



Working Report 2008-29

# Silica Colloids and their Effect on Radionuclide Sorption – A Literature Review

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# **SILICA COLLOIDS AND THEIR EFFECT ON RADIONUCLIDE SORPTION – A LITERATURE REVIEW**

## **ABSTRACT**

Silica sol, commercial colloidal silica manufactured by Eka Chemicals in Bohus, Sweden is a promising inorganic grout material for sealing small fractures in low permeable rock. This literature review collects information about the use of silica sol as an injection grout material, the properties of inorganic, especially silica colloids, colloid contents in granitic groundwater conditions, essential characterization methods and colloid-mediated transport of radionuclides. Objective was to evaluate the release and mobility of silica sol colloids, the effect of the groundwater conditions, the amount of colloids compared with natural colloids in Olkiluoto conditions, radionuclide sorption on colloids and their contribution to radionuclide transport.

Silica sol seems to be a feasible material to seal fractures with an aperture as small as 10 µm in low permeable rock. The silica sol gel is sufficiently stable to limit to water ingress during the operational phase, the requirement that the pH should be below 11 is fulfilled and the compatibility with Engineered Barrier System (EBS) materials is expected to be good. No significant influence on the bentonite properties caused by the silica sol is expected when calcium chloride is used as an accelerator but the influence of sodium chloride has not been examined. No significant release of colloids is expected under prevailing groundwater conditions. The long-term (100 y) stability of silica sol gel has not yet been clearly demonstrated and a long-term release of silica colloids cannot be excluded. The question is the amount of colloids, how mobile they are and the influence of possible glacial melt waters.

The bentonite buffer used in the EBS system is assumed to be a potential source of colloids. In a study in Olkiluoto, bentonite colloids were found only in low salinity groundwater. In general, low salinity water (total dissolved solids < 1 g·L<sup>-1</sup>) favours colloid stability and bentonite colloids can remain stable over long periods. Many techniques and innovative approaches are being applied to give an answer to the question of colloid relevance in a repository system. Several studies have evidenced radionuclide especially actinide sorption on colloids and the mobility of radiocolloids. The main uncertainties remain in the colloidal processes at the bentonite–granite interface, the quantification of colloid generation under realistic repository conditions and establishing a colloid-source term. The synergy of bentonite, organic and inorganic colloids are still unclear. This literature survey on silica sol colloids will be followed-up with experimental studies in order to determine colloid release from silica sol gel, to follow the mobility and stability of silica colloids in groundwater simulates and to study radionuclide sorption on silica colloids.

**Keywords:** Silica sol, inorganic colloids, colloid characterization, radionuclide sorption, migration, granitic groundwater

# SILIKA KOLLOIDIT JA NIIDEN VAIKUTUS RADIONUKLIDIEN SORPTIOON – KIRJALLISUUSSELVITYS

## TIIVISTELMÄ

Silika sooli eli kolloidinen silika on kaupallinen (Eka Chemicals, Bohus, Ruotsi) erittäin pienten kalliorakojen täytteeksi sopiva injektointiaine. Tässä kirjallisuusselvityksessä on koottu yhteen saatavilla oleva tieto silika soolin käytöstä injektioaineena, tieto epäorgaanisista kolloideista erityisesti piikolloideista, kolloidien määrästä graniittisen kallion pohjavesissä, tärkeimmistä kolloidien karakterisointimenetelmistä ja kolloideihin kiinnittyneiden radionuklidien kulkeutumisesta. Tavoitteena oli arvioida piikolloidien muodostumista silika soolista, kolloidien stabiilisuutta, pohjavesiolosuhteiden vaikutusta, piikolloidien määrää verrattuna Olkiluodon luontaisiin kolloideihin, radionuklidien sorptiota kolloideihin sekä osuutta radionuklidien kulkeutumiseen.

Silika sooli on käyttökelpoinen aine kallioperän pienten rakojen sulkemiseen, jopa avaumaltaan 10 µm:n rakoihin asti. Geelitynyt silika sooli on riittävän stabiilia rajoittamaan veden tunkeutumista tunneliin rakennusvaiheessa. Vaatimus että  $\text{pH} < 11$  täytyy ja aineen arvioidaan olevan yhteensopiva muiden teknisten vapautumisesteiden kanssa. Silika soolin ei odoteta vaikuttavan bentoniitin ominaisuuksiin kun kiihdytinaineena käytetään kalsiumkloridia. Natriumkloridin käytöstä kiihdytinaineena ei ole tutkittua tietoa. Nykyisen kaltaisissa pohjavesiolosuhteissa ei oleteta vapautuvan merkittävästi piikolloideja. Geelityneen silika soolin pitkän ajan (> 100 v.) stabiiliutta ei ole vielä selvästi osoitettu eikä kolloidien vapautumista voida sulkea pois. Epävarmuutena on vapautuneiden kolloidien määrä, niiden liikkuvuus ja mahdollisten jääkauden sulamisvesien vaikutus.

Bentoniittipuskurin oletetaan olevan mahdollinen kolloidien lähde. Olkiluodossa tehdyssä kokeessa, jossa testattiin kolloidien mahdollista vapautumista bentoniitista pohjavesiolosuhteissa, bentoniittikolloideja löytyi vain vähäsuolaisesta pohjavedestä. Yleisesti tiedetään kolloidien olevan pysyviä vähäsuolaisissa pohjavesissä (kokonais suolapitoisuus  $< 1 \text{ g}\cdot\text{L}^{-1}$ ), joissa bentoniittikolloidit saattavat olla stabiileja pitkiäkin aikoja. Monia teknisiä analyysilaitteita ja uudenlaisia lähestymistapoja on sovellettu yritettäessä selvittää kolloidien merkitystä loppusijoitustilan pitkäaikaisturvallisuuteen. Useat tutkimukset ovat osoittaneet radionuklidien, erityisesti aktinidien kiinnittyvän kolloideihin ja radiokolloidien olevan liikkuvia. Arvioitaessa kolloidien vaikutusta suurimmat epävarmuudet liittyvät bentoniitti–graniitti rajapintaan, muodostuvien kolloidien määrään realistisissa loppusijoitusolosuhteissa ja lähdetestin todentamiseen. Yhteisvaikutusta bentoniittikolloidien, epäorgaanisten ja orgaanisten kolloidien välillä ei tiedetä. Kirjallisuusselvitystä seuraa kokeellinen osuus, jossa selvitetään kolloidien vapautumista geelityneestä silika soolista, seurataan kolloidien stabiiliutta simuloituissa pohjavesissä ja tutkitaan radionuklidien sorptiota piikolloideihin.

**Avainsanat:** Silika sooli, epäorgaaniset kolloidit, piikolloidit, kolloidien karakterisointi, graniittinen pohjavesi, radionuklidit, sorptio, migraatio

## TABLE OF CONTENTS

ABSTRACT

TIIVISTELMÄ

LIST OF ABBREVIATIONS

1	INTRODUCTION .....	5
2	SILICA SOL .....	7
	2.1 Properties of silica sol .....	7
	2.2 Grouting with silica sol .....	8
	2.3 Long-term stability of silica sol .....	8
	2.4 Compatibility with EBS .....	9
3	COLLOIDS .....	11
	3.1 Formation of natural silica colloids .....	11
	3.2 Colloid stability .....	12
	3.2.1 DLVO theory .....	12
	3.2.2 Zeta potential .....	13
	3.3 Colloid mobility .....	15
4	COLLOID CHARACTERIZATION METHODS .....	17
	4.1 Colloid separation .....	17
	4.2 Chemical characterization .....	17
	4.3 Concentration .....	19
	4.4 Zeta potential .....	20
	4.5 Size and shape .....	20
	4.5.1 Laser light methods .....	20
	4.5.2 Microscopic Techniques (SEM, FESEM, TEM, AFM) .....	23
	4.6 Comparison of methods .....	24
5	COLLOIDS IN GEOLOGICAL DISPOSAL OF SPENT NUCLEAR FUEL .....	27
	5.1 Finland .....	27
	5.2 Sweden .....	29
	5.3 Switzerland .....	30
	5.4 Canada .....	30
6	COLLOIDS FROM SILICA SOL GEL .....	31
7	COLLOID-MEDIATED RADIONUCLIDE MIGRATION .....	33
	7.1 Colloid interaction with rock surfaces .....	34
	7.2 Colloid diffusion within the rock matrix .....	35
	7.3 Radionuclide sorption onto colloids .....	36
	7.4 Colloid transport .....	37
8	CONCLUSIONS .....	41
	REFERENCES .....	43



## LIST OF ABBREVIATIONS

AFM	Atomic force microscopy
CFM	Colloid Formation and Migration project in GTS
CRR	Colloid and Radionuclide Retardation Experiment in GTS
$d_h$	A hydrodynamic diameter (equivalent sphere diameter)
DLVO	Theory that describe colloid stability and agglomeration rates
EBS	Engineered Barrier System
EDL	Electric double layer
EDS, EDX	Energy-dispersive X-ray spectroscopy
FFFF	Flow field-flow fractionation
FEBEX	Full-scale Engineered Barrier Experiment in GTS
FUNMIG	Fundamental Processes of Radionuclide Migration
GTS	Grimsel Test Site
IC	Ion chromatography
ICP–AES	Inductively coupled plasma atomic emission spectroscopy
ICP–MS	Inductively coupled plasma mass spectroscopy
LIBD	Laser-induced breakdown detection
LLS	Laser light scattering
PCS	Photon correlation spectroscopy
RBS	Rutherford Backscattering Spectrometry
SEM	Scanning electron microscopy
SPC	Single particle counting
TOC	Total organic carbon
TRLIF, TRIFS	Time-resolved laser-induced fluorescence spectroscopy
WDXRF, WDS	Wavelength dispersive X-ray spectroscopy
XRD	X-ray diffractometry





## 1 INTRODUCTION

Cement is predominantly used for permeation grouting in hard rock. However, cement leachate has a high pH value mainly due to leaching of portlandite ( $\text{Ca}(\text{OH})_2$ ), which can be harmful for the EBS system in a repository for spent fuel. Limitation in penetrability for cement-based grouts makes them also less suitable in low permeable rock. In situations where large reduction of the water leakage is required, cement cannot always seal efficiently enough to fulfil the requirements. The minimum fracture aperture that cement can penetrate is around 50–100  $\mu\text{m}$  (Emmelin et al. 2004, Axelsson 2006) and at the planned repository depth, -420 m, in granitic bedrock (Posiva 2006a) it is likely that smaller fractures need to be sealed. The primary requirements for the injection grout is that it should be able to sufficiently seal small fractures, and that the pH of the pore water released from the grout should be less than pH 11 in order to preclude serious deterioration of the basic required properties of bentonite (Boden and Sievänen 2005). A promising non-cementitious inorganic grout material for sealing fractures of apertures of 0.05 mm or less is silica sol. Silica sol<sup>1</sup> is commercial colloidal silica manufactured by Eka Chemicals in Bohus, Sweden (EKA Chemicals). Posiva and SKB have made a preliminary study of silica sol as an injection grout for deep repositories (Boden and Sievänen 2005, Torstenfelt et al. 2005).

In this literature review existing information about inorganic colloids especially silica colloid generation and effects of water properties on silica colloid stability in groundwater as well as radionuclide sorption on colloids are collected. Also essential analytical methods for future experimental work are collected. Objective of the following experimental work is to study the possible release of colloids from silica sol gel and the amount of colloids compared with natural colloids in Olkiluoto conditions. The mobility of released colloids and radionuclide sorption on colloids and effect of colloids on radionuclide transport will be also determined.

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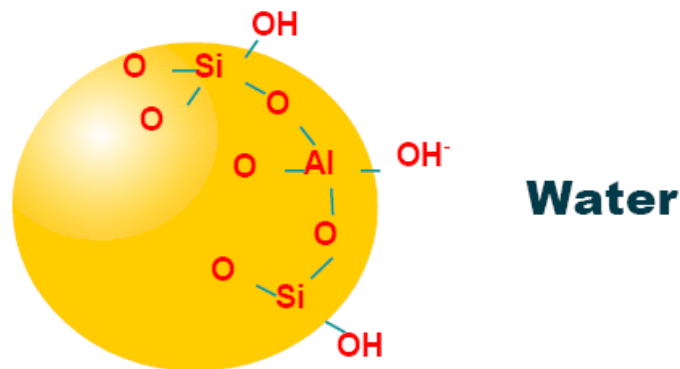
<sup>1</sup> Silica sol is a suspension of silica particles, when a sol is mixed with an accelerator, the particles aggregates and forms a solid gel called here silica sol gel.



## 2 SILICA SOL

### 2.1 Properties of silica sol

Grout consists of a sol of colloidal silica and a salt solution called accelerator. Silica sol is a stable suspension of amorphous particles of silica [ $\text{SiO}_2$ ], which builds randomly distributed [ $\text{SiO}_4$ ]<sup>4-</sup> tetrahedral (Iler 1979). A schematic presentation of silica sol (Eka GEL EXP 36) is given in Figure 2-1. The particles have hydroxylated surfaces, which are insoluble in water. Colloidal silica is manufactured from raw glass heated and diluted with water to make a liquid, and to form water glass, sodium silicate. The colloidal particle size is normally 5–100 nm, and the pH of the solution is 9–11. The viscosity of the sol is similar to water. To use silica sol as a grout, the particles have to aggregate and form a gel within a predictable time. This is done with different kinds of saline solutions; the most common are NaCl and  $\text{CaCl}_2$ . Adding more salt causes quicker gelling. The concentration of the accelerator depends on the properties of the bedrock to be stabilized as groundwater flow, water temperature, salinity of the surrounding water, etc. and on the time required for the sol to gel. Higher salt concentration and temperature result in a shorter gelling time for the sol. When using sodium chloride the concentration of the accelerator solution is normally around 10%. Depending on the conditions when silica sol starts to aggregate, a network made up of the silica particles forms and the water that is present in the sol becomes trapped inside the network. Depending on the ambient temperature, pressure and moisture to which the silica sol is exposed, the trapped water is eventually emitted. In the test at the Äspö Hard Rock Laboratory (Torstenfelt et al. 2005), calcium chloride [ $\text{CaCl}_2$ ] was used as the accelerator instead of sodium chloride as the total chloride concentration will be decreased by about 75% in the gel compared to the sodium chloride accelerator. In evaluation tests for colloidal silica grouted sands performed by Persoff et al. (1999) at Lawrence Berkeley National Laboratory, 5 parts of colloidal silica and 1 part 0.24 M (ca. 2.5%)  $\text{CaCl}_2$ -accelerator was used. The silica sol and NaCl accelerator proposed to be used by Posiva has the brand name “MEYCO<sup>®</sup> MP320” (EKA Chemicals).



