface. The aperture distribution and the mineralogy of the fracture walls are important in giving rise to retention of transported colloids through filtration and sorption. However, detailed description of these factors lay outside the scope of this report.

The mineral surfaces on the fractures are enormous compared with the colloid surfaces in the current case of low concentrations of natural colloids. Scoping calculations have been performed to compare the available sorption areas on the colloid and the bedrock for a 1-metre long fracture with an aperture of 1 mm to 1  $\mu\text{m}$ , colloid concentrations of 1–100  $\mu\text{g/L}$  (representing the spread in background concentrations in Laxemar and Forsmark) and a theoretical montmorillonite colloid specific surface area of around 754  $\text{m}^2/\text{g}$  /Holmboe 2009/. The fractures are seen as tubes with a certain diameter (here the aperture) with a specific length with, and the colloids as to be spherical. Then the smooth surface is simply the length times the circumference of the inlet of the “tube”. Even when the fracture surfaces in these calculations are not attributed any roughness, there is an enormous difference between the colloid and fracture surface, especially in finer fractures with an estimated aperture of 1  $\mu\text{m}$  (Table 3-1). The specific surface area is directly proportional to the sorption sites and the colloids and the minerals are of the same types of materials. Reported  $K_d$ -values for strongly sorbing species on natural colloids and fracture-filling minerals are of the same order of magnitude. For example Am(III), which is an analogue of Eu(III), has reported  $K_d$ -values for granitic rock in the range of  $10^5 \text{ cm}^3/\text{g}$  /Liu and Neretnieks 2006/, while that for Eu(III) is  $10^{5.83} \text{ cm}^3/\text{g}$  on Febex bentonite colloids /Missana et al. 2008/. With similar  $K_d$ -values, the fraction sorbed onto the mineral surface will be directly proportional to the fraction of mineral surface to colloid surface. Nevertheless, this type of comparison is only valid if the elements reach the water bearing fracture on their own i.e not sorbed to montmorillonite colloids. For elements sorbing by reversible cation exchange it is reasonable to believe that the competition between colloid and fracture surface will result in a sorption preference to the fracture surface since the surface area is so much higher. For elements sorbing to montmorillonite colloids by surface complexation where the sorption rate in general are very fast and the desorption rate slow, it is likely that the elements will stick to the colloids through the transport in the fracture if they came into the fracture as sorbed to montmorillonite colloids.

**Table 3-1. Comparison of smooth fracture surfaces and colloid surfaces in a 1 m long fracture of varying aperture. Note that fracture roughness has not been accounted for and therefore the fracture surfaces are underestimated. Also the fracture is assumed to be a tube, with no extension in the longitudinal direction, which is highly unrealistic.**

Fracture aperture (m)	Volume in fracture (m <sup>3</sup> )	Smooth surface area (m <sup>2</sup> )	Natural Colloid Concentration (g/m <sup>3</sup> )	Area Colloid (m <sup>2</sup> )	Ratio Mineral <sub>area</sub> /Colloid <sub>area</sub>
0.001	0.000000785	0.00314	0.001	5.9189·10 <sup>-7</sup>	5,305
0.0001	7.85·10 <sup>-9</sup>	0.000314	0.001	5.9189·10 <sup>-9</sup>	53,050
0.00001	7.8510 <sup>-11</sup>	0.0000314	0.001	5.9189·10 <sup>-11</sup>	530,504
0.000001	7.85·10 <sup>-13</sup>	0.00000314	0.001	5.9189·10 <sup>-13</sup>	5,305,040
0.001	0.000000785	0.00314	0.01	5.9189·10 <sup>-6</sup>	531
0.0001	7.85·10 <sup>-9</sup>	0.000314	0.01	5.9189·10 <sup>-8</sup>	5,305
0.00001	7.85·10 <sup>-11</sup>	0.0000314	0.01	5.9189·10 <sup>-10</sup>	53,050
0.000001	7.85·10 <sup>-13</sup>	0.00000314	0.01	5.9189·10 <sup>-12</sup>	530,504
0.001	0.000000785	0.00314	0.1	0.000059189	53
0.0001	7.85·10 <sup>-9</sup>	0.000314	0.1	5.9189·10 <sup>-7</sup>	531
0.00001	7.8510 <sup>-11</sup>	0.0000314	0.1	5.9189·10 <sup>-9</sup>	5,305
0.000001	7.85·10 <sup>-13</sup>	0.00000314	0.1	5.9189·10 <sup>-11</sup>	53,050

### 3.5 Conditions for colloid transport with time

The conditions for colloid transport of RN can change if the colloid production rate increases, or if colloid consumption decreases. With climate change the flow in the fracture can change, as can the groundwater chemistry. Predictions for future climate change are associated with very high uncertainty. Nevertheless, two main scenarios for climate change during the life span of the repository have been identified for safety assessment analysis /SKB 2007/.

In the first scenario, glacial cycles occur periodically, which could have severe consequences for the repository through:

- Formation of permafrost.
- Changes in the mechanical stress on the bedrock.
- Intrusion of dilute glacial meltwater.
- Intrusion of oxygen during short periods of higher groundwater flow due to intrusion of glacial meltwater.

In the second scenario, the greenhouse effect with associated temperature increase will not have any severe impact on the repository according to predictions. In the colloid transport perspective, a temperature increase could induce a higher production rate of organic colloids. The degradation of organic material in the biosphere may add to humic and fulvic concentrations in the groundwater, but these would have to be transported from the surface down to repository depth. Organic colloid sampling today reveals a clear trend for the organic colloid concentration to decline drastically with depth /Nilsson and Degueldre 2007/.

In the glacial cycle climate scenario, dilute meltwater may intrude with such high flows to repository depth that the older saline groundwater will be pressed away, where the older groundwater and the meltwater will not mix. Also the release of pressure may induce new and fractures with larger aperture. This change in water chemistry overall conditions may result in favorable conditions for colloid stability and higher probability of colloid transport of RN. Under these conditions the bentonite barrier can release colloids, and with a high flow the potential for a high withdrawal rate is also high /Liu and Neretnieks 2006/. The risk is that the mass loss of the bentonite barrier will be significant, which will further endanger buffer functionality.

It is uncertain whether high mass loss is plausible and this is still under consideration in transport and modeling studies /Cheng and Cvetkovic 2009/. In a long-term perspective, the attachment and filtration of colloids in the fracture system may be significant in sealing the fractures, giving a



self-healing system. For strongly sorbing RN with low reversibility, the RN will stay on the colloids for a very long time, if they are released into the fracture already sorbed on a colloid. In dilute waters, such as glacial melt water, the concentration of colloids in solution can certainly be higher than 10–200 µg/L range measured in the present conditions of rather saline waters at Laxemar and Forsmark. The diagrams in Figure 3-1 show that it is reasonable for the groundwater to have colloid concentrations in the mg/L range if intruding meltwater has an ionic strength of 0.001 M. The changes in conditions that could give an impact, especially on bentonite colloid stability in the groundwater at Laxemar and Forsmark, are changes in ionic strength, pH, temperature or exposure to irradiation, with a higher stability for irradiated montmorillonite colloids than the colloids that had not been exposed to radiation /Holmboe et al. 2009/.

### **3.5.1 Expected montmorillonite colloid concentrations outside the bentonite buffer in the glacial scenario**

#### ***Bentonite colloid generation and sedimentation tests***

A number of articles have investigated bentonite colloid generation and sedimentation /Bessho and Degueldre 2009, Degueldre et al. 2009, García García et al. 2009a/. Static tests under no-flow conditions have been initiated to increase understanding of the processes behind the release of colloids from a bentonite bed, without adapting a flow to the system. It is well known that flow can be the driving force for colloid release from a colloidal source. However, a number of processes occur in the vicinity of a colloid bed, such as generation of colloids, diffusion, aggregation, fragmentation and sedimentation of larger aggregates. Sedimentation tests have been run in parallel to investigate whether the same concentration profiles of colloids outside the bed are achieved over time. Since the colloid concentration and size distribution are not intrinsic in the system but rather dependent on the distance to the colloid bed, the term pseudo equilibrium is used, which means that a concentration profile is adapted outside the barrier with the highest concentration closest to the bentonite surface. The published values can be seen as the concentration that could be expected at a certain distance from the bentonite barrier under different conditions. Addition of flow would give transport of colloids away from the bed and new colloids would be released at the bed to achieve equilibrium in the system. The results of all the tests are in general agreement and show that the pseudo equilibrium concentrations as well as the size distribution of colloids will be dependent on the type of bentonite used and the groundwater chemistry. Colloid populations are formed rapidly and the concentrations in numbers of different size classes of colloids are orders of magnitude lower in 0.01 M NaCl than in 0.001 M NaCl solutions. Equilibrium in colloid size distribution takes longer to achieve (100–1,000 h), possibly due to the aggregation of smaller colloids and diffusion from the bed. Similar concentration profiles and colloid size distributions have been achieved in sedimentation and generation tests. According to Bessho and Degueldre /Bessho and Degueldre 2009/, the results indicate that the pseudo-equilibrium states of colloidal dispersion are governed by the final colloid composition and the stability of colloid dispersions in the saline solutions.

#### ***Colloid generation and sedimentation test with Na and Ca-montmorillonite***

/García García et al. 2009b/, performed generation and sedimentation experiments to study the effects of ionic strength, cationic form and elevation on montmorillonite colloid concentration out in suspension. In the generation tests the compacted bentonite were placed in the test tubes, where after water was poured carefully into the test tubes, to avoid to disturb the bentonite surface. In the case of sedimentation, bentonite and water was shaken initially in the test tube and then the bentonite was let to settle. Samples were taken from the middle of the vessels except for the experiments designed to investigate colloid concentration as a function of altitude, where the sampling was performed at 3, 5, 7, 9, 11, 13, and 15 cm from the colloid source. Colloid concentrations were measured with SPC in the size channels 50–100, 150–200, 150–200, 200–300, 300, 500, 500–700, 700–1,000, 1,000–1,500, 1,500–2,000 and 2,000–5,000 nm. From these tests, expected montmorillonite colloid concentrations (7 cm from the bed surface) in mg/L were roughly estimated (Table 3-2). The results show that concentrations of 10 mg/L can be expected in groundwater with an ionic strength of  $\geq 0.001$  M in contact with the bentonite barrier. The concentration drastically decreases with distance and ionic strength, so 10 mg/L can be seen as a rather conservative value. In the case of Ca-montmorillonite, the value is expected to be a factor of 10 lower for an ionic strength of 0.001 M, and too low to be detected by SPC for an ionic strength of 0.01 and 0.1 M.

**Table 3-2. Estimated pseudo-equilibrium concentrations of montmorillonite colloids at a distance of 7 cm from the colloid bed.**

Na	0.001 (M)	0.01 (M)	0.1 (M)
Na-montmorillonite	5.2 ± 0.5 mg/L	0.5 ± 0.1 mg/L	0.2 ± 0.1 mg/L
Ca-montmorillonite	0.4 ± 0.2 mg/L	–	–

### ***Bentonite swelling experiments***

In the SKB Bentonite Erosion project lead by Professor Ivars Neretnieks, investigations on gel formation and subsequent colloid release have been performed whereas all the studies were performed in deionised water. Swelling experiments have been performed with 0.2 g Na-montmorillonite in contact with deionised water in 45 mL bottles. The water very close to the surface of the bottles was collected in 2.5 mL fractions after 41 days. The samples were analyzed with Photon Correlation Spectroscopy (PCS) using a calibration from signal size to concentration /Jansson 2009/. The colloid concentration was found to be fairly constant at 80–100 mg/L for the first 2.5–15 mL of supernatant, after which the concentration started to increase drastically with decreasing distance to the Na-montmorillonite material in the base of the bottles.

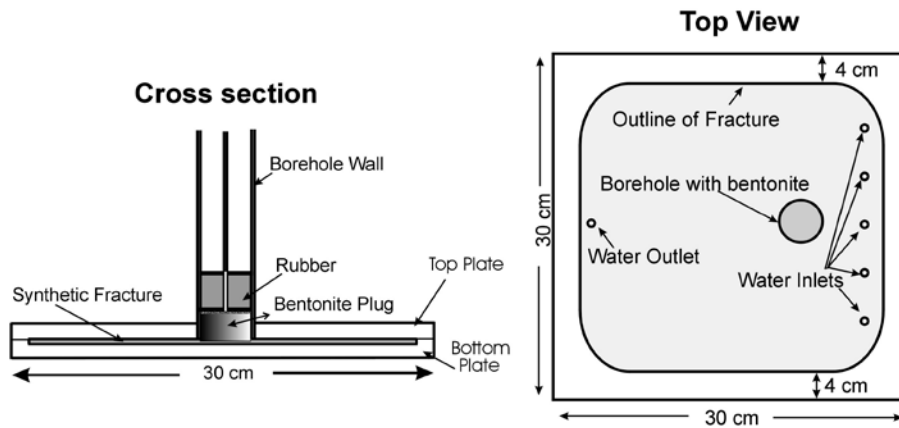
### ***Bentonite gel propagation tests***

To mimic compacted bentonite in contact with groundwater in water-bearing fractures, an artificial fracture in Plexiglas with an aperture of 1 mm was constructed in the same project /Birgersson et al. 2009/. The bentonite was placed in one end of the slabs and saturated. After the bentonite had been fully saturated, deionized water was pumped through the bentonite container with a flow rate of roughly 0.4–0.6 mL/h. In the first test a bentonite with high montmorillonite content was used, with no attempt made to have any cation exchange of the clay. In the second test a bentonite that had been washed twice to remove soluble minerals such as gypsum was used. The dry density in both tests was 1,000 kg/m<sup>3</sup>. The clay dispersed into the fracture in both tests and a clay concentration gradient could be seen in both cases. Downstream samples were collected for colloid concentration analyzes with PCS and SPC. The montmorillonite colloid concentrations throughout the two tests and sample channels were found to be fairly uniform, with concentrations < 200 mg/L.

Other experiments in artificial Plexiglas fractures were set up in the SKB Colloid Transport project in collaboration with NWMO /Vilks and Miller 2009/. A specific objective was to acquire data on the effect of flow rate, bentonite type and groundwater composition on bentonite gel propagation and bentonite colloid erosion. Deionized water and synthetic Grimsel groundwater were used throughout the experimental series. The Grimsel groundwater contained 0.001 M Na<sup>+</sup> and 0.0001 Ca<sup>2+</sup>. In some of the tests the pH was adjusted to 9.6 while in others the pH was not controlled since pH was not expected to give any impact on the bentonite erosion in the specific pH range 8.2–9.6. Na-exchanged, Ca-exchanged and MX-80 bentonite was used, which were mixed with latex colloids. Plugs of a dry density of 2 g/cm<sup>3</sup> with a diameter of roughly 38 mm and a thickness of 10 mm were produced. Latex colloids of different sizes, representative for bentonite colloids, were mixed in with the bentonite. Fluorescent latex colloids are easier to detect than bentonite colloids and will tell in what direction the colloids from the plug have travelled. The clay plugs were installed within a transparent Lexan tube (38 mm inner diameter) intended to simulate a borehole (Figure 3-2). The transparent synthetic fracture had the dimensions of 22×22 cm. To stabilize the bentonite and prevent it from expanding upwards, A rubber packer was installed to keep the bentonite in place and to avoid it from swelling up, out from the fracture. In two tests the fracture was given an incline of 15° to mimic the slope to study the effect of gravity on gel propagation and further colloid release.

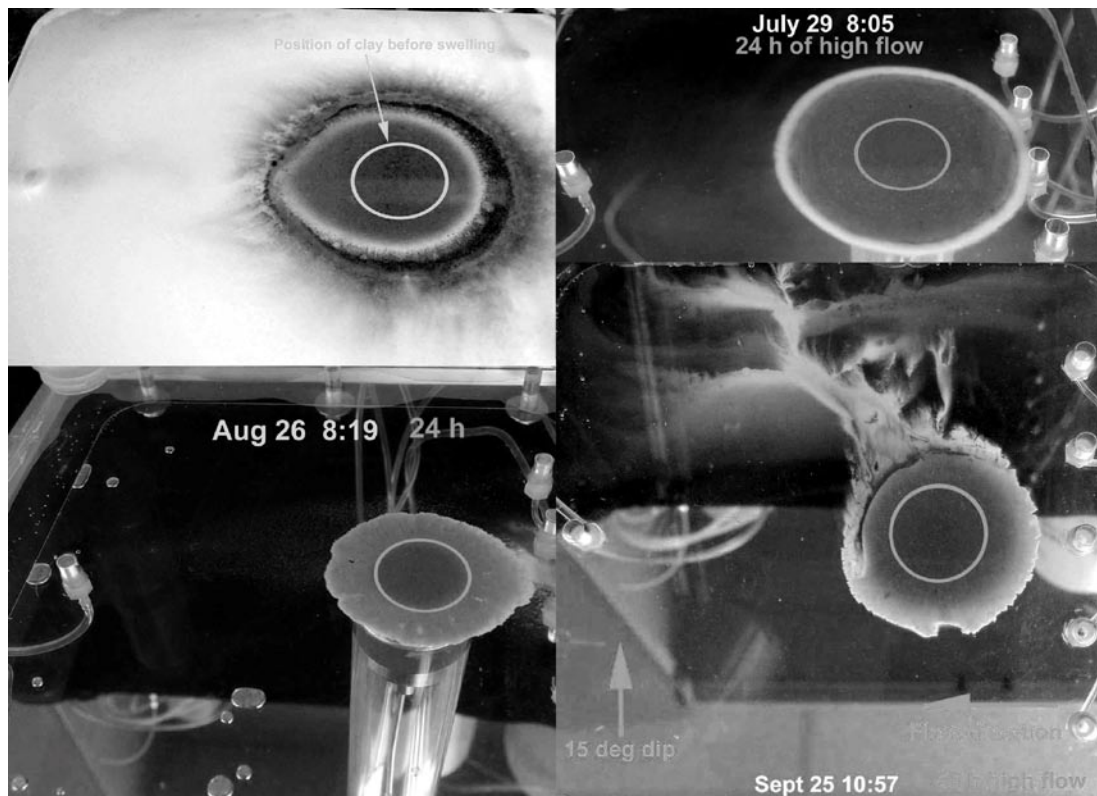
Initially, the fracture was filled with water and bentonite saturation and further swelling were visually monitored for no-flow periods of 23 to 430 h. After that, a low flow of 6 mL/h was applied for 72 to 170 h. The flow was increased to 44 mL/h for a 24 to 50 h period to test for flow velocity effects on bentonite erosion and transport. Finally, the flow was stopped and the artificial fracture was opened and the bentonite deposits examined.