**Figure 2-1.** Schematic figure of the silica sol Eka Gel EXP36 (Torstenfelt et al. 2005).

## 2.2 Grouting with silica sol

Silica sol has been studied by Axelsson (2006), Funehag and Fransson (2006) and Funehag and Gustafson (2008a, 2008b). These studies show that silica sol can penetrate fractures with an aperture of at least 10  $\mu\text{m}$ . Silica sol (Cembinder U22) was used as injection grout in some experiments in the Hallandsås, Sweden. The results showed that colloidal silica is feasible as a sealing material for fractures as small as 9  $\mu\text{m}$ . The non-grouted rock had a median inflow of 70  $\text{L}\cdot\text{min}^{-1}$ , when grouted with cement inflow was reduced to 2  $\text{L}\cdot\text{min}^{-1}$  and after grouted with silica sol the water inflow was further reduced to 0.2  $\text{L}\cdot\text{min}^{-1}$ . The hydraulic conductivity was reduced from  $3.0\cdot 10^{-6} \text{ m}\cdot\text{s}^{-1}$  for the non-grouted to  $5.0\cdot 10^{-8} \text{ m}\cdot\text{s}^{-1}$  for the cement grouted, down to  $1.1\cdot 10^{-9} \text{ m}\cdot\text{s}^{-1}$  for the silica sol grouted rock mass. This can be compared to sparsely fractured deep rock where a hydraulic conductivity of  $10^{-9}$  to  $10^{-10} \text{ m}\cdot\text{s}^{-1}$  or less is not uncommon. Although these tests were preliminary they demonstrated that silica sol can be used to seal fractures to low conductivity.

Lin (2006) has studied colloidal silica transport mechanisms for the passive site stabilization of liquefaction soils. The purpose of the study was to determine whether colloidal silica grout could be delivered uniformly over long distances in an adequate concentration to stabilize the sand, to understand the mechanisms of colloidal silica transport through liquefiable sands, and to evaluate numerical modelling methods for simulating colloidal silica transport in the subsurface. Column tests were performed to investigate variables affecting colloid transport, including the pH and ionic strength of the colloidal mixtures, viscosity and gelling behaviour of colloidal silica, the flow rate of the fluid and the type of the liquefiable media. Samples of the treated soils recovered from the column tests after the colloidal silica gelled were tested for unconfined compressive strength. A numerical modelling of colloidal silica transport through the soil column was also evaluated. Column tests showed that viscosity was the most important factor governing transport of gelling colloidal silica grouts in saturated porous media. Colloidal silica could be delivered throughout the 0.9 m, 3 m and 9 m columns in an adequate concentration as long as the viscosity remained low during injection. The ionic strength and pH affect the transport of gelling colloidal silica grouts because they influence the gelling time and hence the viscosity of the grout. The hydraulic gradient and hydraulic conductivity of the porous media influenced the transport rate of colloidal silica grouts, but not as significantly as viscosity. Column tests also showed that normalized chloride concentration is an excellent indicator of the percentage of colloidal silica in solution.

## 2.3 Long-term stability of silica sol

The compressive strength of silica sol gel increases over time. Experiments have shown that the compressive strength increased for up to about 3 years from around 0.35 MPa directly after gelling to 1.2 MPa after ca. 3 years stored at 20 °C and 100% relative humidity. At the same time practically no dissolution or changes in permeability were observed. Persoff et al. (1999) observed that samples immersed in water continued to gain strength for one year, but samples immersed in organic solution aniline or water saturated with aniline weakened in strength. For silica sol gel tested in perchloroethylene (PCE), carbon tetrachloride ( $\text{CCl}_4$ ), water saturated with these or mixtures of

these, or in HCl diluted to pH 3, no change in sample strength was observed. The stability of the gel is not expected to be significantly influenced by variations in the groundwater salinity. Possible variations in groundwater salinity would however influence the gelling time, thus, it is important to perform sufficient tests with the correct groundwater salinity prior to applying the silica sol *in situ*. If the gel is dried, the material will be brittle and have low resistance to mechanical movement. If for some reason the gel dries after being applied in the rock, then rock movements would seriously degrade the gel. If a dried undisturbed gel is re-saturated quick tests have shown that it will become even more brittle and fall apart, but this behaviour and how it affects the properties of the gel have yet to be studied (Funehag and Fransson 2006).

## 2.4 Compatibility with EBS

The compatibility of silica sol with cement is expected being good (Torstenfelt et al. 2005). Silica in the form of water glass or as dry powder is used as cement stability enhancing material. Chemical similarity between silica sol and water glass predicts that cement and silica sol will perform well together. With the use of calcium chloride as the accelerator, silica sol will contribute to transferring sodium bentonite to the calcium form. A mixed sodium-calcium bentonite will have different properties than a pure Na-bentonite. The main difference is that the sodium bentonite sorbs a larger amount of interlamellar water than the calcium bentonite. Calcium bentonite is therefore less expandable and feature lower swelling pressures at lower densities (Posiva 2006b). All calcium in the accelerator is available in the silica sol and will be released to the surrounding water at a rate depending on the concentration gradient and the surrounding water flow. The impact of the silica sol calcium compared with calcium in the groundwater and released from concrete is dependent on the proportion of available silica sol, concrete and groundwater. The pH of the pore water released from the silica sol was below 11 at leach tests except for experiments using distilled water, which is an unlikely situation in the field. Thus, the requirement that the pH should be below 11 is fulfilled if silica sol is used. According to Torstenfelt et al. (2005) no other effects caused by the colloidal silica are foreseen to have a significant influence on the bentonite properties. However, in Olkiluoto sodium chloride will be used as an accelerator, which might have influence on bentonite (montmorillonite) erosion.



### 3 COLLOIDS

Colloids are very small particles between 1 nm and 1  $\mu\text{m}$  in diameter. Organic and inorganic colloids are present in natural groundwater but colloids can also be produced from degraded Engineered Barrier System (EBS) materials such as the bentonite clay barrier and copper or steel container. The colloid dimensions of less than 1  $\mu\text{m}$  result in a very high surface-to-volume ratio. Therefore, surface chemistry is very important in the study of colloidal systems. Colloids are usually classified as natural colloids from the fracture filling material, bentonite colloids derived from the EBS, homogeneous radio-colloids ( $\text{PuO}_2$ ) and heterogeneous radio-colloids e.g. radionuclides attached to bentonite colloids (Alonso et al. 2006).

#### 3.1 Formation of natural silica colloids

In natural groundwater silica colloids are formed by dissolution from silica-based minerals. The dissolution kinetics of solid oxides and deposition of dissolved species depend on the surface charge density. The interaction between charged colloidal particles is governed by the diffuse part on the electric double layer (EDL). Vogelsberger et al. (1999) have found dissolution dependence on time, pH and ionic strength when applying the general kinetic dissolution model to experimental data.

Icopini et al. (2005) have studied the silica oligomerization rate in batch reaction experiments utilizing solutions with two ionic strengths of 0.01 M and 0.24 M, between pH 3 and 11. The most rapid oligomerization rate was at near-neutral pH for all ionic strengths. Increasing the initial concentration of silica increased the oligomerization rate although in solution with similar pH and initial silica concentrations, the steady-state concentrations of molybdate-reactive silica were also similar regardless of ionic strength. These results support the interpretation that in some natural solutions, e.g. at low and high pH and at low ionic strength, colloidal silica particles are relatively stable.

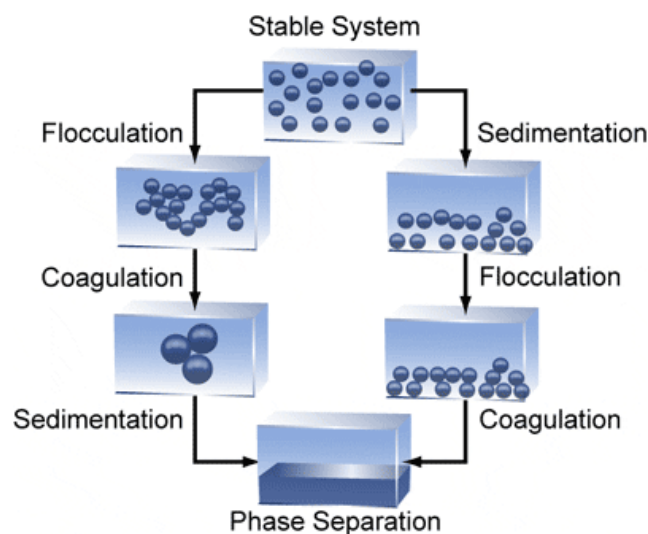
The kinetics of the formation and precipitation of colloidal silica from geologically relevant aqueous solutions was investigated by Conrad et al. (2007). Their work provides the first kinetic models for the appearance and evolution of colloidal silica over time under environmentally relevant conditions. Changes in the rate of formation of silica colloids depended on the degree of supersaturation, ionic strength and pH of the experimental solutions while the stability of the colloidal fraction was largely controlled by the pH of the solution. The results indicate that primary silica nanocolloidal particles appear to be approximately 3 nm in diameter and can account for a large portion, up to 65% of the total silica present in aqueous solutions at low pH (3–4) regardless of ionic strength and at neutral pH in low ionic strength aqueous systems. Larger aggregates of the primary nanocolloids were also observed to range in size from 30 to 40 nm. The results elucidate the environmental conditions under which the colloidal fraction is important and should be considered when investigating the dissolution and precipitation behaviour of silica and silica-based minerals. Characterizing changes in the particle diameter, structure and reactivity of colloidal silica are needed to more accurately and completely understand their impact on geochemical processes in a natural system.

### 3.2 Colloid stability

In a stable colloidal system, the particles resist flocculation or aggregation and exhibit a long being. This will depend upon the balance of the repulsive and attractive forces that exist between particles as they approach one another. The particles in colloidal dispersion may adhere to one another and form aggregates of successively increasing size that may settle out under the influence of gravity. An initially formed aggregate is called a floc and the process of its formation flocculation. If the aggregate changes to a much denser form, it is said to undergo coagulation. An aggregate usually separates out by sedimentation. Usually coagulation is irreversible whereas flocculation can be reversed by the process of deflocculation. Figure 3-1 schematically represents processes involved in a colloidal system.

#### 3.2.1 DLVO theory

Well-known Derjaguin, Landau, Verwey and Overbeek (DLVO) theory (Swanton 1995) suggests that the stability of a colloidal system is determined by the sum of the van der Waals attractive (VA) and electrical double layer repulsive (VR) forces that exist between particles as they approach each other due to the Brownian motion they are undergoing. This theory proposes that an energy barrier resulting from the repulsive force prevents two particles approaching one another and adhering together. If the particles collide with sufficient energy to overcome that barrier, the attractive force will pull them into contact where they adhere strongly and irreversibly together. If the particles have sufficiently high repulsion, the dispersion will resist flocculation and the colloidal system will be stable. However if a repulsion mechanism does not exist then flocculation or coagulation will eventually take place. In high salt concentrations, there is a possibility that a much weaker and potentially reversible adhesion between particles exists together. These weak flocs are sufficiently stable not to be broken up by Brownian motion, but may dissociate under an externally applied force such as vigorous agitation.



**Figure 3-1.** Processes that deal with the stability of colloidal systems by Derjaguin, Landau, Verwey and Overbeek (Malvern Instruments Ltd.).



There are two fundamental mechanisms that affect colloidal dispersion stability. Steric repulsion involves polymers added to the system adsorbing onto the particle surfaces and preventing the particle surfaces coming into close contact. If enough polymers adsorb, the thickness of the coating is sufficient to keep particles separated by steric repulsions between the polymer layers. At those separations the van der Waals forces are too weak to cause the particles to adhere. Electrostatic or charge stabilization is the effect on particle interaction due to the distribution of charged species in the system.

The potential relevance of colloids for radionuclide transport is highly dependent on their stability. DLVO theory basically considers that the interaction between two colloids is governed both by the Van der Waals-type attractive interaction and the repulsive force due to interaction of the double layers of the particles. The DLVO theory is generally applied to describe colloid stability and agglomeration rates, however, it is demonstrated that the application of DLVO models to heterogeneous natural systems has its limitations (Swanton 1995). It was observed that the prediction of bentonite colloid stability by a simple DLVO approach deviates from experimental findings (Missana and Adell 2000). The coagulation kinetics of natural bentonite colloids studied by means of time-resolved light scattering techniques revealed that even though bentonite particles have a high intrinsic negative charge over a wide pH range, their stability behaviour is clearly pH dependent. This is mainly due to the pH dependent charge developed at edge sites. Only at high pH ( $\text{pH} \geq 8$ ) the edge sites are negatively charged and thus impose a high colloidal stability to clay dispersions. It was also shown that a high bivalent cation concentration would decrease bentonite colloidal stability, in agreement with observations found for other natural colloids (Degueudre et al. 1996b, 2000).

In general, low salinity waters ( $<10^{-3}$  M) favoured the stability of bentonite colloids (Missana et al. 2003). It was observed that the bentonite colloids remained stable in waters of low salinity over long periods. To evaluate the stability of colloids under natural conditions it is necessary to conduct site-specific studies over long-term periods. The relevance of salinity on colloid provenance in granite groundwater has been recently confirmed by applying the very sensitive Laser Induced Breakdown Detection technique (LIBD) on-site, e.g., in Forsmark in Sweden (Bergelin et al. 2007).

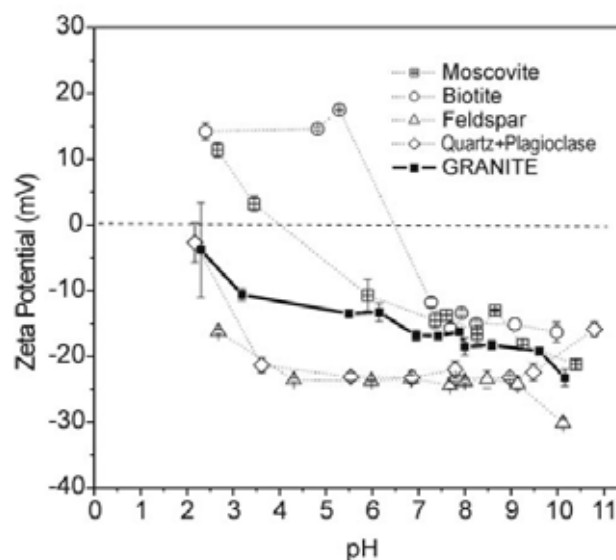
### **3.2.2 Zeta potential**

Zeta potential ( $\zeta$ -potential) is a measure of the magnitude of the repulsion or attraction between particles. It brings detailed insight into the dispersion mechanism and is the key to electrostatic dispersion control. Parameters that determine stability can be identified by measuring zeta potential, particle size, pH and conductivity (Sonnefeld et al. 2001). In order to investigate the role of zeta potential of mineral grains in the initial deposition kinetics of colloidal particles in geochemically heterogeneous porous media, experiments with colloidal silica particles flowing through columns packed with chemically heterogeneous sand were carried out (Elimelech et al. 2000). Chemical heterogeneity was introduced by modifying the surface chemistry of a fraction of the quartz sand grains via reaction with aminosilane. Experimental initial colloid deposition rates and resulting collision efficiencies were compared to theoretical predictions based on the measured average zeta potential of the chemically heterogeneous sand. It was

shown that colloid deposition kinetics are controlled by the degree of patch wise chemical heterogeneity and that use of the measured zeta potential of the granular porous medium in theoretical predictions leads to erroneous results.

The zeta potentials measured for the granite and minerals such as biotite, muscovite, feldspar and a mixture of quartz and plagioclase, are plotted as function of the pH in Figure 3-2. It can be seen that whereas the granite has, on average, a negative surface charge over the whole pH range, the major minerals composing the granite as quartz–plagioclases or feldspars present a similar negative behaviour. However, the micas, such as biotite or muscovite, present a positive charge at  $\text{pH} < 6$ . Considering the colloid sizes ( $< 1 \mu\text{m}$ ), a single particle will not be affected by the average rock surface charge but by the specific charge of a certain mineral (Song and Elimelech 1994, Song and Singh 2005, Song et al. 2004).

In groundwater probed at the Äspö hard rock laboratory, it was found that at ionic strength values  $> 0.2 \text{ mol}\cdot\text{L}^{-1}$ , natural colloid concentrations can drop to very low values ( $< 25 \mu\text{g}\cdot\text{L}^{-1}$ ) (Hauser et al. 2002). Temperature effects in the repository case may affect colloid stability. In the near field of a nuclear repository, the temperature can raise up to  $150 \text{ }^\circ\text{C}$ . It is well known that increasing the temperature promotes colloid aggregation, but a complete understanding of the contributing mechanisms is still lacking, e.g., increases in Brownian motion, variations in surface charge and influences from the temperature dependent electrolyte behaviour (Mohtadi and Rao 1973, Luckham and Rossi 1999). This agglomeration will significantly affect settling rates and transport or retention but quantification will be difficult due to the uncertainties to define the actual temperature at the different locations, in the near field and in the barriers during the time periods after the closure of a spent nuclear fuel repository.



**Figure 3-2.** Z-potential as function of pH measured for granite and for its different minerals and a mixture of quartz–plagioclase (Alonso et al. 2006).

In a FEBEX (Full Scale Barrier Experiment) experiment, where the thermo–hydro–mechanical behaviour of the compacted bentonite barrier was studied *in situ*, it was demonstrated that a temperature gradient develops from 100 °C at the waste form surface, over 85 °C at the canister–bentonite barrier to about 30 °C at the bentonite–granite interface (Missana et al. 2003). In the course of time, temperature gradients can significantly influence not only properties of the bentonite barrier but also the colloid stability and should take into account for the evaluation of the colloid contribution to radionuclide transport in the near field.

### 3.3 Colloid mobility

The colloid mobility is highly dependent on colloid stability in different chemical environments. In crystalline rocks, colloid transport is expected to mainly take place by advection in conductive fractures. Due to surface charge colloid transport is significantly different to that of a solute e.g. colloids have no interactions with the rock surfaces. The colloid mobility and transport is difficult to describe and there are many aspects to be considered such as water flow, geochemical conditions and colloid size distribution. Also the nature of the surrounding rock surfaces and of the colloids interactively determine whether colloids are retained or not within the rock (Saiers et al. 1994, Yan et al. 1995).

The colloid mobility has been scarcely investigated in transport experiments. In a field-scale migration experiments at AECL's Underground Research Laboratory (URL) Vilks et al. (1997) have studied the transport of silica colloids within a fracture zone compared with conservative tracers (I<sup>-</sup>, Br<sup>-</sup>). These tests demonstrated that colloidal silica can migrate through open fractures over the distances of 17 m under the induced average flow velocities of 1.6 and 2.9 m·h<sup>-1</sup>. Results of laboratory experiments in granite fractures (Vilks and Bachinski 1996) have shown that changes in a flow direction can produce significant differences in elution profiles and in the recovery of colloidal and conservative tracers. Both in field-scale and laboratory-scale experiments, colloids exhibited different transport properties from conservative tracers.

The bentonite colloid transport within a granite fracture has been investigated by complementary laboratory (Missana et al. 2003, Schäfer et al. 2004) and *in situ* studies at Grimsel Test Site within the Colloid and Radionuclide Retardation Experiment (CRR) (Hauser et al. 2002, Möri et al. 2003, Geckeis et al. 2004). The influence of the bentonite colloids on radionuclide transport within a granite fracture was studied under *in situ* conditions in the Grimsel underground laboratory by applying a hydraulic dipole using injection flow of 10 mL·min<sup>-1</sup> and extraction flow of 150 mL·min<sup>-1</sup>. Bentonite colloids generated from bentonite backfill material were found to be stable. The injected bentonite colloids showed a recovery of 80–90% after passing through the 2.23 m long dipole flow field. Colloid-mediated transport was shown to be faster than the transport of dissolved species. The migration behaviour of the tri- and tetravalent actinides americium and plutonium was strongly mediated by the bentonite colloids and recovery increased from 20–30% in the absence of bentonite colloids to 60–80% in the presence of bentonite colloids.

In accompanying laboratory column studies, a granite core from the Grimsel Test Site, which contains a longitudinal fracture, was used for transport studies. In all experiments, it was demonstrated that colloid presence indeed influences radionuclide transport within the fracture. It was shown that a fraction of the bentonite colloids moved always unretardedly, other colloids eluted retardedly and a colloid fraction was filtered in the medium. The different behaviours were dependant on the flow conditions and on colloid sizes. Within the CRR project the description of colloid and radionuclide transport experiments by applying available transport models, accounting for different parameters was satisfactory (Möri et al. 2003, Kosakowski 2004). However, it was pointed out that the underlying mechanisms that lead to colloid retardation and filtration were still not understood. An adequate description of colloid-mediated transport within natural media requires the identification and quantification of colloid retention mechanism accounting both for the colloid and medium main characteristics.

## 4 COLLOID CHARACTERIZATION METHODS

Many techniques have been applied to separate a colloidal fraction and characterize the properties of colloids. Different methods have been combined to get complementary information about colloid concentration, size and shape. Generally used methods for chemical characterization are inductively coupled plasma mass spectroscopy (ICP–MS), inductively coupled plasma atomic emission spectroscopy (ICP–AES), energy-dispersive X–ray spectroscopy (EDS or EDX) and X–ray diffractometry (XRD). Standard methods for the determination of colloid concentration and size distributions are based on laser light as single particle counting (SPC), photon correlation spectroscopy (PCS) and laser-induced breakdown detection (LIBD). Microscopic techniques as scanning electron microscopy (SEM) and atomic force microscopy (AFM) have been used to investigate both the sizes and shapes of particles.

### 4.1 Colloid separation

Generally used methods for colloid separation are membrane filtration (ultra filtration) and ultra centrifugation. Flow field–flow fractionation (FFFF) is a technique in which the separation of colloids is achieved in a laminar carrier flow under the action of a flow field, which is perpendicular to the carrier flow (Thang et al. 2001). The movement of colloidal species in the laminar carrier flow is determined by their diffusion coefficient and, thus, their size. No stationary phase is required meaning that a less extent of the interaction effects of sample components with equipment surfaces is expected. Depending on the particle properties and concentration, different detectors have been applied to record the particle size distribution, e.g. ICP–MS (Geckeis et al. 2003), UV/VIS (Gimbert et al. 2005), PCS and LIBD (Bouby et al. 2002, Thang et al. 2000).

Colloid cake is a flat membrane on which colloids are isolated by filtration. Colloids on the membrane are analyzed without filter dissolution by gravimetry or XRD. Gravimetry has its limits due to the mass of collected colloids. In principle some 0.5 mg of colloid should be collected to determine colloid concentration accurately for a given membrane cut off size e.g. 100 nm. This condition limits the use of this technique because of membrane clogging. X–ray diffraction is also limited by the mass of colloids collected, their degree of crystallinity and crystal diffraction properties. Finally, after filter cake dissolution (14 M HNO<sub>3</sub>) the leached phase may be analyzed as described above. To avoid systematic errors, ideally the colloid cake should be thick enough to neglect membrane blank. In all cases, the mass required for analysis remains a major problem because, during cross–filtration, the separation process passes from a plain filtration to a gel filtration thus changing the cut off.

### 4.2 Chemical characterization

ICP–MS and ICP–AES are generally used methods for chemical composition analyses. These multi element analysis methods are highly sensitive and capable to determining a range of elements in the part per trillion levels. Difference between these methods is that ICP–MS spectrometer can be used to analyze also solid samples. Solid samples are introduced into the ICP by a laser ablation system. ICP–MS is also capable of monitoring isotopic speciation for the ions. ICP–AES has been routinely used for Na, K,

Ca, Mg, Sr, Ba, Fe, Ti, S, Al, Si and P analysis. ICP–MS has been used for trace analysis of rare earth elements, Th and U as well as for Sn, Zr, Pd and Se. Supra pure HNO<sub>3</sub> is added to the water samples on site prior to transfer to the laboratory for analysis by ICP–MS and ICP–AES. Ion chromatography (IC) has been used to analyze anions (Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>) (Degueldre et al. 2003). Inorganic carbon can be determined on- or off-line together with total organic carbon (TOC, Dohrman unit). TOC is measured by persulfate wet oxidation under UV irradiation allowing detection down to the ng·mL<sup>-1</sup>. Analyses could also be performed on the concentrate to assess whether ion retention occurs during colloid sampling. In principle the elemental composition of the colloidal phase should be obtained from the fluid phase analysis of the filtrate, the concentrate or the groundwater. However, artefact generation and colloid attachment on the filters limit the use of this procedure (Degueldre et al. 1996a).

EDS (EDX) or wavelength dispersive X-ray spectroscopy (WDXRF or WDS) is an analytical tool used for chemical characterization based on the detection of X-rays produced by the interaction of electrons with the sample matter. An electron or photon beam is focused on the atom of the sample containing ground state unexcited electrons situated in probability shells around the nucleus. The incident beam excites an electron in a lower energy state, prompting its ejection and resulting in the formation of an electron hole within the atom electronic structure. An electron from an outer, higher-energy shell then fills the hole and the excess energy of that electron is released in the form of an X-ray. The release of X-rays creates spectral lines that are highly specific to individual elements and the X-ray emission data can be analyzed to characterize the sample. EDS equipment are commonly connected with scanning electron microscopes.

WDXRF (WDS) is a method used to determine the energy spectrum of an X-ray radiation. It is mainly used in chemical analysis, in an X-ray fluorescence spectrometer or in an electron microprobe. The X-rays emitted by the analyzed object are collimated by parallel copper blades and irradiate a known single crystal. The single crystal diffracts the photons, which are collected by a detector, usually a scintillation counter or a proportional counter. The single crystal and the detector are mounted on a goniometer, which is a device similar to a traditional XRD. It is usually operated under vacuum to reduce the absorption of low-energy photons by air and thus increase the sensitivity to the detection and quantification of light elements between boron and oxygen.