**Figure 3-2.** Schematic diagram of the synthetic fracture and bentonite placement.

Photos from on the clay plugs in the different condition show that the gel propagation and colloid release have distinct appearances in the different experimental conditions (Figure 3-3). The gel propagation and colloid release is strongly connected to bentonite type, flow rate, aperture width, groundwater composition and gravity. As expected, the Ca-montmorillonite did not expand extensively in the gel phase in comparison to the MX-80 and the Na-montmorillonite because of the only mechanisms of crystalline swelling and the lack of osmotic swelling (or at least the osmotic swelling is marginal). The flow rate had a significant impact as expected, with the higher colloid release at



**Figure 3-3.** Bentonite gel propagation and further erosion under varying conditions.

Upper left: MX-80, DIW, 5 mm aperture.

Upper right: MX-80, synthetic Grimsel groundwater, 5 mm aperture.

Lower left: Ca-montmorillonite, synthetic Grimsel groundwater, 1 mm aperture.

Lower right: MX-80, synthetic Grimsel groundwater, 1 mm aperture, fracture incline 15. The montmorillonite colloid concentrations were sampled in the water outlet over time, with the reported concentrations obtained at steady state (Table 3-3).

higher flows. In the wider aperture (5 mm), the bentonite gel expanded faster than in the aperture of 1 mm. The gel propagation and further colloid release is attributed strongly to the groundwater chemistry. Interesting to note that even the low ionic strength of the synthetic Grimsel groundwater gave a significant impact with a low gel propagation compared with the tests performed in deionized water. Gravity had a major impact, with colloids released in the direction of the slope (Figure 3-3, lower right photo). Note that the outlet for sampling was not in the direction of the slope and elevated concentrations would most likely have been found in the direction of the slope, whereas the samples from the outlet contained colloid concentrations in the same range as was found in the parallel test without a fracture incline.

As can be seen in Table 3-3, the colloid concentrations at steady state never exceeded 20 mg/L when Grimsel GW was used in the set-up. Furthermore, the colloid concentrations were the same in the outlets for low and high flow, except in the test with a 5 mm aperture using deionized water.

### **Glacial water composition**

It is hard to predict the ionic composition of a future glacial meltwater intruding to repository depth. Nevertheless, the chemical composition with glacial meltwaters from now existing glaciers can be used as standards. G.H Brown 2002 has published data on the chemical composition of meltwaters from eighteen existing glaciers (Table 3-4.). These meltwaters have not been in contact with the ground. This means that exceeding concentrations than the ones reported in the table could be expected if this kind of water reaches repository depth since glacial meltwaters enrich in chemistry over the distance from the ice and snowmelt to the emergence in the glacier portal /Brown 2002/.

**Table 3-3. Montmorillonite colloid concentrations sampled in the outlet at steady state.**

Test	Parameters	Montmorillonite Colloids (mg/L)		Latex Colloids (mg/L)	
		6 mL/h	44 mL/h	6 mL/h	44 mL/h
2	Wyoming bentonite DIW 5 mm aperture 1 µm blue latex	20 to 200	150 to 480	0.02 to 0.04	0.04 to 0.55
4	Wyoming bentonite Grimsel water 5 mm aperture 220 nm YG latex	4 to 16	0 to 9	0.48 to 0.65	0.30 to 0.70
5	Wyoming bentonite Grimsel water 1 mm aperture 220 nm YG latex	0.3 to 7	2.0 to 4.7 reached steady-state at 3	0.10 to 0.43	0.25 to 0.38
6	Ca montmorillonite Grimsel water 1 mm aperture 220 nm YG latex	0.2 to 2.2	0.2 to 0.6 reached steady-state at 0.5	0.02 to 0.06	0.04 to 0.08
7	Wyoming bentonite Grimsel water 1 mm aperture 220 nm YG latex fracture dips 15°	0.2 to 3.7	0.5 to 1.0 reached steady-state at 1	0.01 to 0.11	0.02 to 0.04
8	Na montmorillonite Grimsel water 1 mm aperture 220 nm YG latex fracture dips 15°	0 to 1.8	0 to 0.15	0.07 to 0.12	0.04 to 0.07

**Table 3-4. Ca<sup>2+</sup> and Na<sup>+</sup> concentrations in glacial meltwaters from existing glaciers /Brown 2002/.**

	Ca mM	±	Na mM	±	Divalent mM	±	Monovalent mM	±
Bench Glacier (Alaska)	0.28	0.01	0.03	0.00	0.29	0.01	0.09	0.00
Haut Glacier d'Arolla (Switzerland)	0.16	0.16	0.02	0.03	0.17	0.16	0.03	0.03
Nigardsbreen (Norway)	0.01	0.01	0.02	0.02	0.01	0.01	0.02	0.02
Gornergletscher (Switzerland)	0.12	0.10	0.03	0.03	0.17	0.13	0.04	0.05
Walcott Glacier (Antarctica)	0.38	0.53	0.06	0.08	0.43	0.54	0.07	0.09
Koettlitz Glacier (Antarctica)	0.04	0.01	0.02	0.02	0.04	0.01	0.03	0.02
Howchin Glacier (Antarctica)	0.60	0.14	0.49	0.25	0.68	0.14	0.54	0.25
Ward Glacier (Antarctica)	0.39	0.05	1.16	0.56	0.54	0.06	1.26	0.56
Berendon (Canada)	0.21	0.34	0.00	0.01	0.22	0.34	0.01	0.01
Tsanfleuron (Switzerland)	0.32	0.02	0.00	0.00	0.37	0.02	0.01	0.00
Chhota-Shigri (India)	0.08	0.09	0.05	0.04	0.10	0.09	0.08	0.05
Scott Turnerbreen (Svalbard)	0.11	0.09	0.43	0.63	0.20	0.13	0.44	0.63
Fjallsjökull (Iceland)	0.12	0.03	0.08	0.09	0.14	0.04	0.08	0.09
Chamberlain (USA)	0.09	0.11	0.01	0.00	0.13	0.13	0.01	0.01
Engabreen (Norway)	0.18	0.27	0.11	0.20	0.19	0.27	0.13	0.20
Grimsvotn (Iceland)	0.18	0.01	0.48	0.02	0.24	0.01	0.49	0.02
Austre Okstindbreen (Norway)	0.17	0.07	0.08	0.12	0.19	0.07	0.09	0.12
Argentière (France)	0.13	0.23	0.05	0.08	0.14	0.23	0.06	0.08

The glacial meltwater from these eighteen sites has Ca<sup>2+</sup> concentrations in the range of 0.01 to 0.60 mM and Na<sup>+</sup> concentrations ranging from 0 to 1.6 mM. Assumingly Mg<sup>2+</sup> and K<sup>+</sup> have the same effect on bentonite gel propagation and further colloid release as Ca<sup>2+</sup> and Na<sup>+</sup> and should therefore also be taken into account. Relating these values to CCC-values for Ca<sup>2+</sup> (0.0001 M) and Na<sup>+</sup> (0.001) M on montmorillonite colloids, it is two of the eighteen specific cases with concentrations below the CCC values.

In the different studies presented, the montmorillonite colloid concentrations outside the barrier are strictly coupled to the groundwater chemistry and in particular the concentrations of the dominating cations Ca<sup>2+</sup> and Na<sup>+</sup>. The difference in expected concentration in a groundwater with the composition of deionized water and a Grimsel type of groundwater is a magnitude of 10, i.e 200 mg/l instead of 20 mg/l. According to inventories of existing glacier meltwaters, the Grimsel type is more representative than deionized water, and it is more likely that glacier meltwaters will have a Ca and Na concentration that will not favor montmorillonite colloid stability. The pH in the Grimsel water is fairly high (9.6), however the difference in pH from neutral to Grimsel pH is not expected to give any effect on colloid stability /García García et al. 2010/. However, the expected concentrations outside the bentonite barrier for the case with deionized water serves as a conservative case.