XRD is used as an adjunct to chemical analysis in the identification of the constituents of the mixtures of crystalline phases, e.g. in minerals, cements and alloys. Bragg's law ( $2d \sin\theta = n\lambda$ ) describes how the angle of diffraction ( $\theta$ ) of an X-ray beam focused on a crystal is related to wavelength ( $\lambda$ ) and the periodic distance ( $d$ ) between atoms in the crystal. Since periodic atomic distance is unique to individual crystalline compounds, Bragg's law predicts that compounds will have unique diffraction patterns. Several types of diffractometers have been developed to analyze various materials such as single crystals, powders, flat plates, thin films, or liquids. The sample is irradiated with either copper or cobalt characteristic X-rays generated at high voltage. The X-rays are focused by a series of slits onto a flat sample area of about 1 cm<sup>2</sup>. Diffraction angles are measured by moving the X-ray source and detector on a goniometer, a device that rotates about the sample. A computer interactively controls the goniometer movement, data recording, and data reduction. Diffraction patterns are matched with a well-

maintained commercial database of over 60000 compounds and with patterns published in peer-reviewed journals.

Time-resolved laser-induced fluorescence (TRLIF, TRLFS) spectroscopy has been used to study the electronic structure of molecules and their interactions. The principle is based on pulsed laser excitation followed by temporal resolution of the fluorescence signal which leads to the elimination of short lifetime disturbing fluorescence. Excitation resolution obtained by the proper choice of the laser wavelength makes possible to distinguish between more species since a particular excitation of a given species is not shared by other species. Emission fluorescence gives the characteristic spectra of the fluorescent free or complexed cation and fluorescence lifetime is characteristic of its environment such as complexation or quenching. TRLIF provides useful information on the chemical species present in solution and it is quite useful for actinide and lanthanide complexation and sorption studies. TRLIF has been successfully used to investigate Cm (III) interaction with calcite (Stumpf and Fanghänel 2002), for the spectroscopic characterization of different species of europium (Plancque et al. 2003) and study the sorption of Eu(III) onto kaolinite and montmorillonite (Tertre et al. 2006) and non-porous silica (Takahashi et al. 2006).

### 4.3 Concentration

Single particle counting (SPC) has been a normally used technique to determine colloid concentration. Particles are counted and analyzed with respect to size based on the intensity of scattered light which the colloids produce in the unit laser beam tar (10 mW, wavelength: 488 nm). Degueldre et al. (1996a) have analyzed natural groundwater samples which needed a significant dilution in ultra pure water according to the colloid concentration. Information was displayed as a cumulative distribution given in equation Eq. 4-1:

$$[\text{coll}] = \int_{\varnothing(m)}^{\varnothing(M)} \frac{d[\text{coll}]}{d\varnothing} d\varnothing \quad (\text{Eq. 4-1})$$

where  $\varnothing$  (m) are the smallest (e.g. 100 nm) and  $\varnothing$  (M) the largest (e.g. 1000 nm) nano particle sizes analyzed. The results were treated with a calculation code called COLIAT (COLloid Linear Analytical Treatment) in order to calculate the colloid number concentration [coll] for a given size range and normal size distribution. To express the colloid number concentration in colloid mass concentration ( $\mu\text{g}\cdot\text{mL}^{-1}$ ) requires an assumption to be made as to an average colloid density  $\rho$  (e.g.  $2\text{ g}\cdot\text{cm}^{-3}$ ), and their shape which was assumed to be spherical. Linear extrapolation of the distribution will underestimate the colloid concentration. Yoon and Lueptow (2006) have used a detection method based on fluorescent dye bound colloidal silica particles and fluorescence excitation-emission spectroscopy to quantify the concentration of colloidal silica suspensions. Fluorescence intensity increased with increasing particle size diameters ranging from 7 nm to 22 nm. Fluorescence intensity increased with increasing pH above 9 for the negatively charged particles and decreased with decreasing pH below 5.5 for the positively charged particles.

## 4.4 Zeta potential

No direct method for the experimental determination of zeta potential exists. It can be calculated using theoretical models and an experimentally determined electrophoretic mobility (Ryan and Gschwend 1994, Toikka and Hayes 1997, Yoon and Lueptow 2006) or dynamic electrophoretic mobility which are measurable parameters. The basic microelectrophoresis system is a cell with electrodes to which a potential is applied. An electric field is applied across the dispersed particles, which will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential. Velocity is measured using Laser Doppler Velocimetry (LDV) technique. The frequency shift or phase shift of an incident laser beam caused by these moving particles is measured as the particle mobility, and this mobility is converted to the zeta potential by the application of the Smoluchowski or Huckel theories. The most known and widely-used theory for calculating zeta potential from experimental data is that developed by Smoluchowski for electrophoresis. Theory is valid for dispersed particles of any shape and concentration.

Zeta potential can also be determined by applying widely used electroacoustic phenomenon colloid vibration current and electric sonic amplitude (Sadasivan et al. 1998, Dukhin et al. 2005). Intensity of electroacoustic effects is determined by dynamic electrophoretic mobility which depends on zeta potential. Difference between dynamic electrophoretic mobility and electrophoretic mobility is a frequency; electrophoretic mobility is a low frequency limit of the dynamic electrophoretic mobility. Electroacoustic techniques are able to perform measurements in intact samples, without dilution but give only a single average value for zeta potential, whereas techniques based on electrophoretic mobility provide information on the distribution of zeta potential.

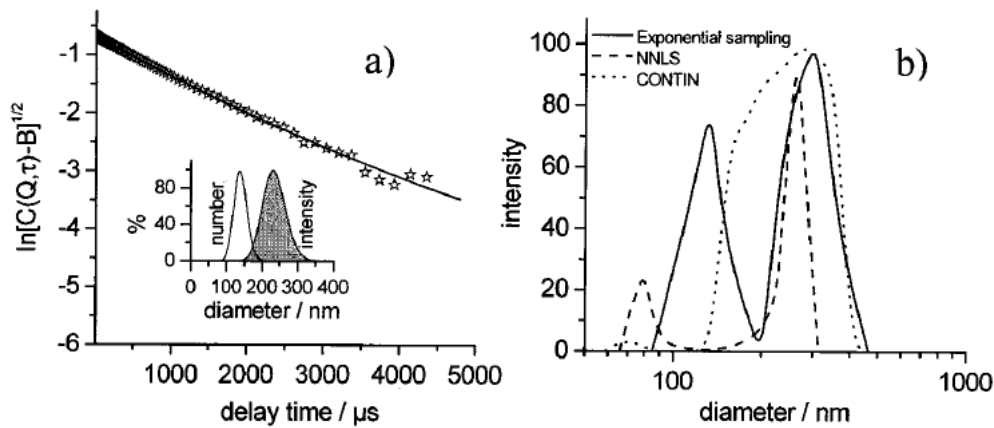
## 4.5 Size and shape

### 4.5.1 Laser light methods

Laser light methods belong to the standard methods for the determination of colloid concentration and size distributions. Laser light scattering (LLS) and laser back scattering (BSC) methods measure Brownian motion and relate it to the size of the particles. Brownian motion is the movement of particles due to random collision with the molecules of the liquid. Small particles move quickly and large particles move more slowly. The intensity of the scattered light strongly depends on the hydrodynamic particle diameter ( $d_h$ ). A hydrodynamic diameter ( $d_h$ ) is an equivalent sphere diameter derived from a measurement technique involving hydrodynamic interaction between the particle and fluid. PCS known also as dynamic light scattering (DLS) is one of the most commonly applied non-destructive colloid sizing methods.

Photon correlation spectroscopy (PCS) application to the characterization of natural aquatic colloids was reviewed and assessed by Fillela et al. (1997). PCS is based on the analysis of the temporal fluctuation of the scattered laser light intensity originating from the Brownian movement of dispersed particles. The relationship between the size of the particle and its speed is defined using the Stokes–Einstein equation.





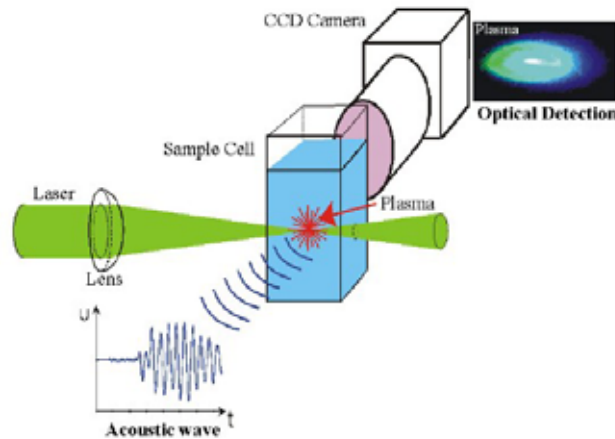
**Figure 4-1.** PCS size distribution analysis of FEBEX bentonite colloids: (a) weighted quadratic cumulant analysis (QC) of the autocorrelation function  $C(Q, \tau)$ . (b) Size distribution analysis by the ill-conditioned inverse Laplace transformation methods (Plaschke et al. 2001).

A hydrodynamic diameter ( $d_h$ ) of ideal spherical colloids can be calculated by computer assisted evaluation of the intensity from experimental measured autocorrelation function (ACF,  $C(Q, \tau)$ ). The determined hydrodynamic diameter  $d_h$  strongly depends on the volume and the shape of the particles. Analytical expressions have been developed to consider ellipsoidal, cylindrical, or wormlike geometrical shapes. PCS is very insensitive for small particles in the presence of larger sized particles, which produce the major part of the scattering light intensity. Thus, evaluation of autocorrelation function for natural samples with complex composition and wide size distribution range becomes very difficult (Figure 4-1).

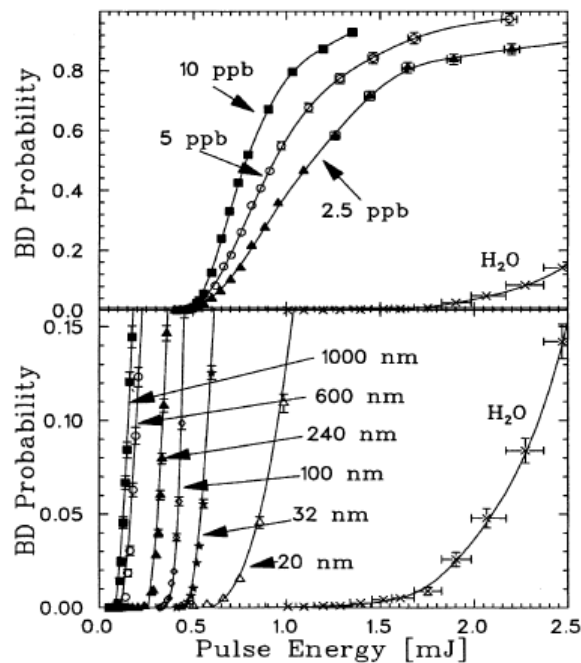
Laser-induced breakdown detection (LIBD) is a very sensitive method for the direct detection of colloids at the lowest concentration level. The principle of operation is illustrated in Figure 4-2. LIBD is based on the plasma generation on single particles by a focused, pulsed laser beam and the detection of produced shock waves or plasma light emissions. The laser-induced breakdown effect and the principles of LIBD are described in detail in references (Bundschuh et al. 2001a, 2001b, 2005a, 2005b, Walther et al. 2002). The laser power density required to induce the breakdown of a dielectric medium resulting in plasma formation is significantly lower for solid matter than for liquids. Unless the laser pulse power density exceeds the breakdown threshold ( $P_{A,crit}$ ) of the solvent in colloidal dispersion, the plasma is generated almost exclusively on colloids.

The evaluation of the number of breakdown events per number of laser shots results in a breakdown probability, which is dependent on both particle concentration and size. The probability of a breakdown initiation on an individual particle depends on the laser power density which affects the number of particle-borne electrons. These initial electrons are accelerated in the electromagnetic field of the laser beam and cause an electron avalanche by additional ionization. With increasing particle size, lower laser power density is needed to induce a dielectric breakdown in a particle. The spatial distribution of the individual breakdown events within the focal area of the laser beam is found to be dependent on the particle diameter and independent of the particle

concentration. The width of the breakdown volume along the laser beam axis called effective focal length,  $L_z(P)$  can be taken as a measure for the mean colloid size.  $L_z(P)$  is defined as the length where 99.7% of the plasma events are found. To determine  $L_z(P)$ , the light emission of single plasmas is detected by a microscope charge-coupled device (CCD) camera system.



**Figure 4-2.** LIBD, principle of operation: plasma is ignited selectively on colloids in solution by a tightly-focused pulsed laser. Its expansion causes an acoustic wave which can be detected by a piezoelectric receiver. The emitted light is observed and spatially resolved by a CCD camera (Walther 2003).



**Figure 4-3.** The breakdown probability is plotted as a function of the laser pulse energy,  $E$  [mJ]. Bottom: the threshold of curves increases with the decreasing particle size of polystyrene reference colloids. Top: while the threshold remains unchanged, the slope changes with the colloid concentration (particle size 32 nm) (Walther et al. 2002).

The use of reference colloids e.g. polystyrene particles of well-defined diameters provides a calibration for relating breakdown thresholds to particle size. A mean particle diameter of sample colloids is obtained by comparison the  $L_z(P)$  of the sample colloids with that of the polystyrene reference particles. Based on the known mean particle diameter of the sample colloids, the particle concentration can be calculated from the breakdown probability. The calibration measurement of polystyrene reference particles is shown in Figure 4-3. The threshold energy, ET [mJ], of the curve is the laser pulse energy where the first breakdown events occur. The threshold energy increases with decreasing particle size, and an unknown size can be determined from its threshold energy when the breakdown threshold is plotted as a function of the particle size. Devices for a mobile LIBD arrangement are described and have been applied also in field studies (Hauser et al. 2002, 2005).

#### **4.5.2 Microscopic Techniques (SEM, FESEM, TEM, AFM)**

Scanning electron microscopy (SEM) is a type of electron microscope which produces the high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for determining the surface structure of the sample. In SEM, electrons are thermionically emitted from a tungsten or lanthanum hexaboride ( $\text{LaB}_6$ ) cathode and are accelerated towards an anode. In FESEM electrons are emitted by field emission (FE). Tungsten is used because of the highest melting point and lowest vapour pressure of all metals allowing it to be heated for electron emission. The electron beam, an energy ranging from a few hundred eV to 50 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam in a raster fashion over a rectangular area of the sample surface. Through these scattering events, the primary electron beam effectively spreads and fills a teardrop-shaped volume, known as the interaction volume, extending from less than 100 nm to around 5  $\mu\text{m}$  into the surface. Interactions in this region lead to the subsequent emission of electrons which are then detected to produce an image.

The transmission electron microscopy (TEM) is based on the same basic principles as the light microscope but uses electrons instead of light. Due to much lower wavelength of electrons it is possible to get a resolution order of a few angstroms ( $10^{-10}$  m). TEM uses electrons that travel through vacuum in the column and electromagnetic lenses focus the electron beam. The electron beam travels through a very thin slice of the specimen, electrons hit a fluorescent screen and project the highly-magnified image onto a phosphor screen or special photographic film in which different parts are displayed in varied darkness according to their density.

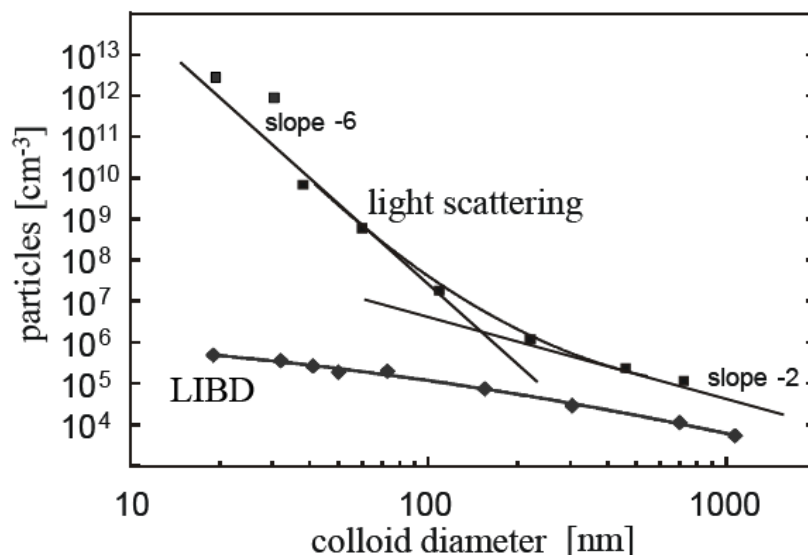
Atomic force microscopy (AFM) is a relatively new imaging technique for studying the morphology of nano particles. The non-contact mode of AFM is a technique that uses oscillating cantilevers to maintain a constant distance between a tip and sample. Compared with electron microscopy, AFM offers more flexibility in sample preparation, three-dimensional images and in some cases better image resolution. AFM has been applied to investigate environmental particles such as humic colloids (Plaschke et al. 1999), clay particles (Degueldre 1997) and the interaction of an iron oxide sphere

with silica flat immersed in a dilute electrolyte solution (Toikka et al. 1996). AFM requires the prior deposition of colloids onto a plane surface.

Plaschke et al. (2001) have investigated FEBEX bentonite particles on the mineral surface of cleaved mica. Muscovite mica has flat, atomically smooth surface with a negative charge at intermediate pH. Colloids were allowed to adsorb from the bentonite suspension with a colloid concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$  to the mica surface. The mica sheets were then withdrawn from the solution and thoroughly rinsed with de-ionized water in order to remove any non-adsorbed bentonite or residues from salt crystals, and the mica samples were then dried in an oven. The AFM software was then applied for image processing for levelling images in a horizontal plane (Plaschke et al. 1999). Particle size data like area, volume and average height was exported and processed for the calculation of particle size distribution. Particle diameters were calculated from the particle areas by assuming disk-shaped particles. Since the lateral resolution of AFM is limited by the size of the AFM tip, these diameters were corrected by a geometrically estimated tip artefact which is described in the literature.

#### 4.6 Comparison of methods

The application of different colloid characterization methods is a prerequisite to get complementary information about colloid size and shape, which is essential for the understanding of natural colloidal systems. For the applied methods, the raw size data have to be corrected in order to consider chemical composition and shape of the colloids as well as instrumental artefacts. A comparison of the size information requires the prior definition of the diameter types that are obtained by the individual methods. Microscopic techniques have the advantage that both the sizes and shapes of particles become visible in the images.



**Figure 4-4.** The detection limit of LIBD in comparison to the conventional light scattering (Bundschuh et al. 2001).

Compared to PCS LIBD provides a much higher sensitivity with respect to particle number densities, particle concentration, and particle dimensions. The detection limits of the LIBD are compared with conventional light scattering in Figure 4-4. LIBD provides many orders of magnitude lower detection limits for small colloids and the possibility to study colloids also in the size range from 1–10 nm in very dilute concentrations. A minimum detectable particle radius of  $r_{\min} = 0.64 \pm 0.33$  nm has been shown by calculation (Bundschuh, et al. 2001). LIBD can be applied from the border range for the transition of molecular species to colloids at about 1 nm to the size, where stability of colloids limits to sedimentation at  $\leq 1000$  nm. Even though LIBD provides an averaged number weighted particle size, a particle size distribution is not yet available.

AFM and SEM are the only imaging methods that provide within the inherent instrumental uncertainties the direct shape and geometric dimensions of the colloids. SEM is a well-established method but it is not very appropriate for the investigation of flat structures with low contrast in an atomic number. Preparation of SEM samples like drying, evaporation, or coating the sample specimen with a conductive metal layer may distinctly disturb the colloidal system. AFM overcomes some of these limitations because non-conducting materials can be directly investigated in air or even in liquids. Particle sizes and shapes can be determined simultaneously from the nanometer to micrometer range. A number weighted particle size distribution can be calculated from a number of images. A size distribution obtained in this way is quite a time-consuming procedure and implies relatively poor statistics due to the small number of analyzed particles. Furthermore, distinct artefacts coming from size and shapes of AFM tips have to be taken into consideration. However, the major strength of AFM is to visualize the morphologies of the nanometer sized particles and necessary information about particle shapes needed by the other methods for an appropriate shape correction is provided.

In contrast to the other methods, FFFF is based on a physical fractionation of particles according to their size resulting in a complete size distribution of the bulk of particles in the sample. Combined with ICP–MS, the method allows a mass sensitive particle analysis over a widely linear measuring range that is not provided by light scattering detectors. The relative mass-weighted size distribution obtained from FFFF–ICP–MS is in fair agreement with the mass-weighted distribution calculated from AFM particle dimensions. The FFFF–ICP–MS combination will determine the element composition of the colloidal species as a function of their size, including direct mass-weighted information and delivering insight into the chemical properties of the colloidal species. To compare the different investigation methods, it has to be taken into account that the colloid size obtained by AFM and LIBD gives direct information about the number-weighted mean particle diameters, whereas FFFF–LLS and PCS give direct information on the intensity-weighted particle diameters. For a comparison of differently weighted particle diameters, the shape of the particles has to be considered in an appropriate way. In the case of LIBD and FFFF, a size calibration has usually been made and the measured sizes are related to that of spherical polystyrene particles. Hydrodynamic diameters ( $d_h$ ) provided by PCS measurement are derived from the particle diffusion coefficient by applying Stoke's law.

Plaschke et al. (2001) have studied FEBEX bentonite colloids from the Grimsel Test Site. The sizes of bentonite colloids released into the groundwater of low ionic strength were characterized by PCS, LIBD, AFM, SEM and FFFF. It was pointed out that the size information given by the different colloid characterization methods strongly depends on the shape of particles and only the shape-corrected size values can be compared in a reasonable way. They assumed that FEBEX bentonite colloids are disks with a 1/10-height-to-diameter proportion, which was in fair agreement with the AFM results. The diameter obtained by LIBD for disk-shaped particles by the above described two-dimensional evaluation of the breakdown events in the laser focus depends on the maximum cross section of the particle. To compare the mass-weighted FFFF-ICP-MS size distribution with that calculated from the AFM results, it is necessary to convert the FFFF size information related to spherical reference colloids to that of disk-shaped particles. As expected for natural colloid suspension, the FEBEX bentonite sample seems to have a rather broad number size distribution of disk-shaped particles in the range of 10 to > 300 nm. In the broad size distribution, PCS typically overestimates the larger sized particles, maximum in the intensity size distributions > 200 nm. On the contrary AFM and LIBD are focused on the large number of small-sized colloids, mean particle diameters 73 nm (AFM) and 67 nm (LIBD). Small-sized colloids play a minor role in the mass weighted intensity distributions, maximum in the distribution curves: 235 nm (FFFF-ICP-MS) and 180 nm (AFM). Results obtained by the different analyzing principles are valuable, fairly consistent and include more detailed information about the colloidal sample. The study emphasized that complementary results of different analytical methods are required for a reasonable interpretation of more complex colloidal size distributions as typically found in natural aquatic systems.

## 5 COLLOIDS IN GEOLOGICAL DISPOSAL OF SPENT NUCLEAR FUEL

Colloid sampling and characterization related to geological disposal of spent nuclear fuel have been carried out in many countries e.g., in Switzerland (Degueldre et al. 1996a), Germany (Kim et al. 1992, Buckau et al. 2000), Canada (Vilks et al. 1991, 1993), United States (Triay et al. 1996, Kersting et al. 1999, George et al. 2000, Contardi et al. 2001), Spain (Turrero et al. 1995), Sweden (Düker and Ledin 1998, Laaksoharju and Wold 2005, Nilsson and Degueldre 2007) and Finland (Laaksoharju et al. 1994, Vuorinen and Hirvonen 2005, Takala and Manninen, 2006b). Degueldre et al. (2000) presents and discusses groundwater colloid results from various geological formations ranging from crystalline to sedimentary, from organic rich to organic poor systems and from subsurface to very deep aquifers.

The bentonite barrier is considered a potential source of colloids. Bentonite colloid generation at a spent nuclear fuel repository has been investigated at a laboratory scale by means of column experiments simulating the granite–bentonite boundary, both at dynamic and under quasi-static water flow conditions (Missana et al. 2003). The main results were the demonstration of the detachment of solid particles ( $> 1 \mu\text{m}$ ) and colloids ( $< 1 \mu\text{m}$ ) and the observation of their mobilization by an induced water flow. Under dynamic conditions, the colloidal fraction was mainly composed of bentonite particles with sizes of 300 nm. Colloid concentration was mainly depending on the flow conditions but widely independent on the chemical variations suggesting that the colloid generation was mainly induced by mechanical erosion on the clay surface. In quasi-static experiments, it was observed that the extrusion of the clay from the compacted barrier resulted in a local loss of density and at a sufficient high hydration degree lead to clay colloid detachment. High groundwater flow produces mechanical forces that favour the detachment of colloidal particles (Ryan and Gschwend 1994). Flow rates in a repository are believed to be low so that such processes are considered less relevant. In order for bentonite erosion to take place, the viscous force exerted by the flowing water on the particles of the clay gel must exceed the average particle bond strength in the order of  $10^{-13}$  to  $10^{-12}$  N for the waters of low salinity (Pusch 1985).

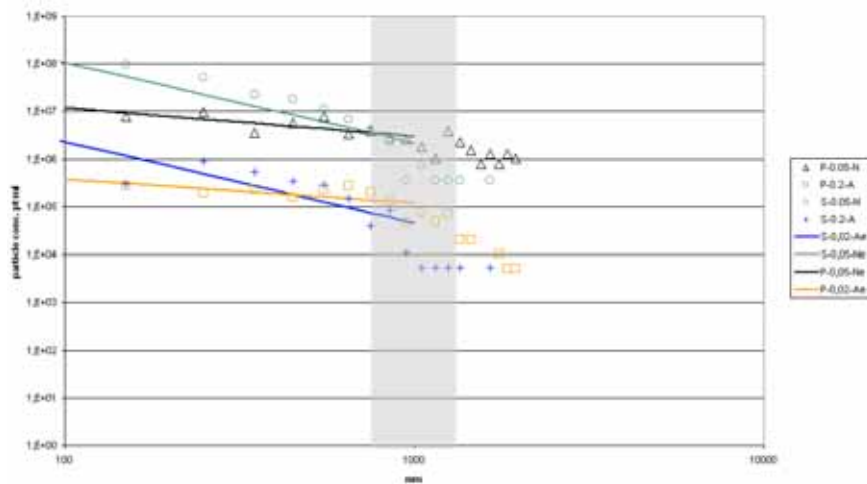
The analysis of natural colloids in the water is in many cases difficult due to their small size ( $< 1\text{--}2 \text{ nm}$ ) and their low concentration. Studies aiming to analyze and to quantify colloid populations are basically subjected to the resolution of analytical techniques available. Natural colloid concentrations in crystalline systems can vary over wide ranges. They depend on geochemical conditions and are influenced by the existence of geochemical gradients and mechanical disturbances. A specific in-site determination is required, since it is considered that even a really small colloid concentration could have an effect on the contaminant migration if the colloids are mobile.