## 4 Sorption of the prioritized elements montmorillonite colloids

In the early lifetime of the repository, colloid transport of radionuclides appears to be unlikely since the natural background colloid concentrations are low, in the magnitude of  $\mu\text{g/L}$ , and due to the rather high salinity colloids will not stay stable in solution for a long time. As already mentioned, the conditions may drastically change in the event of intrusion of dilute glacial meltwater to repository depth, with higher flow velocities than at present. The functionality of the bentonite barrier can be jeopardised if bentonite colloids are released and transported away from the buffer. In the event of a leaking canister, radionuclides that are strongly sorbed to the bentonite might be mobilised with released colloids. The strength of sorption to the colloids is crucial, as the sorption and desorption rates. If the sorption is strong and fast and desorption slow, the RN may travel long distances quite rapidly with the colloids. If, on the other hand, the sorption is weak and desorption is rather fast, it is more likely that the RN will sorb to the fracture surfaces instead. Therefore  $K_d$ -values and sorption kinetics are needed as input in modeling colloid transport of RN.

### 4.1 Definition and restrictions in $K_d$ -values

A  $K_d$ -value is a measure of sorption and is defined as the ratio between the element sorbed per unit of absorbent to the amount of element in solution.

The distribution coefficient  $K_d$ , can be calculated from experimental data from sorption experiments using the equation:

$$K_d = (C_0 - C_e) / C_e \cdot V/m \quad (4-1)$$

$C_0$  = initial concentration of sorbent out in solution.

$C_e$  = concentration of sorbent at equilibrium out in solution.

$V$  = volume of solution.

$m$  = weight of solid/colloid.

The units are given in  $\text{m}^3/\text{kg}$  or  $\text{cm}^3/\text{g}$ .

For deriving an accurate  $K_d$ -value the surface sorption sites,  $A$ , has to be in excess to avoid saturation effects. The derived  $K_d$ -values have to be independent of the element concentration and the reaction should be reversible.

The rate constant forward for sorption is  $k_2$  (second order kinetics since RN has to collide with a colloid) and rate constant backward for desorption is  $k_{-1}$  (first order kinetics since it is the complex releasing RN),

$$K = K_d = (k_2 / k_{-1}) \quad (4-2)$$

When  $k_2 \gg k_{-1}$ , as often the case in natural systems the reaction can be seen as irreversible (depending on appointed time scale). Although in the case of a very high  $K_d$  and the reverse rate is very slow, it does not mean that the attachment of the RN to the colloid is not reversible. A change in RN concentration, pH or ionic strength can shift the equilibrium. The ability of the sorbed RN to respond to the change in equilibrium is the measure of reversibility. In cases where desorption is slow it is difficult to perform experiments to observe desorption in reasonable time periods. This is of course especially crucial in a system as the repository of spent nuclear fuel, where transport of radionuclides are important for very long time scales and these data are needed for safety assessment calculations. However, if the  $K_d$  and the rate constant for sorption are given the rate of desorption can be derived from Equation 4-2. The desorption rate constant can be neglected when it is very small compared to the sorption rate.

The conditional  $K_d$ -value is specific to the particular experimental conditions as pH, temperature, ionic strength with one type of adsorption site and one type of sorbant. In practice the  $K_d$ -values obtained come from a system with mixed minerals and sites. The sensitivity to these parameters is coupled to the sorption mechanism, where elements sorbing by cationic exchange are very sensitive to for example the ionic strength and will react on that accordingly. Drastic changes in pH from neutral to acid pH ranges can change the sorption mechanism for elements sorbing by surface complexation to cationic exchange. However, small changes in the neutral pH range will not affect the system.

Uncertainties on different levels will be attached to the  $K_d$ -values using them in transport calculations. In the case of  $K_d$ -values for colloids the following uncertainties can be identified:

The experimental error accounting for deficiencies in the measurement method itself and additional processes not fully quantified in the experimental evaluation is most often attached to the  $K_d$  literature value. A representative error is for example Pu(V) sorption to montmorillonite  $10^{5.37 \pm 0.18}$  at pH 9.5 /Missana et al. 2008/.

The conditional nature of  $K_d$  requires different estimates of this parameter for each set of geochemical conditions of potential relevance along the potential migration path for a radionuclide. As is not feasible to measure sorption for every set of conditions, the derivation of  $K_d$  must rely on data derived from representative model systems. /Ochs et al. 2006/. The pH affects mainly sorption by surface complexation (except for its effect in determining surface charge), while ionic strength affects sorption by ion exchange. Also the Eh is important, especially then considering the speciation of the elements sorbing.

The  $K_d$ -value is colloid specific. The data are scarce, and  $K_d$ -values are not available for different types of montmorillonite, as Ca- and Na-montmorillonite. Especially this will be important for elements sorbing by ionic exchange.

The size distributions of the colloids will affect the specific size and the number of sorption sites. Smaller sized colloids with higher specific area will contain a larger number of sorption sites per mass than the larger colloids. This is certainly problematic since  $K_d$ -values are normalized per mass and not to surface area. Using a  $K_d$ -value obtained for one size distribution applying it on another will introduce a large error in the predicted sorptivity. Due to the lack of data concerning surface areas and size distributions for which  $K_d$  data in the literature are available, conversion of mass normalized to surface area normalized values is not feasible. This error is identified as the largest error attached to the  $K_d$ -value.

The range of the  $K_d$ -values for the different elements in Table 4-1 will give an estimate of the spread due to varying colloid size distributions, varying chemical conditions, different montmorillonites and varying analysis techniques. The  $K_d$ -values are not normally distributed why median number and not the mean in this range will represent the best estimate.

In literature data  $R_d$  is often used instead of  $K_d$  and is used to indicate that it is not known if experiments feeding the data managed to reach equilibrium.

## 4.2 Prioritized elements

A list of prioritized elements for which data on  $K_d$ -values and sorption kinetics are needed has been drawn up by SKB. The criteria used in its ranking were the yearly dose to the near zone based on the spent fuel inventory, radiotoxicity and half-life. The list is as follows, in descending order of priority:

Pu, Th, Am, Pb, Pa, Ra, Np, Cm, Ac, Tc, Cs, Nb, Ni, Pd, Se, Sn, Zr and U.

### 4.3 Chemical characteristics of the prioritized elements

The oxidation state of the RN naturally governs sorption onto colloids. The groundwater will be reducing for the majority of the lifetime of the repository. However, in the construction phase of the repository, oxygen will be introduced into the system and will be consumed in hundreds of years according to calculations. In the climate scenario with glacial cycles, it cannot be excluded that oxygen might penetrate the repository environment. These transient periods of oxidizing conditions are particularly interesting, since colloid transport of RN in this scenario is considered to be associated with the highest risk. Therefore, the sorption data for redox-sensitive elements are presented in this report for both the oxidative and reductive species where data are available. The chemical characteristics for the priority elements are presented below. The characteristics have been taken from /Carbol and Engkvist 1997/ if not stated otherwise.

#### **Plutonium (Pu)**

##### **Actinide**

Half-life:  $^{238}\text{Pu}$  87.74 y,  $^{239}\text{Pu}$   $2.411 \cdot 10^4$  y,  $^{240}\text{Pu}$  6,563 y,  $^{241}\text{Pu}$  13.2 y,  $^{242}\text{Pu}$   $3.763 \cdot 10^5$  y

Oxidation state under reducing conditions: Pu(III) /Allard et al. 1983/ and Pu(IV)

Oxidation state under oxidizing conditions: Pu(IV), Pu(V) and Pu(VI)

Pu(IV) has a tendency to form true colloids, which will influence the sorption values from experiments.

#### **Thorium (Th)**

##### **Actinide**

Half-life:  $^{229}\text{Th}$  7,340 y,  $^{230}\text{Th}$   $7.54 \cdot 10^4$  y,  $^{232}\text{Th}$   $1.405 \cdot 10^{10}$  y

Oxidation state under reducing and oxidizing conditions: Th(IV)

#### **Americium (Am)**

##### **Actinide**

Half-life:  $^{241}\text{Am}$  432.7 y,  $^{242\text{m}}\text{Am}$  141 y,  $^{243}\text{Am}$  7,380 y

Oxidation state under reducing and oxidizing conditions: Am(III)

#### **Lead (Pb)**

##### **Post-transition element**

Half-life:  $^{202}\text{Pb}$   $10^{4.7}$  y,  $^{204}\text{Pb}$   $1.4 \cdot 10^{17}$  y

Oxidation state under oxidizing and reducing conditions: Pb(II)

#### **Radium (Ra)**

##### **Alkaline earth metal**

Half-life:  $^{226}\text{Ra}$  1,602 y,  $^{228}\text{Ra}$  5.75 y

Oxidation state under reducing and oxidizing conditions: Ra(II)

#### **Protactinium (Pa)**

##### **Actinide**

Half-life:  $^{231}\text{Pa}$   $3.276 \cdot 10^4$  y

Oxidation state under reducing and oxidizing conditions: Pa(V)

The chemistry of Pa is not well known. However sorption onto quartz and aluminium oxide is reported to be very strong above pH 6, between 1 and 10 m<sup>3</sup>/kg /Allard et al. 1979/.

### **Neptunium (Np)**

#### **Actinide**

Half-life:  $^{237}\text{Np}$   $1.55 \cdot 10^5$  y

Oxidation state under reducing conditions: Np(IV), Np(V)

Oxidation state under oxidizing conditions: Np(V), Np(VI), Np(VII)

### **Curium (Cm)**

#### **Actinide**

Half-life:  $^{237}\text{Cm}$   $1.56 \cdot 10^7$ ,  $^{238}\text{Cm}$   $3.4 \cdot 10^5$ ,  $^{244}\text{Cm}$  18.11 y,  $^{245}\text{Cm}$  8,500 y,  $^{246}\text{Cm}$  4,730 y,  $^{250}\text{Cm}$  9,700 y

Oxidation state under reducing and oxidizing conditions: Cm(III)

### **Actinium (Ac)**

#### **Actinide**

Half-life:  $^{227}\text{Ac}$  21.77 y

Oxidation state under reducing and oxidizing conditions: Ac(III)

There are very few chemical data on Actinium, but its analogue in the lanthanides can be used to assess chemical properties.

### **Technetium (Tc)**

#### **Transition metal**

Half-life:  $^{99}\text{Tc}$   $2.13 \cdot 10^5$  y

Oxidation state under reducing conditions: Tc(IV), probably in the form  $\text{TcO}(\text{OH})_2\text{H}_2\text{O}_{\text{aq}}$ .

Oxidation state under oxidizing conditions: Tc(VII) in the form of  $\text{TcO}_4^-$

### **Cesium (Cs)**

#### **Alkali metal**

Half-life:  $^{135}\text{Cs}$   $3 \cdot 10^6$  y,  $^{137}\text{Cs}$  30 y

Oxidation state under reducing and oxidizing conditions: Cs(I)

### **Zirconium (Zr)**

#### **Transition metal**

Half-life:  $^{93}\text{Zr}$   $1.53 \cdot 10^6$  y

It is not well known in what species Zr will exist in reducing groundwater. However in reducing conditions and oxidizing conditions Zr(IV) is believed to be the existing oxidation state. Zr can also form true colloids.

### **Nickel (Ni)**

#### **Transition metal**

Half-life:  $^{59}\text{Ni}$   $7.5 \cdot 10^4$  y,  $^{63}\text{Ni}$   $10^2$  y

Oxidation state under reducing and oxidizing conditions: Ni(II)

Ni is an analogue to Co because of the similarities in the ionic radius and charge. Ni sorption is dominated by surface complexation with a minor part sorbing by cationic exchange.



## **Uranium (U)**

### **Actinide**

Half-life:  $^{233}\text{U}$   $1.59 \cdot 10^5$  y,  $^{234}\text{U}$   $2.45 \cdot 10^5$  y,  $^{235}\text{U}$   $7.04 \cdot 10^8$  y,  $^{236}\text{U}$   $2.34 \cdot 10^7$ ,  $^{238}\text{U}$   $4.47 \cdot 10^9$  y

Oxidation state under reducing conditions: U(IV, VI), U(IV) dominate in highly reducing conditions as  $\text{U}(\text{OH})_4$  and in oxidizing to mildly reducing conditions the U(VI) is dominating. There are very few data available on sorption of U(IV), but Th(IV) can here be used as an analogue.

## **Tin (Sn)**

### **Metal**

Half-life:  $^{126}\text{Sn}$   $1 \cdot 10^5$  y

The aqueous speciation of Sn is not well known. In oxidizing conditions the Sn(IV) is the major oxidation state. In reducing condition Sn will reduce from Sn(IV) to Sn(II).

## **Selenium (Se)**

### **Non metal**

Half-life: The determination of the half life give disparate values in different sources. The half-life ranges from for  $^{79}\text{Se}$  varies in  $10^{4.8}$ – $10^{6.0}$  years.

The aqueous chemistry of Se is rather complex known, but most probably Se will exist as  $\text{SeO}_3^{2-}$  or  $\text{SeO}_4^{2-}$  in reducing conditions, which indicates that Se sorption will be marginal. True colloids can most plausible form.

## **Palladium (Pd)**

### **Transition metal**

Half-life:  $^{107}\text{Pd}$   $6.5 \cdot 10^6$  y

Oxidation state under reducing and oxidizing conditions: Pd(II)

## **Nb (Niobium)**

### **Transition metal**

Half-life:  $^{94}\text{Nb}$   $2.03 \cdot 10^4$  y

Oxidation state under reducing and oxidizing conditions: Nb(V), Nb(III and IV) also exist.

## **4.4 $K_d$ -values for the prioritized elements**

In the table below  $K_d$ -values for the prioritized elements are listed with the experimental conditions in the sorption experiments from which the  $K_d$ -values are derived.



**Table 4-1.  $K_d$ -values listed for the prioritized elements.**

Elements	Colloid	pH	IS (M)	Redox sensitive	Eh	$K_d$ -value (cm <sup>3</sup> /g)	Reference
<b>Pu</b>				Yes			
Pu(IV)	Febex (Ca dominated bentonite) mean size 200–250 nm	9.2–9.6	0.001		Anaerobic	10 <sup>5</sup>	/Geckeis et al. 2004/
Pu(V)	Smectite (92% 100–200 nm), (natural water)	8.2	0.005		–	6.4·10 <sup>3</sup>	/Lu et al. 1998/
Pu(V)	Smectite (92% 100–200 nm), (synthetic water)	8.5	0.005		–	3.8·10 <sup>4</sup>	/Lu et al. 1998/
Pu(IV) (true colloid)	Smectite (92% 100–200 nm), (natural water)	8.2	0.005		–	3.5·10 <sup>3</sup>	/Lu et al. 1998/
Pu(IV) (true colloid)	Smectite (92% 100–200 nm), (synthetic water)	8.5	0.005		–	1.4·10 <sup>5</sup>	/Lu et al. 1998/
Pu(V) or Pu(IV) not known in what form	Ca-montmorillonite colloids	8.3				7·10 <sup>5</sup>	/Lu et al. 2003/
Pu (IV)	Febex (Ca dominated bentonite) mean size 200–250 nm	9.5	0.001		–200 mV	10 <sup>5.37</sup>	/Missana et al. 2008/
Recommended value Pu(IV) sorption	Sorption of Pu(IV) as true colloid not included in the recommended value					Range 10 <sup>5.0</sup> –10 <sup>5.37</sup> Best estimate 10 <sup>5.2</sup>	
Recommended value Pu(V) sorption						Range 10 <sup>3.80</sup> –10 <sup>4.58</sup> Best estimate 10 <sup>4.4</sup>	
<b>Th</b>				No			
Th(IV)	MX-80 in solution. Not specific colloid fractions.	7	~0.1		Anoxic and red	~10 <sup>5.3</sup> (taken from plot)	/Grambow et al. 2006/
	However performed in such a way that it is colloid sorption observed.	8				~10 <sup>5.3</sup> (taken from plot)	/Grambow et al. 2006/
	Sorption between pH 2–11.	9				~10 <sup>5.3</sup> (taken from plot)	/Grambow et al. 2006/
Recommended value Th(IV) sorption						Range 10 <sup>5.3</sup> Best estimate 10 <sup>5.3</sup>	
<b>Am</b>				No			
Am(III)	Kunipiel bentonite (Na-bentonite). Used bulkbentonite.	9.4	Deionized (60°C)			A 1.2·10 <sup>4</sup> B 1.0·10 <sup>5</sup> C 1.1·10 <sup>5</sup>	/Baston et al. 1999/
	Centrifuged the solution before analyzing A and filtered through 450 nm B and 10,000 MW filter C.	9.4	Deionized (60°C)			A 3.0·10 <sup>4</sup> B 4.6·10 <sup>4</sup> C 3.0·10 <sup>4</sup>	/Baston et al. 1999/
	Kunipia,Na-bentonite, 4–450 nm	8	0.001		N <sub>2</sub> -atm	4·10 <sup>6</sup> –9·10 <sup>7</sup>	/Iijima et al. 2008/
	Kunipia,Na-bentonite, 4–450 nm	10	0.001		N <sub>2</sub> -atm	5·10 <sup>7</sup> –2·10 <sup>8</sup>	/Iijima et al. 2008/
	Marl. 5–500 nm.	8.6	0.02		310 mV	(1–3)·10 <sup>6</sup>	/Degueldre et al. 1994a/
	Montmorillonite	8	0.01		?	(0.5–5)·10 <sup>5</sup>	/Degueldre et al. 1994b/
	Febex. Ca-montmorillonite. mean size 200–250 nm.	9.2–9.6	0.001		Anaerobic	2·10 <sup>6</sup>	/Geckeis et al. 2004/