### 5.1 Finland

In Olkiluoto three colloid sampling methods were tested by Laaksoharju et al. (1994). Total inorganic colloid content (size  $1\text{--}1000 \text{ nm}$ ) in Olkiluoto was  $184 \pm 177 \mu\text{g}\cdot\text{L}^{-1}$  consisting of clay minerals, silica, pyrite, goethite and magnesium oxide. The concentration of organic substances was around  $10 \mu\text{g}\cdot\text{L}^{-1}$ . Vuorinen and Hirvonen (2005) have studied bentonite as a potential source of colloids in Olkiluoto by testing

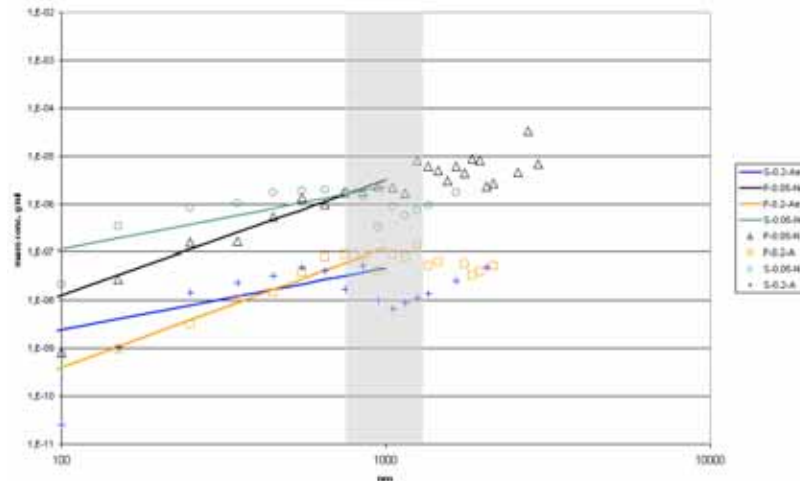
the colloid formation of bentonite in contact with different groundwater at the site. Groundwater samples ( $[Cl^-]$  was  $0.8 \text{ g}\cdot\text{L}^{-1}$  and  $2.6 \text{ g}\cdot\text{L}^{-1}$ ) collected before interaction with bentonite indicated that iron and aluminium were associated with colloidal species with  $\text{SiO}_2$ , clay mineral and/or calcite colloids. The estimated size range was from 50 nm to 400 nm and the estimated concentration of the Fe-associated colloids was  $800 \mu\text{g}\cdot\text{L}^{-1}$  and that of the Al-associated colloids  $4 \mu\text{g}\cdot\text{L}^{-1}$ . After bentonite interaction bentonite colloids were found only in low salinity ( $\sim 2 \text{ g}\cdot\text{L}^{-1}$ ) groundwater. The size of bentonite colloids varied from 50 nm to 200 nm.

The formation and investigation of inorganic and organic colloids and the colloid sampling and analysing techniques has been reviewed by Takala and Manninen (2006a). They have also tested different filtering methods and membranes in order to determine the colloid concentration and to characterize the composition of the colloid phase at ONKALO groundwater station ONK-PVA1 at Olkiluoto (Takala and Manninen 2006b). The particle size distributions (Figure 5-1) were determined from SEM micrographs by counting observed particles and dividing the particles into size groups. The particle concentration (Figure 5-2) was determined with the single particle counting (SPC). Differences in the colloid concentration were explained by the different pore size, structure and the material of the Anopore and Nuclepore membranes. The colloid concentration  $200\text{--}400 \mu\text{g}\cdot\text{L}^{-1}$  was comparable to the concentrations of samples collected from similar environments (Laaksoharju et al. 1994, Düker and Ledin 1998). The lower colloid concentration than that reported by Vuorinen and Hirvonen (2005) was explained by different sampling methods. Vuorinen and Hirvonen based their colloid concentration estimation on the difference in the chemical compositions of the filtrates, while Takala and Manninen calculated the concentration using the single particle analysis method.



**Figure 5-1.** Size distribution ( $\text{pt}\cdot\text{mL}^{-1}$ ) obtained by a single particle analysis of the micrographs. The continuous lines represent the size distribution estimates calculated from the Pareto power law. The grey area represents the cut-off of the  $1\text{-}\mu\text{m}$  prefilter. The particles larger than 1000 nm are sampling artefacts caused by, e.g., the agglomeration of smaller particles. (Takala and Manninen 2006).





**Figure 5-2.** Colloid mass concentration distribution ( $\text{g}\cdot\text{mL}^{-1}$ ). The continuous lines represent the mass concentration estimates calculated from the Pareto power law (Takala and Manninen 2006).

## 5.2 Sweden

In an international colloid project at the Äspö Hard Rock Laboratory (HRL) in Sweden the role of bentonite as a colloid source was studied, the background colloid concentration at Äspö HRL was verified and the potential for colloid formation and transport in natural groundwater concentrations was investigated (Laaksoharju and Wold 2005). The colloid project consisted of laboratory experiments with bentonite, background field measurements of natural colloids, borehole specific bentonite colloid stability experiments and a fracture specific transport experiment. It was concluded that the bentonite colloid stability is strongly dependent on the groundwater ionic strength. Natural colloids are organic degradation products such as humic and fulvic acids, inorganic colloids (clay, calcite, iron hydroxide) and microbes. Microbes form few but large particles and their concentration increase with increasing organic carbon concentrations. The small organic colloids are present in very low concentrations in deep granitic groundwater. The concentrations can be rather high in shallow waters. The colloid concentration decreases with depth and salinity, since colloids are less stable in saline waters. The colloid content at Äspö is less than  $300 \mu\text{g}\cdot\text{L}^{-1}$ . The colloid content at repository level is less than  $50 \mu\text{g}\cdot\text{L}^{-1}$ . The groundwater variability obtained in the boreholes reflects well the natural groundwater variability along the whole HRL tunnel (Walther et al. 2002).

In a site investigation program at Forsmark, Hauser et al. (2005) have performed a colloid analysis in groundwater samples. Samples collected in a stainless steel cylinder avoiding water contact with the atmosphere. Colloids were analyzed in INE by LIBD using a closed flow-through detection cell. Groundwater batch samples were collected for the chemical analysis (ICP–AES, ICP–MS) and for the detection of inorganic carbon and dissolved organic carbon. Track-etched polycarbonate filter samples were taken for colloid analysis with SEM/EDX. The water was highly saline with about  $4500 \text{mg}\cdot\text{L}^{-1}$  chloride. Average colloid diameters of 105–270 nm and mass concentrations of 1.1– $6.8 \mu\text{g}\cdot\text{L}^{-1}$  were determined. In a recent study by Nilsson and Degueldre (2007) natural groundwater colloids were sampled by micro-filtration of water samples collected from

a granitic groundwater and maintained at the *in situ* thermodynamic conditions. The on-line procedure allowed working at the well head avoiding the generation of artefacts produced by pH changes due to CO<sub>2</sub> exchange, yielding potential carbonate precipitation, or by O<sub>2</sub> contaminations yielding oxidized insoluble phases. Micro-filtration of the colloids was carried out after the on-line long-term measurements of chemical and physical parameters in the unbroken sample water line. Colloid samples were characterized by SEM. At deep granitic groundwater conditions, natural colloids occurred sparsely. The colloid concentration for sizes ranging from 50 to 500 nm was  $C_{col} \sim 1 \mu\text{g}\cdot\text{L}^{-1}$ . These colloids were clay with an average size smaller than 200 nm. For the Na–Ca–Cl groundwater (pH 7.53, ionic strength  $\sim 10^{-1}$  M), the colloid concentration values were comparable with values reported in the literature.

### 5.3 Switzerland

In Switzerland colloid sampling and characterization have been carried out in the Grimsel Test Site area (Transitgas Tunnel), Northern Switzerland (Leuggern, Zurzach) and the Black Forest (Bad Säkingen, Menzenschwand) (Degueldre et al. 1989, 1996a, 1996b). The groundwater colloids in granitic systems were predominantly composed of phyllosilicates and silica originating from the aquifer material. Under constant hydrogeochemical conditions, the colloid concentration did not exceed  $0.1 \mu\text{g}\cdot\text{mL}^{-1}$  when the calcium concentration is larger than  $10^{-4}$  M and the sodium concentration is larger than  $10^{-2}$  M. However, under transient chemical or physical conditions, such as geothermal or tectonic activity, colloid generation may be enhanced and the colloid concentration may reach  $10 \mu\text{g}\cdot\text{mL}^{-1}$  or more if both calcium and sodium concentrations are low ( $< 10^{-4}$  M and  $< 10^{-2}$  M respectively). Resuspension from fissures or fractures was observed as well. The colloid size distribution yields information about their stability. For a representative deep crystalline water ( $[\text{Ca}] = 3.5 \cdot 10^{-4}$  M,  $[\text{Na}] = 1.4 \cdot 10^{-2}$  M,  $[\text{TOC}] = 3 \cdot 10^{-6}$  M), the colloid concentration was  $< 0.1 \mu\text{g}\cdot\text{mL}^{-1}$  and around  $0.01 \mu\text{g}\cdot\text{mL}^{-1}$  in Zurzach water for sizes ranging from 100 nm to 1000 nm.

### 5.4 Canada

In Canada Vilks et al. (1991, 1993) have characterized natural colloids (1–450 nm) and suspended particles ( $> 450$  nm) in groundwater of the Whiteshell Research Area and Cigar Lake uranium deposit to evaluate their potential role in radionuclide transport through fractured granite. The concentrations of colloids between 10 nm and 450 nm ranged between  $0.04$  and  $1 \text{ mg}\cdot\text{L}^{-1}$ . The average colloid concentration from the deeper saline waters ( $0.46 \text{ mg}\cdot\text{L}^{-1}$ ) was not significantly different from the average concentration in the shallower Na–Ca–HCO<sub>3</sub> waters ( $0.27 \text{ mg}\cdot\text{L}^{-1}$ ). The concentrations of suspended particles varied from  $0.04$  to  $14 \text{ mg}\cdot\text{L}^{-1}$ . The range of suspended particle concentration in the shallower Na–Ca–HCO<sub>3</sub> waters ( $0.05$ – $14 \text{ mg}\cdot\text{L}^{-1}$ ) was greater than in deep saline waters ( $0.04$ – $1.4 \text{ mg}\cdot\text{L}^{-1}$ ). The particles consisted mainly of low and high temperature alteration mineral including carbonate, clays, Fe–Si oxides, quartz, and potassium feldspar and albite. Cigar Lake groundwater contained particles in all sizes ranging from 10 nm to 20  $\mu\text{m}$ ; most samples contained a relatively high concentration of colloids in the 100–400 nm size range. Particle compositions were similar to the composition of minerals in the sandstones and ore body, suggesting that particles in groundwater are generated by the erosion of fracture–lining minerals.

## 6 COLLOIDS FROM SILICA SOL GEL

Torstenfelt et al. (2005) have measured the release of colloids from silica sol gel. They used sodium chloride (0.1 mM and 0.1 M) or calcium chloride (33.3 mM) as the accelerator and tested four leaching solutions: distilled water, 0.1 mM NaCl, 0.1 M NaCl and 33.3 mM CaCl<sub>2</sub>. When measuring the colloid and silicon concentrations after 21 days contact time, in the 0.1 mM NaCl leaching solution the colloid concentration was 0.6 mg·L<sup>-1</sup> and the silicon concentration 0.17 mM. In the 0.1 M NaCl leaching solution the colloid concentration was 0.22 mg·L<sup>-1</sup> and the silicon concentration 0.07 mM. In the 33.3 mM CaCl<sub>2</sub>, the colloid concentration was under the detection limit and the silicon concentration about 0.02 mM. After about one month leaching using calcium chloride as the accelerator, colloid concentrations varied from slightly less than 0.5 mg·L<sup>-1</sup> in distilled water to less than 0.1 mg·L<sup>-1</sup> for the more saline leaching solutions. The mean particle diameter varied between 60 nm in distilled water up to 120 nm in 0.1 M NaCl. No colloids were detected in the 33.3 mM CaCl<sub>2</sub> leaching solution and no mean particle diameter could be measured.

The results by Torstenfelt et al. (2005) confirm earlier experience with colloids in groundwater. According to Laaksoharju et al. (1995), in water containing more than 4 mg·L<sup>-1</sup> Ca or 23 mg·L<sup>-1</sup> Na, the colloid concentration in the water will be insignificant. SKB-SR 97 (SKB 1999) states that the expected calcium concentration in deep granitic bedrock will be between 10 and 2000 mg·L<sup>-1</sup>, while for Na the expected concentrations range from 100 to 2100 mg·L<sup>-1</sup>. In addition, the use of either NaCl or CaCl<sub>2</sub> accelerators will increase the ionic strength in the fractures during injection. Amorphous silica in the temperature range of 0–25 °C has a solubility of 50–150 mg·L<sup>-1</sup> SiO<sub>2</sub>; thus, a colloid concentration of 0.1 mg·L<sup>-1</sup> as measured by Torstenfelt et al. (2005) is low. Since the natural silica concentration is much higher than measured using silica sol, silica sol is not expected to increase the concentration levels of silica to any appreciable extent. Also the natural calcium and sodium concentrations in the surrounding groundwater are high enough to suppress colloid formation.

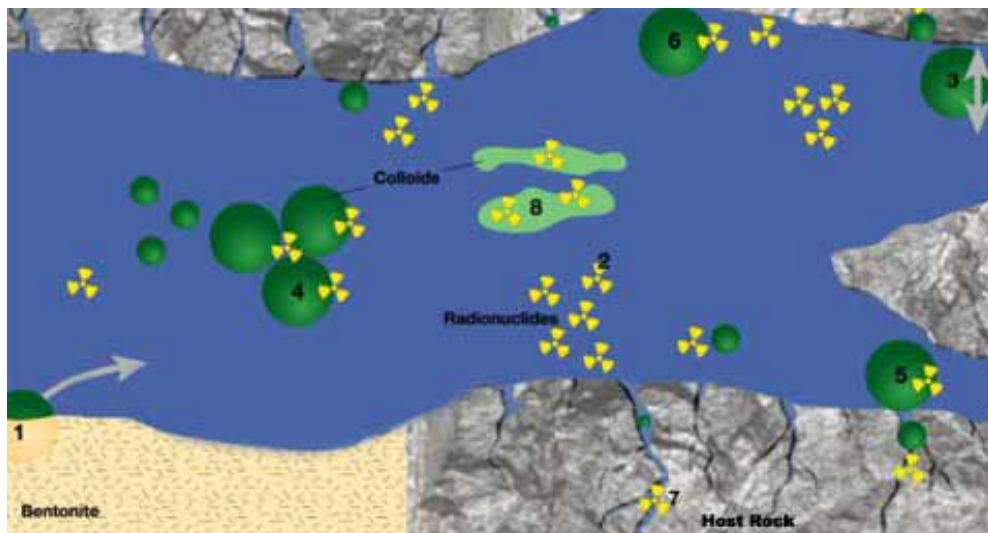
The main conclusion from the colloid investigations was that the concentration of colloids released from silica sol gel is generally low, less than 1 mg·L<sup>-1</sup>. In the non-buffered leaching solutions pH varied between 8 and 11. The more diluted the leaching water is, the higher pH. In pure water, the pH value rises to above 11. Since the colloid release in general was very low, it is difficult to draw certain conclusions from the impact of different ionic media on the release of colloids but some trends, though. The more saline the solution was, the less colloids were released. Somewhat fewer colloids were released when silica sol gel was produced with calcium as cation than sodium as cation in the accelerator. Calcium chloride reduced the silica colloid release but there was not a big difference in silica colloid release when using sodium chloride or calcium chloride as leaching solution. The use of sodium chloride as an accelerator might influence on bentonite dispersion in water and indirectly the formation of colloids.



## 7 COLLOID-MEDIATED RADIONUCLIDE MIGRATION

It is generally accepted that colloid-mediated transport of radionuclides may be significant to the long-term performance of a spent nuclear fuel repository. Many studies have demonstrated that the aqueous speciation of tetravalent actinides is very often dominated by colloids (Olofsson et al. 1982, Kim and Kanellakopulos 1989, Lieser et al. 1990). Actinide transport investigations in a laboratory column (Artinger et al. 1998) or in a block (Vilks and Baik 2001) experiments and field-scale studies (Novikov et al. 2006) have shown that colloid transport can enhance the actinide migration and has to be considered in the long-term safety assessment of a spent nuclear fuel repository. Inorganic colloids, e.g. silicates or clay minerals, are ubiquitous in natural aquatic systems and therefore contribute to the aquatic chemistry and to the migration of groundwater trace components (Degueldre et al. 1996a, 1996b). The relevance of colloids in promoting the transport of long-lived radionuclides from a waste disposal site has to be assessed by taking into account the hydrogeochemical situation, the properties of the colloidal species, and the interaction of the contaminant with the colloids.

The migration mechanisms of colloids and radionuclides in a water conducting fracture are illustrated in Figure 7-1. The mechanisms involved are: Generation of inorganic colloids (1), radionuclide dissolution in groundwater (2), sorption/desorption of colloids onto/from rock surfaces (3), sorption of radionuclides onto colloids (4), filtration of colloids (5), colloid size preventing penetration into pore space of rock (6), diffusion of radionuclides into the pore space of rock (7) and sorption of radionuclides onto the organic colloids or incorporation of radionuclides into the organic colloids (8). In general, all processes that contribute to eliminating colloids from the aqueous phase are comprised in term filtration that can be due to physical-chemical interactions or to mechanical processes (dead-end pores, cavities, etc.).



**Figure 7-1.** Schematic diagram of migration mechanisms of colloids and radionuclides in a water conducting fracture (Nagra Grimsel Test Site).

Colloid matrix diffusion is not considered as a filtration mechanism, but it is theoretically included in many transport models as responsible for the observed colloid retention (Smith and Degueldre 1993). In general, it is not easy to weigh up these different mechanisms involved in colloid retardation from advective flow. In a review article Ryan and Elimelech (1996) present theories describing colloid migration, laboratory experiments designed to test theories and applications to colloid mobilization and transport experiments in natural groundwater systems. Colloid retention on fracture surfaces is mostly theoretically described by introducing an empirical filtration factor in the transport equation, which accounts for any mechanism (Moreno et al. 1998, Cvetkovic et al. 2004). This underlines the necessity for gaining a deeper understanding about the colloid filtration mechanisms and the need for determining experimental filtration parameters.

### 7.1 Colloid interaction with rock surfaces

Colloid retention is based on colloid–rock interactions, and can be evaluated using a dimensionless attachment factor,  $a$ , which is determined as a ratio of particle attachment rate to particle collision rate. In Swiss crystalline formation, the determined colloid attachment factor was large due to high sodium and calcium concentrations which restrict the stability and mobility of the colloid population. For montmorillonite colloids and for  $1.4 \cdot 10^{-2}$  M Na and  $3.5 \cdot 10^{-4}$  M Ca, the attachment factor,  $a$ , was nearly 1 at pH 8 (Degueldre et al. 1996b). The surface based colloid distribution coefficient between rock and water,  $K_a$ , was  $0.1 \text{ cm}^{-1}$  in  $10^{-2}$  M Na solutions. It was expected to be larger than  $10 \text{ cm}^{-1}$  in the deep granitic groundwater conditions which contributes to slowing down their mobility. That study was limited to granitic formation waters and did not describe the situation in other aquifers.

The evaluation of the surface area available for colloid retention is a fundamental parameter due to the presence of different minerals, pore size distribution and roughness of heterogeneous granite surface (Toran and Palumbo 1992, Saiers et al. 1994). Colloid interactions with the rock surfaces are expected to be influenced by the charge of colloids and the heterogeneous charge distribution of the rock due to the presence of different minerals. Heterogeneity effects on colloid–rock surface interactions have been studied theoretically (Grindrod 1993) and experimentally by the  $\mu$ -Particle Induced X-Ray Emission ( $\mu$ PIXE) technique (Alonso et al. 2003a). Studies were performed by contacting granite sheets to colloid solutions under various chemical conditions to analyze the sorbed colloids on granite surfaces. The granite areas were in contact with europium-traced bentonite colloids at pH 5. Europium presented almost 100% sorption onto the clay colloids, and no desorption from the bentonite colloids to the granite surface was detected within the experimental times, thus europium acts as bentonite colloid indicator. Europium labelled bentonite colloids presented a clear relationship with the iron presence, usually related to minerals like biotite or other micas. This was in agreement with an expected attractive electrostatic interaction between positively charged minerals and negatively charged colloids when  $\text{pH} = 5$ . Even in the case where both the colloids and rock surface should electrostatically repel each other, colloid deposition was as well detected.  $\mu$ PIXE allowed not only detection the colloids but also of the mineral phases responsible for the colloid attachment. Results showed that the

measured colloid–rock surface interactions could be explained by repulsive and attractive interactions between charged colloid and surface-charged minerals.

Elimelech (1991) and Swanton (1995) have considered a number of explanations for the observed discrepancies between theory and experiments. Retention was insensitive to flow rates; other considered explanations included a distribution of surface potential, hydrodynamic effects and surface roughness. The disparities were not completely resolved even when those effects were included. It was suggested that the discrepancies with regard to particle size effects were related to the failure of DLVO theory to account for the dynamics of particle interactions. The values calculated for the deposition velocities, accounting for gravitation effects, could neither explain the observed deposition, and it was suggested that in general, particle repulsion reduces sedimentation by blocking effects (Song and Elimelech 1993, Liu et al. 1995).

Possibly the geochemical conditions favoured the colloid aggregation, e.g. increasing the sedimentation rate by the filter ripening phenomenon (Yao et al. 1971). Also chemical effects, like surface (co)precipitation, may enhance the colloid–rock interactions when favourable electrostatic interactions do not exist. The kinetics of the attachment or detachment of colloids to mineral surfaces and the nature and potential reversibility of this interaction are relevant for the understanding about the processes affecting radiocolloid mobility. Complementary studies on colloid–rock interactions with different techniques as AFM (Toikka and Hayes 1997) and X–ray based techniques could help to quantify the mechanisms that lead to colloid filtration in the rock. The up-scaling from laboratory experiments to *in situ* is an issue that need to be evaluated as well for assessing the relevance of colloid–mediated transport.

Crist et al. (2004) have developed a real time pore–scale visualization method of studying the sorption of colloids at the air–water interface. The method is based on the light transmission technique for fingered flow studies in packed sand infiltration chambers combined with high–resolution, electro-optical hardware and imaging software. Infiltration and drainage of suspensions of hydrophilic negatively charged carboxylated latex micro spheres provided to compel visual evidences that colloid retention in sandy porous media occurred via trapping in the thin film of water where the air–water interface and the solid interface meet, the air–water–solid interface. This modified theory of trapped colloids was able to explain the apparent discrepancy between the experimental evidences of hydrophilic colloids seemingly partitioning to the air–water interface. It also explains more recent findings that suggest this type of colloid does not adsorb at the air–water interface.

## 7.2 Colloid diffusion within the rock matrix

Due to very low porosity (0.2–1%) of crystalline rock colloid diffusion is considered a minor mechanism and expected to depend on colloid size distribution and rock matrix pore space. A method based on the ion nuclear beam technique Rutherford Back-scattering Spectrometry (RBS) (Ryan 2004) was applied to assess whether colloids are able to diffuse within the rock. The method allowed experimentally obtaining bentonite colloid (~ 250 nm) diffusion within a low permeability medium (Alonso et al. 2003a, 2003b, Patelli et al. 2006). Apparent diffusion coefficients,  $D_a \approx 7.5 \cdot 10^{-17} \text{ m}^2 \cdot \text{s}^{-1}$ , were

clearly slower than those measured for europium,  $D_a \approx 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$  (Alonso et al. 2006). Colloid diffusion in granite and the effect of colloid size was measured using gold colloids of different sizes from 2 nm to 250 nm (Alonso et al. 2006, 2007). It was found that colloid diffusion was dependent on size. The measured apparent diffusion coefficient,  $D_a$ , was  $7 \cdot 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$  for 2 nm and  $0.5 \cdot 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$  for 100 nm colloids. 250 nm colloids did not diffuse within the rock, emphasizing the influence of the pore size on the colloid size ratio. Based on the properties of granite, the estimated effective diffusion coefficient,  $D_e$ , was  $1.75 \cdot 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$  for 2 nm colloids. Diffusion coefficients measured for gold colloids in granite were about five orders of magnitude lower than values for weak or non-sorbing solutes under the same experimental conditions. The void pores accessible to transport decreased as particles accumulated thus hindering the access of other colloids and restricting diffusion. Clogging time presented a linear dependence with the particle diameter, confirming that at higher diameters, the saturation begins earlier. From this relationship it was possible to estimate the maximum particle size of 123 nm that can access to the granite in the experimental conditions. Evidently, a diffusion coefficient of such magnitude, and the observed colloid limited access, discards colloid diffusion as the main factor responsible for colloid filtration. However, the possibility of introducing experimental values in theoretical transport codes can help to identify and quantify other filtration mechanisms.

### 7.3 Radionuclide sorption onto colloids

The distribution of radionuclide ions between mobile colloidal and immobile rock phases determines radionuclide mobility. It can be quantified by batch experiments that determine the distribution coefficients,  $K_d$ , the distribution ratio of radionuclide between solid and liquid phase. The distribution coefficients ( $K_d$  in  $\text{mL} \cdot \text{g}^{-1}$ ) for several radionuclides, obtained at different contact times for the sorption of several elements onto bentonite colloids are presented in the literature (Geckeis et al. 2004, Missana et al. 2004). The  $K_d$  value gives a degree of sorption, but does not provide information on the sorption mechanism and it is argued to be conservative. Irreversible sorption would be favourable to safety, so neglecting it tends to over-estimate releases to the biosphere. Many repository performance assessments commonly use an assumption of reversible radionuclide sorption on the solid surface. Irreversible sorption on colloids may increase releases if colloids are sufficiently mobile. Significant sorption/desorption hysteresis was observed for the cesium sorption onto smectite and therefore can not be considered totally reversible within the laboratory time scale (Missana et al. 2004).

The study of radionuclide sorption mechanisms onto colloids requires the identification of the sorbing species and bonds. Techniques such as the Nuclear Magnetic Resonance (NMR) spectroscopy and X-Ray Photoelectron Spectroscopy (XPS) are sometimes applied to identify the different sorption mechanisms (Kim et al. 1994). The Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy technique is also applied to identify poly-nuclear surface species, mono, bi-dentate surface complexes and to differentiate inner and outer-sphere species (Sylwester et al. 2000, Dähn et al. 2002). Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is also applied to study the uptake mechanisms (Stumpf and Fanghänel 2002, Panak et al. 2003, Tertre et al. 2006) of trivalent actinides and lanthanides. Some studies revealed the formation of new solid phases on the surface that incorporate radionuclides (Stumpf and Fanghänel 2002). The



sorption mechanisms for the experimentally observed partly very slow sorption and desorption kinetics are unknown. In batch experiments containing dispersed colloids, a strong decrease of sorption on the granite and secondary phase minerals of a granite fracture was observed. The decrease was notable for the tri- and tetravalent actinide ions, and to a minor extent also for uranium in the oxidation state VI and cesium (Geckeis et al. 2004). To quantify the radionuclide/rock surface interactions, rock matrix heterogeneities have to be taken into account (Siitari-Kauppi et al. 1997, Missana et al. 2006).