Elements	Colloid	pH	IS (M)	Redox sensitive	Eh	K <sub>d</sub> -value (cm <sup>3</sup> /g)	Reference
	MX-80 in solution. Not specific colloid fractions.	7	0.1		Anoxic and red	~10 <sup>4.7</sup> (taken from plot)	/Grambow et al. 2006/
	however performed in such a way that it is colloid sorption observed.	8				~10 <sup>5.2</sup> (taken from plot)	/Grambow et al. 2006/
	Sorption between pH 2–11	9				~10 <sup>5.1</sup> (taken from plot)	/Grambow et al. 2006/
	Natural colloids. Consist mainly of organics. (Not included in the range of values which the median K <sub>d</sub> is estimated from)	8.3	0.013			6.8·10 <sup>4</sup> –1.2·10 <sup>5</sup>	/Vilks and Baik 2001/
Recommended value Am(III) sorption						Range 10 <sup>4.08</sup> –10 <sup>8.30</sup> Best estimate 10 <sup>5.1</sup>	
<b>Pa</b>				Yes			
Pa(V)	Kunipiel bentonite (Na-bentonite). Used bulk bentonite.	10.1	DI (21°C)			A. > 2.1·10 <sup>5</sup> B. > 2.6·10 <sup>5</sup> C. > 3.5·10 <sup>5</sup>	/Baston et al. 1999/
	Centrifuged the solution before analyzing and filtered through 450 nm and 10,000 MW filter. Denoted A. B. C	10.1	DI (21°C)			A. > 1.9·10 <sup>5</sup> B. > 1.9·10 <sup>5</sup> C. > 2.6·10 <sup>5</sup>	/Baston et al. 1999/
		9.4	DI (60°C)			A. 7.6·10 <sup>3</sup> B. 8.1·10 <sup>3</sup> C. > 2.9·10 <sup>5</sup>	/Baston et al. 1999/
		9.4	DI (60°C)			A. 9.9·10 <sup>3</sup> B. > 3.2·10 <sup>5</sup> C. > 3.3·10 <sup>5</sup>	/Baston et al. 1999/
	Separation of the < 0.5 µm size of the bulk bentonite.					10 <sup>4.8</sup>	/Bradbury and Baeyens 2006/
Recommended value Pa(V) sorption						Range (21°C) 10 <sup>4.8</sup> –10 <sup>5.4</sup> Best estimate (21°C) 10 <sup>5.3</sup>	
<b>Np</b>				Yes			
Np(V)	Febex. Ca-montmorillonite. mean size 200–250 nm.	9.2–9.6	0.001		Anaerobic	< 5·10 <sup>3</sup>	/Geckeis et al. 2004/
Np(IV)	Kunipielbentonite. (Na-bentonite). mean size 450 nm.	8	0.01		Anaerobic	2.7·10 <sup>4</sup>	/Nagasaki et al. 1999/
Np(V)	Ca-montmorillonite. mean size 100 nm.	8.2–8.9	0.003		430 mV	10–100	/Runde et al. 2002/
Recommended value Np(IV) sorption						Range – (only one value) Best estimate 10 <sup>4.4</sup>	
Recommended value Np(V) sorption						Range 10–10 <sup>3.70</sup> Best estimate 10 <sup>3.4</sup>	

Elements	Colloid	pH	IS (M)	Redox sensitive	Eh	K <sub>d</sub> -value (cm <sup>3</sup> /g)	Reference
<b>Cm</b>				No			
Cm(III)	MX-80 in solution. Not specific colloid fractions	7	~0 and 0.008		Anoxic and red	10 <sup>4.2</sup>	/Grambow et al. 2006/
	however performed in such a way that it is colloid sorption observed.	8		10 <sup>4.2</sup>		/Grambow et al. 2006/	
	Sorption between pH 2–11.	8.5		10 <sup>4.4</sup>		/Grambow et al. 2006/	
	Ca-montmorillonite. < 2 mm. Sorption on bentonite. yet performed in such way that the sorption on colloids observed	7	0.1	~10 <sup>6.3</sup>		/Rabung et al. 2005/	
Recommended value Cm(III) sorption						Range 10 <sup>4.2</sup> –10 <sup>6.3</sup> Best estimate 10 <sup>4.3</sup>	
<b>Ac</b>				No			
Ac(III)	MX-80 in solution. Not specific colloid fractions	7	~0.03		Anoxic and red	10 <sup>3.6</sup>	/Grambow et al. 2006/
	however performed in such a way that it is colloid sorption observed.	8		10 <sup>4.4</sup>		/Grambow et al. 2006/	
	Sorption between pH 2–11.	9		10 <sup>5.4</sup>		/Grambow et al. 2006/	
	Kunipiel bentonite (Na-bentonite). Used bulkbentonite.	10.1	DI (21°C)	No		A 5.4·10 <sup>4</sup> B 5.8·10 <sup>4</sup> C 9.4·10 <sup>4</sup>	/Baston et al. 1999/
	Centrifuged the solution before analyzing and filtered through 450 nm and 10,000 MW filter.	10.1	DI (21°C)			A 3.4·10 <sup>4</sup> B 5.9·10 <sup>4</sup> C 13·10 <sup>4</sup>	/Baston et al. 1999/
		9.4	DI (60°C)			A 1.1×10 <sup>4</sup> B 3.1·10 <sup>4</sup> C 16·10 <sup>4</sup>	/Baston et al. 1999/
		9.4	DI (60°C)			A 2.1·10 <sup>3</sup> B 5.0·10 <sup>4</sup> C 9.3·10 <sup>4</sup>	/Baston et al. 1999/
Recommended value Ac(III) sorption						Range (20°C) 10 <sup>3.6</sup> –10 <sup>5.4</sup> Best estimate (20°C) 10 <sup>4.8</sup>	
<b>Pb</b>				Yes			
Pb(II)	MX-80 in solution. Not specific colloid fractions	7	~0.03		Anoxic and red	~10 <sup>4.0</sup> (taken from plot)	/Grambow et al. 2006/
	however performed in such a way that it is colloid sorption observed.	8		~10 <sup>4.5</sup> (taken from plot)		/Grambow et al. 2006/	
	Sorption between pH 2–11.	9		~10 <sup>5</sup> (taken from plot)		/Grambow et al. 2006/	
Recommended value Pb(II) sorption						Range 10 <sup>4</sup> –10 <sup>5</sup> Best estimate 10 <sup>4.7</sup>	

Elements	Colloid	pH	IS (M)	Redox sensitive	Eh	K <sub>d</sub> -value (cm <sup>3</sup> /g)	Reference
<b>Ra, Sr</b> (used as analog for Ra)				No			
Ra(II) (Sr(II))	Natural groundwater colloids. Size distribution 40–1,000 nm.	9.6	0.001			0.6·10 <sup>3</sup>	/Viłks and Degueudre 1991/
	Natural groundwater colloids. mainly organic. Size distribution 1–450 nm.	8.3	0.013			4.4·10 <sup>2</sup> –1.2·10 <sup>3</sup>	/Viłks and Baik 2001/
	Na- montmorillonite colloids from Avanlea bentonite. Two mixed size fractions with mean sizes 54 to 310 nm.	8.3	0.013			1.2·10 <sup>4</sup>	/Viłks and Baik 2001/
Recommended value Ra(II) sorption						Range –only one value from montmorillonite Best estimate 10 <sup>4.1</sup>	
<b>Tc</b>				Yes			
Tc(IV)	MX-80 in solution. Not specific colloid fractions however performed in such a way that it is colloid sorption observed.	7	~0.03		Anoxic and red	10 <sup>4</sup>	/Grambow et al. 2006/
	Sorption between pH 2–11	8				10 <sup>4.2</sup>	/Grambow et al. 2006/
		9				10 <sup>3.8</sup>	/Grambow et al. 2006/
Recommended value Tc(IV) sorption						Range 10 <sup>3.8</sup> –10 <sup>4.2</sup> Best estimate 10 <sup>4</sup>	
<b>Cs</b>				No			
Cs(I)	Febex. Ca-montmorillonite. mean size 200–250 nm.	9.2–9.6	0.001		Anaerobic	10 <sup>3.94</sup>	/Geckeis et al. 2004/
Cs(I)	Febex. Ca-montmorillonite. mean size 250 ± 50 nm.	9.5	0.001		Anaerobic Eh (–200 mV)	10 <sup>3.94</sup>	/Missana et al. 2004/
Cs(I)	MX-80 in solution. Not specific colloid fractions, however performed in such a way that it is colloid sorption observed.	7–9?	~0.03		Anoxic and red	~10 <sup>2.5</sup> (taken from plot) ~10 <sup>2.2</sup> (taken from plot)	/Grambow et al. 2006/
Recommended value Cs(I) sorption						Range 10 <sup>2.2</sup> –10 <sup>3.94</sup> Best estimate 10 <sup>3.7</sup>	
<b>Zr</b>				No			
Zr(OH) <sub>3</sub> <sup>+</sup>	MX-80 in solution. Not specific colloid fractions, however performed in such a way that it is colloid sorption observed.	8	~0.05		Anoxic and red	10 <sup>6.7</sup> Large spread in the data set. At pH 8 values from 10 <sup>4.3</sup> –10 <sup>8</sup>	/Grambow et al. 2006/
Recommended value Zr(IV) sorption						Range 10 <sup>4.3</sup> –10 <sup>8</sup> 10 <sup>6.7</sup> – Best estimate	
<b>Ni</b>				No			
Ni(II)	MX-80 in solution. Not specific colloid fractions, however performed in such a way that it is colloid sorption observed.	8	0.03 pH 8 and pH 9 (experimental data from pH 3–11)		Anoxic and red	10 <sup>3.8</sup> (pH 8) 10 <sup>4.2</sup> (pH 9)	/Grambow et al. 2006/