Sorption of fission product radionuclides, Cs-137 and Sr-90, by Savannah River Site sediments impregnated with colloidal silica was studied by Hakem et al. (2004). Permeation grouting with colloidal silica gel is a potentially effective technique for creating hydraulic barriers to prevent the advective migration of radioactive contaminants in shallow permeable sediments. Batch sorption measurements with Cs<sup>+</sup> and Sr<sup>2+</sup> and silica gel and two kaolinitic sediments were conducted to evaluate the effectiveness of silica gel grouted barriers in the controlling transport of fission product radionuclides through sorption and diffusion. Sorption experiments were conducted both in the presence and in the absence of silica gel. Cesium and strontium concentrations varied between 10<sup>-3</sup> to 10<sup>-8</sup> M and 10<sup>-4</sup> to 10<sup>-8</sup> M, respectively. The pH values after one day varied for each experiment and ranged from 3.6 to 6.6. The pH of the solutions was buffered by the sediments and/or silica gel, and changed little over the duration of the experiments. The fraction of both cesium and strontium retained on the solids increased with decreasing radioelement concentration.

Lu and Mason (2001) have investigated the sorption and desorption behaviour of radioactive strontium on Ca-montmorillonite and silica colloids, and the effect of ionic strength of water on the sorption of strontium. Batch sorption experiments were conducted using Sr-85 as a surrogate for Sr-90 and groundwater from DP Canyon, Yucca Mountain, Nevada, and deionized water. The results showed that 92–100% of the Sr-85 was rapidly adsorbed onto Ca-montmorillonite colloids in all three waters. The ionic strength and Ca<sup>2+</sup> concentration in groundwater significantly influenced the adsorption of Sr-85 onto silica colloids. Desorption of Sr-85 from Ca-montmorillonite colloids was slower than from silica colloids.

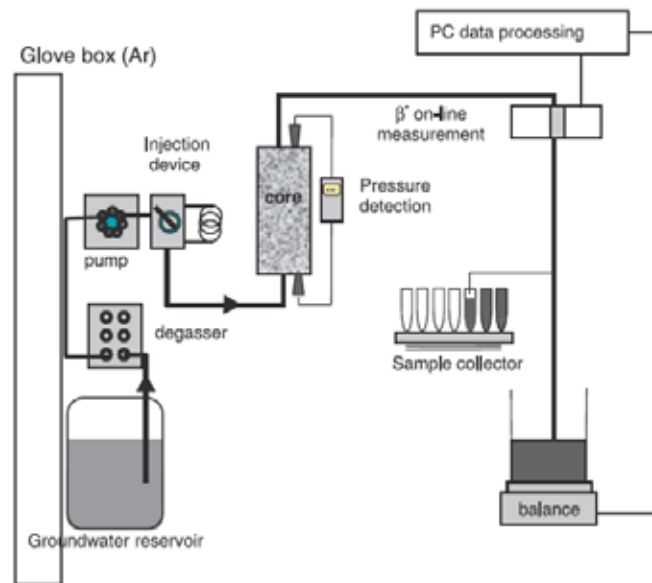
#### **7.4 Colloid transport**

At present, there are several projects running to elucidate colloid transport mechanisms, which demonstrate the particular interest in eliminating the uncertainties related to the colloid problem in the vicinity of a spent nuclear fuel repository. Various smectitic clays are in discussion as the backfill materials of EBS due to their swelling properties preventing water access to the waste and their strong sorption properties toward dissolved radionuclide species. A potential scenario in this repository setup is the mobilization of colloids at the EBS–groundwater interface, possibly promoting the transport of actinides by colloid migration. Especially under the low ionic strength conditions typical for granitic groundwater systems, colloids can be stabilized by their surface charge. To assess their migration properties and their potential role as radionuclide carriers, it is necessary to characterize the morphology and size distribution of such colloids.

At Nagra's Grimsel Test Site (GTS) colloid transport has been examined in two projects. The Colloid Formation and Migration project (CFM) aims to analyze the colloid generation and migration at the bentonite–groundwater interface in the underground laboratory as close as possible under realistic conditions. The next step (Phase II) in the CFM project of the bentonite/tracers/radionuclide emplacement has been planned to start in 2008. The colloid and radionuclide retardation (CRR) experiment is dedicated to study the *in situ* migration behaviour of actinides and fission products in the absence and presence of bentonite colloids in fractured rock. In the next period of CRR (Phase VI) several decades or several orders of magnitude longer experimental durations have been planned.

Within the EU project FUNMIG started in January 2005, the colloid issue is studied within different work packages. Field evidences of bentonite colloid generation at the FEBEX site are investigated and the mechanism related to colloid-borne migration is addressed. The FEBEX project was developed to demonstrate the feasibility of a compacted bentonite barrier, studying their thermo-hydro-mechanical behaviour. After already 7 years of continuous activity it is likely that in the vicinity of the gallery the bentonite barrier could have produced bentonite colloids that can be mobilized along the hydraulic field by advection.

Schäfer et al. (2004) have performed a core migration experiment in a granite fracture from the Grimsel Test Site. The solutions with  $10^{-6}$  M U(VI),  $10^{-8}$  M Th(IV) and  $10^{-8}$  M Eu(III) with and without addition of  $2 \text{ mg}\cdot\text{L}^{-1}$  bentonite colloids were injected using flow velocities  $46 \text{ m}\cdot\text{y}^{-1}$ ,  $94 \text{ m}\cdot\text{y}^{-1}$  and  $187 \text{ m}\cdot\text{y}^{-1}$ . Flow field–flow fractionation and ultrafiltration measurements showed that Th(IV) and Eu(III) were associated with colloids in both spiked natural groundwater with and without bentonite colloid addition. Measurements showed that U(VI) was not colloid borne. The partly unretarded U(VI) migration observed at short contact times (1–2 h) diminished under near natural groundwater velocities ( $46 \text{ m}\cdot\text{y}^{-1}$ ) and only a weak retardation ( $R_f = 19.5$ ) could be observed. Furthermore, the U(VI) mass recovery decreased with increasing contact time and was as expected unaffected by bentonite colloid addition. A groundwater colloid–mediated Th(IV)/Eu(III) migration without bentonite colloid addition could be confirmed in the core experiments but only at fast groundwater flow rates. Experiments at a water flow rate of  $94 \text{ m}\cdot\text{y}^{-1}$  demonstrated a partially bentonite colloid–mediated transport of Th(IV) 27% mass recovery and Eu(III) with 37% mass recovery. At long tracer residence times in the flow field, no breakthrough of colloidal Th(IV)/Eu(III) could be observed in both runs, indicating the strong dependence of reaction kinetics on their mobility. Reference colloid experiments using fluorescence dye labelled carboxylated polystyrene micro spheres (25 nm, 50 nm and 100 nm) revealed in general a higher recovery of smaller colloid size classes increasing with groundwater velocity. Additionally, an earlier peak arrival time of colloids and colloid-associated Th(IV) and Eu(III) was observed with respect to the conservative tracer HTO in all experiments due to pore-size or charge exclusion effects. In general, the colloid recoveries found in the laboratory core experiments were lower than those obtained in the field studies. The decrease of colloid mobility with increasing residence time suggests the occurrence of colloid attachment to the rock surfaces even under the colloid stabilizing groundwater conditions.



**Figure 7-2.** Setup of core migration experiments under argon inert gas conditions in a glove box. (Schäfer et al. 2004).

DiCarlo et al. (2006) have studied colloid transport and retention by *in situ* measurements using synchrotron X-ray fluorescence and  $\text{Cd}^{2+}$  ions attached to clay colloids. Synchrotron X-rays were used to cause the cadmium to fluoresce and by measuring the fluorescence and attenuation of the X-rays simultaneous *in situ* water saturations and colloid concentrations on the timescales of tens of seconds were obtained. The technique was used to study the transport of colloids consisting of sodium and calcium form montmorillonite clays through a preferential flow path in uniform well-sorted sand. This flow path had both saturated and unsaturated zones that travel downward with time. Sodium montmorillonite colloids showed slight retention in the sand while the calcium montmorillonite colloids were retarded with respect to the wetting front. By comparing the results with those obtained by infiltrations with a cadmium solute it was found that the retention of the colloids seen in the unsaturated portion of the column was no greater than that seen in the saturated portion.

To prove that colloid-mediated transport of radionuclides in a potential repository host rock may be significant to the long-term performance of a waste repository: colloids must be present, mobile and stable under the given groundwater conditions, radionuclide association with the colloids must take place and the association must be irreversible. The results for the CRR test in shear zone conditions indicated that the answer to the first four requirement was probably affirmative (Möri et al. 2003). Colloid formation was confirmed in a laboratory under dynamic and quasi-stagnant groundwater conditions, implying that colloids may be produced even in the absence of strong erosion forces. The concentration of colloidal material generated at the interface was observed to increase with increasing water flow. The injected bentonite colloids travelled along a 2.23 m flow path suggesting colloid mobility. Bentonite colloids showed high stability under the experimental groundwater conditions and the colloid size distribution was found to be rather constant over a period of approximately five months. Experimental findings from CRR experiment showed that bentonite colloids

influenced *in situ* retardation behaviour of tri- and tetravalent actinides in a significant way. Requirement about reversibility or irreversibility of radionuclide-colloid association must be investigated further in a simple system and the other processes examined in CRR, must be investigated in repository relevant conditions.

Alonso et al. (2006) have discussed whether colloids contribute to the radionuclide transport. They have reviewed the studies carried out to elucidate the colloid contribution to radionuclide migration, focused on the role of bentonite colloids formed at the bentonite–host rock interface in a spent nuclear fuel repository and considering an emplacement in crystalline rock. Many uncertainties still exist and as a result most performance assessment studies either treat such scenarios conservatively or do not include the influence of colloids in the calculations for evaluating the long-term behaviour of a high-level radioactive waste, basically due to the lack of quantitative data.

## 8 CONCLUSIONS

Colloidal silica called silica sol is a promising inorganic grout material for sealing small fractures in low permeable rock instead of cement-based grouts. Silica sol seems to be a feasible material to seal fractures with an aperture as small as 10  $\mu\text{m}$ . The silica sol gel is sufficiently stable to prevent water flow through the sealed fractures. The compatibility of silica sol with EBS materials is expected to be good. Chemical similarity between silica sol and water glass predicts that cement and silica sol will perform well together. The requirement that the pH should be below 11 is fulfilled if silica sol is used. No significant influence on the bentonite properties caused by the silica sol is expected when calcium chloride is used as an accelerator. The influence has not been examined when sodium chloride is used as an accelerator. No significant release of colloids is expected because the calcium and sodium concentrations in the groundwater are expected to be high enough to suppress colloid formation. The long-term stability of silica sol gel has not yet been clearly demonstrated and a long-term release of silica colloids cannot be excluded. If a dried undisturbed gel is saturated again, tests have shown that it will become even more brittle and fall apart releasing colloidal particles. The purpose of the colloidal silica is to limit water ingress during the operational phase and it is not with the intention of having a long-term sealing effect. The role of colloids might not be significant until the possible release of radionuclides has taken place. The question is the amount of colloids and how mobile they are.

In granitic groundwaters, the total natural inorganic and organic colloid contents are reported being low ( $< 1 \text{ mg}\cdot\text{L}^{-1}$ ). This was also the case for the only sample collected so far from deep groundwater at Olkiluoto. Natural inorganic colloids consist of clay minerals, silica, pyrite, goethite and magnesium oxide. The bentonite buffer used in the EBS system is assumed to be a potential source of colloids. In a study in Olkiluoto to test whether bentonite might generate colloids in contact with the groundwater of different salinity, bentonite colloids were found only in low salinity groundwater. In general, low salinity water (total dissolved solids  $< 1 \text{ g}\cdot\text{L}^{-1}$ ) favours colloid stability and it has been observed that bentonite colloids remain stable in low salinity waters over long periods. Size resolution and detection limits depend for all methods on the nature of the sample and the composition of the colloids. A very critical point in colloid analysis is sampling and sample storage. Sorption onto sample vial surfaces, redox reactions for example by oxygen access to the sample, etc. can decrease or strongly increase the colloid population in the sample. The optimum characterization of colloids, therefore, requires the application of *in situ* analytical techniques. Sampling and analysis in the laboratory always holds the risk of artefacts.

Colloid-mediated transport of radionuclides may contribute to the long-term performance of a spent nuclear fuel repository. During the last decades, great progress has been made to quantify the colloid contribution to radionuclide migration theoretically and by conducting experimental studies in a laboratory and *in situ*. Many techniques and innovative approaches are being applied to give an answer to the question of colloid relevance in a repository system. Several studies have evidenced radionuclide sorption on colloids and the mobility of radiocolloids. The main uncertainties remain in the colloidal processes at the bentonite–granite interface, the quantification of colloid generation under realistic repository conditions and

establishing a colloid-source term. Mechanisms of radionuclide sorption onto colloids and rock surfaces at enhanced contact times are not yet clear which may complicate the application of common sorption model approaches. Sorption reactions where radionuclide interaction with the colloidal phase is characterized by a very slow radionuclide desorption rate may lead to an enhanced colloid-mediated radionuclide transport over large distances, provided the colloids are stable and mobile. The synergy of bentonite, organic and inorganic colloids are still unclear. Therefore, laboratory experiments in relevant conditions are needed to elucidate the underlying sorption mechanisms.

This literature survey on silica sol colloids will be followed-up with experimental studies in order to determine colloid release from silica sol gel, to follow the mobility and stability of silica colloids in groundwater and to study radionuclide sorption on silica colloids. The plan is to use the following procedure: silica gel samples will be stored in contact with low-mineralized groundwater simulates, colloid release will be followed by taking samples and analyzing the colloid size distribution and concentration, the stability of colloids will be identified by measuring particle size distribution, zeta potential, pH and conductivity. Malvern Zetasizer Nano equipment will be used to determine colloidal particle size distribution applying the dynamic light scattering method and zeta potential based on dynamic electrophoretic mobility. Chemical composition will be analyzed by ICP-MS spectrometry or of the dried colloid cake by X-ray diffraction and by gravimetry. The size and shape of colloids will be also investigated by concentrating colloids on membranes, which can be determined by scanning electron microscopy.

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