Elements	Colloid	pH	IS (M)	Redox sensitive	Eh	K <sub>d</sub> -value (cm <sup>3</sup> /g)	Reference
Recommended value Ni (II) sorption						Range 10 <sup>3.8</sup> –10 <sup>4.2</sup> Best estimate 10 <sup>4.0</sup>	
<b>U</b>				Yes			
U(IV)	MX-80 in solution. Not specific colloid fractions, however performed in such a way that it is colloid sorption observed.	8			Anoxic and red	10 <sup>4.5</sup> (pH 8) 10 <sup>4</sup> (pH 9)	/Grambow et al. 2006/
Recommended value U(IV) sorption						Range 10 <sup>4</sup> –10 <sup>4.5</sup> Best estimate 10 <sup>4.3</sup>	
U(VI)	Febex. Ca-montmorillonite. mean size 250 ± 50 nm.	9.5	0.001		Anaerobic Eh (–200 mV)	10 <sup>2.91–3.21</sup> *CaCO <sub>3</sub> 19.5–23.6	/Missana et al. 2004/
U(VI)	Febex. Ca-montmorillonite. mean size 200–250 nm.	9.2–9.6	0.001		10 <sup>2.91</sup>	10 <sup>2.91</sup>	/Geckeis et al. 2004/
Recommended value U(VI) sorption						Range 10 <sup>2.91–3.21</sup> Best estimate 10 <sup>2.91</sup>	
<b>Sn</b>				Yes			
Sn(IV)	Na-smectite		0.1			10 <sup>5.6</sup>	/Bradbury and Baeyens 2004/
	No information					Range – Best estimate 10 <sup>5.6</sup>	
<b>Se</b>				Yes			
Se						Selenium would exist as SeO <sub>3</sub> <sup>2-</sup> or SeO <sub>4</sub> <sup>2-</sup> and the sorption is therefore low.	
<b>Pd</b>						See Ni(II)	Based on the oxidation state and that Pd is a transition metal it seems reasonable to assume the same sorption mechanism and the same K <sub>d</sub> for Pd(II) as Ni(II).
Recommended value Pd(II) sorption						Range 10 <sup>3.8</sup> –10 <sup>4.2</sup> Best estimate 10 <sup>4.0</sup>	
<b>Nb</b>						See Pu(V)	Based on the oxidation state it seems reasonable to assume the same sorption mechanism and the same K <sub>d</sub> for Nb(V) as Pu(V).
Recommended value Nb(V) sorption						Range 10 <sup>5.58</sup> –10 <sup>5.81</sup> Best estimate 10 <sup>5.7</sup>	

## 5 Sorption kinetics data from the literature

The  $K_d$ -values for elements on colloids only represent the distribution of elements between liquid and solid phase but reveals no information on the sensitivity of the system. A high  $K_d$ -value represents a higher tendency for the element to coordinate to the surface than to be out in the solution. It does not give any information how strong the bond/interaction with the surface is and how easy it can be released if the conditions in the surroundings change. For colloids to be able to facilitate the transport of the prioritized elements, fast and strong sorption and slow desorption is the prerequisite, and therefore the kinetics, rate constants for sorption and desorption are needed. In general terms, surface complexation is considered as strong sorption, and cation exchange as weaker sorption since in surface complexation chemical bonds are formed and in cation exchange the cations are bound to the surface by weaker electrostatic forces. Also, the elements sorbing by surface complexation have a higher preference to mineral surfaces than elements sorbing by cation exchange. Elements with higher oxidation states than (II) have a tendency to sorb by surface complexation. Desorption data are often just available for one point in time. If sorption/desorption tests have reached equilibrium, and the surface of the sorbent have been in excess to the sorbent, the  $K_d$ -value is directly related to the rate sorption and desorption rate through:

$$K_d = (k_2/k_{-1}) (\text{conc}^{-1}) \quad (5-1)$$

$k_2$  sorption rate constant ( $\text{conc}^{-1}\text{time}^{-1}$  when applying second order kinetics)

$k_{-1}$  desorption rate constant ( $\text{time}^{-1}$  when applying first order kinetics )

Knowing the  $K_d$ -value gives the relation between the rate constant for sorption and desorption. Since the time to reach sorption equilibrium is roughly known and the solid to volume ratio ( $\text{conc}$ ) given,  $k_2$  can be estimated by multiplying  $\text{conc}^{-1}$  and  $\text{time}^{-1}$  and the  $k_{-1}$  will fall out from the above equation when the  $K_d$  is known. In theory the second order rate constant should not vary with solid to volume ratio, however they sometimes do reflecting the difficulty to perform an accurate experiment. This way of deriving the rate constants is very approximate and gives high uncertainties that will be attached to the rate constants. However, it gives an idea on the magnitudes of the sorption and desorption rates.

Note that unless otherwise stated experimental conditions for the tests can be found in the table of  $K_d$ -values (Table 4-1).

### ***Pu(IV, V)***

Pu(IV) and Pu(V) are sorbing to clay colloids by surface complexation with high  $K_d$ -values. The sorption of Pu(IV) and Pu(V) is fast and the desorption considerably slower.

The desorption tests were performed by separating the colloids in the end of the sorption tests by centrifuging the suspensions. Then the colloids were contacted again with Pu-free water. These data demonstrate that the sorption rate is much faster than the desorption rate, however, the data set is too small to calculate sorption and desorption rates directly.

From the sorption and desorption data /Lu et al. 1998/ sorption and desorption rate values can be derived if assuming that sorption equilibrium is reached in 96.7 hours. Still, the rates have to be seen as rough estimates since the kinetic analysis is performed on only three observations.

**Table 5-1. Sorption and desorption of Pu(V) over time /Lu et al. 2003/.**

Time (h)	% sorbed	Time(d)	% RN desorbed fraction
4	4–7	1	11–13
476	68–79	32	15–19
489	68–79	293	20–21

**Table 5-2. Sorption and desorption of Pu over time in two different types of groundwater.**

Element	Time (h)	% sorbed	Time (days)	% desorbed
<b>Pu(V)</b>	8.3	70	2	0.16
<b>pH 8.2</b>	16.7	80	15	0.33
	33.3	85	50	0.44
	96.7	90	86	0.53
			107	0.60
			128	0.68
			150	0.74
<b>Pu(V)</b>	8.3	72	2	0.45
<b>pH 8.5</b>	16.7	82	15	0.64
	33.3	90	50	0.91
	96.7	97	86	1.02
			107	1.13
			128	1.28
			150	1.42

Estimated rate constants for the two cases when colloid concentration, i.e S/V-ratio is 0.2 g/l.

**Pu(V) pH 8.2**

$$k_2 \sim 263 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 4 \cdot 10^{-4} \text{ h}^{-1}$$

**Pu(V) pH 8.5**

$$k_2 \sim 247 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 6 \cdot 10^{-4} \text{ h}^{-1}$$

For sorption of Pu(IV) a rough estimation has been performed with a  $K_d$ -value and solid to volume ratio from /Geckeis et al. 2004/.

**Pu(IV) pH 9.6**

$$k_2 \sim 435 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 4.35 \cdot 10^{-3} \text{ h}^{-1}$$

### **Th(IV)**

No relevant kinetic data found in the literature. Th is expected to sorb by surface complexation and the reversibility is therefore low. A rough estimation of the sorption rate ( $k_1$ ) and desorption rate ( $k_{-1}$ ) is performed through the listed  $K_d$ -value of  $10^5 \text{ cm}^3/\text{g}$ . An often used solid to volume ratio in sorption experiment is 1:200, and sorption equilibrium is reached very fast in maybe 1 hour.

$$k_2 \sim 200 \text{ h}^{-1} \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 2 \cdot 10^{-3} \text{ h}^{-1}$$

### **Am(III)**

No accurate kinetic analysis can be performed since there are not complete data sets available. However, a rough estimation is performed from  $K_d$ -values for Am matching with the recommended value  $10^6 \text{ g}/\text{cm}^3$  /Geckeis et al. 2004/. With a  $K_d$ -value of  $2 \cdot 10^6 \text{ g}/\text{cm}^3$  and a solid to volume ratio of 2.3g/l the rough estimations of rate constants were obtained.

$$k_2 \sim 435 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 2 \cdot 10^{-3} \text{ h}^{-1}$$

Eu(III) can be seen as an analogue to Am(III) and was shown to irreversibly sorb to  $\text{Al}_2\text{O}_3$  on 100–200  $\mu\text{m}$  particles at pH 5. Am is sorbing by surface complexation to montmorillonite colloids and the reversibility is very slow. /Xu et al. 2005/.

No data were found on Pa sorption kinetics in the literature whereas a rough estimation of the rate constants has been performed with the  $K_d$ -value  $1 \cdot 10^5 \text{cm}^3/\text{g}$  and solid to volume ratio 1:200.

$$k_2 \sim 20 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 2 \cdot 10^{-6} \text{ h}^{-1}$$

### **Np(V)**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Rough estimates are performed from  $K_d$ -values and solid to volume ratios. Np(V)  $K_d$ -value and solid to volume ratio from /Geckeis et al. 2004/.

$$k_2 \sim 435 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 4.35 \cdot 10^{-1} \text{ h}^{-1}$$

### **Np (IV)**

$K_d$ -value and solid to volume ratio from /Nagasaki et al. 1999/

$$k_2 \sim 1.0 \cdot 10^{-2} \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 4.610^{-7} \text{ h}^{-1}$$

### **Cm(III)**

No data were found on Cm sorption kinetics in the literature. Rough estimations on rate constants have been performed on data from /Grambow et al. 2006/ at pH 8.

$$k_2 \sim 100 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 6 \cdot 10^{-3} \text{ h}^{-1}$$

### **Ac(III)**

No data were found on Ac sorption kinetics in the literature. Rough estimations on rate constants have been performed on data from /Grambow et al. 2006/ (1) and /Baston et al. 1999/ (2).

1. pH 8

$$k_2 \sim 100 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 6 \cdot 10^{-3} \text{ h}^{-1}$$

2. pH 10.1, 21°C

$$k_2 \sim 20 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 3.7 \cdot 10^{-4} \text{ h}^{-1}$$

### **Pb(II)**

No information on solid to volume ratio is given in /Grambow et al. 2006/, whereas the assumption is made that 1 g/l was used. The rate constants derived are:

$$k_2 \sim 200 \text{ h}^{-1} \text{cm}^3 \text{g}^{-1}$$

$$k_{-1} \sim 6 \cdot 10^{-3} \text{ h}^{-1}$$

### **Ra(II)**

No data were found on Ra sorption kinetics in the literature and data for Sr were used since Sr is an analogue of Ra (Table 5-3).

For Sr there is faster sorption and slower desorption on Ca-bentonite than on Na-bentonite. Sorption tests were carried out in three types of groundwater (Table 5-3) with < 1,000 nm Ca-bentonite. After 1 h. 91–98% sorbed and then remained constant.



**Table 5-3. Desorption of Sr from Ca-bentonite under different conditions.**

Time (days)	Water 1	Water 2	Water 3
10	3.8	0.6	0.1
30	6.8	1.2	0.4
60	10.2	1.8	0.7
90	16.5	2.9	1.1

**Table 5-4. Water conditions in the Sr tests.**

Water	1	2	3
pH	7.8	8.0	8.0
Ca <sup>2+</sup> (ppm)	78.2	13.3	< 0.01
Na <sup>+</sup> (ppm)	156	46	< 0.01

/Abd El-Rahman et al. 2006/

Sr and presumably also Ra sorb by cationic exchange and are very sensitive to changes in the surrounding environment. No data were found on Sr and montmorillonite sorption kinetics in the literature. Rough estimations on rate constants have been performed on data from /Vilks and Degueldre 1991/.

Rough rate constants derived are:

$$k_2 \sim 333 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 0.03 \cdot 10^{-3} \text{ h}^{-1}$$

#### **Tc(IV)**

Tc sorbs strongly by surface complexation under reducing conditions, however under oxidizing conditions the Tc is most probable more mobile. No data were found on Tc(IV) sorption kinetics in the literature and rough estimations were therefore calculated from sorption data from /Grambow et al. 2006/. The solid to volume ratio varied in the experiment why two sets of rate constants are derived with the highest and the lowest solid to volume ratios used in the experiments.

$$k_2 \sim 2.5 \cdot 10^5 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.004 g/l)}$$

$$k_{-1} \sim 15 \text{ h}^{-1}$$

$$k_2 \sim 1 \cdot 10^4 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.1 g/l)}$$

$$k_{-1} \sim 0.63 \text{ h}^{-1}$$

#### **Cs(I)**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Rough estimates are performed from  $K_d$ -values and solid to volume ratios.

$K_d$ -value and solid to volume ratio from /Geckeis et al. 2004/.

$$k_2 \sim 435 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 0.05 \text{ h}^{-1}$$

Desorption of Cs from Febex bentonite has been performed where the  $K_d$ -values increased, which is interpreted as that the sorption is not completely reversible. Since Cs is sorbed by cation exchange, an increase in ionic strength will give a decrease of Cs sorbing to the montmorillonite surfaces.

$K_d$ -value and solid to volume ratio (2g/l) from /Missana et al. 2004/.

$$k_2 \sim 500 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 0.06 \text{ h}^{-1}$$

$K_d$ -value and solid to volume ratio from /Grambow et al. 2006/.

$$k_2 \sim 2,000 \text{ h}^{-1} \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.5 g/l)}$$

$$k_{-1} \sim 6.3 \text{ h}^{-1}$$

$$k_2 \sim 250 \text{ h}^{-1} \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 4 g/l)}$$

$$k_{-1} \sim 0.8 \text{ h}^{-1}$$

### **Zr(IV)**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Rough estimates are performed from  $K_d$ -values and solid to volume ratios.

$K_d$ -value and solid to volume ratio from /Grambow et al. 2006/.

$$k_2 \sim 10^7 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.01 g/l)}$$

$$k_{-1} \sim 2 \text{ h}^{-1}$$

$$k_2 \sim 10^6 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.1 g/l)}$$

$$k_{-1} \sim 0.2 \text{ h}^{-1}$$

### **Ni(II)**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Rough estimates are performed from  $K_d$ -values and solid to volume ratios.

$K_d$ -value and solid to volume ratio from /Grambow et al. 2006/.

$$k_2 \sim 2,000 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.5 g/l)}$$

$$k_{-1} \sim 0.2 \text{ h}^{-1}$$

$$k_2 \sim 250 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 4 g/l)}$$

$$k_{-1} \sim 0.025 \text{ h}^{-1}$$

### **U(IV,VI)**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Rough estimates are performed from  $K_d$ -values and solid to volume ratios.

$K_d$ -value and solid to volume ratio from /Grambow et al. 2006/.

### **U(IV)**

$$k_2 \sim 3 \cdot 10^5 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.004 g/l)}$$

$$k_{-1} \sim 17 \text{ h}^{-1}$$

$$k_2 \sim 1 \cdot 10^4 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1} \text{ (S/V 0.1 g/l)}$$

$$k_{-1} \sim 0.5 \text{ h}^{-1}$$

$K_d$ -value and solid to volume ratio (2 g/l) from /Missana et al. 2004/

### **U(VI)**

$$k_2 \sim 3 \text{ h}^{-1} \text{ cm}^3 \text{ g}^{-1}$$

$$k_{-1} \sim 0.003 \text{ h}^{-1}$$

### **Sn(IV)**

No accurate kinetic analysis could be performed since no complete sorption data sets are found in literature.

**Se**

No accurate kinetic analysis could be performed since complete sorption data sets are not found in literature. Selenium would most plausibly as  $\text{SeO}_3^{2-}$  or  $\text{SeO}_4^{2-}$  or selenat and the sorption as anion will be small.

***Pd(II)***

No accurate kinetic analysis could be performed since no sorption data sets are found in literature. Ni(II) can be seen as an analog for Pd(II)

***Nb(V)***

No accurate kinetic analysis could be performed since no sorption data sets are found in literature. Pu(V) can be seen as an analog for Nb(V).

Note that these estimated rate constants for the elements are only rough estimates and a very large uncertainty is attached to these values.

## 6 Concluding remarks

This compilation clearly demonstrates that there is a lack of accurate data on RN sorption to colloids (in particular montmorillonite colloids). It is obvious that the  $K_d$ -values for RN sorbing to colloids should be normalized to specific surface area, and not to mass since the number of colloids greatly differ in a certain mass if the colloids are large or if they are small. A way to get around that would be to specify exactly which size ranges of colloids were used in the sorption experiments, however the size distributions are instead often not well defined or very wide. Further, to see if the sorption actually has reached equilibrium and how fast equilibrium is reached, more precise experiments are needed as well as desorption experiments as such. Kinetic data are just not available. In spite of the fact that there are a lot of pitfalls in the way to get these data, colloid sorption has to be looked upon in a more precise way to really be able to predict how the colloids can affect RN transport in a deep geological repository.

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