Role of inorganic colloids generated in a high-level deep geological repository in the migration of radionuclides: Open questions

Incertidumbres asociadas al papel de los coloides generados en un almacenamiento geológico profundo de residuos de alta actividad en la migración de radionucleidos

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Abstract

Do colloids contribute to the radionuclide (RN) transport in a high level radioactive waste repository (HLWR)? The fact is that, during the last decades, many theoretical and experimental studies, at laboratory and *in-situ* scale, have been devoted to give an answer to this question. However, many uncertainties still exist and as a result most performance assessment (PA) 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 HLWR, basically due to the lack of quantitative data.

The aim of this paper is to review the studies carried out during the last years to elucidate the colloid contribution to the RN migration, paying special attention to the role of bentonite colloids, formed at the bentonite/host rock interface in a HLWR and considering an emplacement in crystalline rock. The main uncertainties and present research projects and future research strategies will be highlighted.

Keywords: Radioactive waste repository, bentonite, granite, colloids, generation, mobility, filtration.

Resumen

¿Contribuyen los coloides al transporte de radionucleidos (RN) en un almacenamiento de residuos radiactivos de alta actividad? Lo cierto es que durante las últimas décadas multitud de estudios, tanto teóricos como experimentales, a escala de laboratorio e in-situ, se han dedicado a intentar dar una respuesta a esta pregunta. A pesar de los esfuerzos dedicados, existen todavía grandes incertidumbres y por ello, la mayoría de los estudios de evaluación de comportamiento (PA) de un almacenamiento no incluyen el efecto que los coloides pueden tener en el transporte de RN, básicamente por la escasez de datos cuantitativos al respecto.

El objetivo de este trabajo es hacer una revisión de los distintos estudios llevados a cabo los últimos años para elucidar el papel que juegan los coloides en el transporte de RN, prestando particular atención a los coloides de bentonita, que pueden generarse en la interfaz bentonita/roca de un almacenamiento. Se destacarán las principales incertidumbres asociadas, y los estudios y proyectos que actualmente se están realizando, haciendo hincapié en las futuras estrategias de investigación en esta área.

Palabras clave: Almacenamiento de residuos radiactivos, bentonita, granito, coloides, generación, movilidad, filtración.

1. Introduction

A geological repository for high-level radioactive waste (HLWR) consists on a multi-barrier system, emplaced hundred meters deep in a geological medium. In the main repository concepts, the waste would be located in metal canisters surrounded by a layer of compacted clay, i.e. bentonite. These engineered barriers constitute the *near field* of the repository. As host geologic formation, clays, crystalline rocks or salts are mainly considered, constituting the *far field* of the repository. In principle, it is expected that the canisters and the whole repository isolate the waste from the biosphere. Even in case of a canister failure, the compacted bentonite barrier will serve to stop or retard the radionuclide (RN) transport because of its high sorption capability for many radionuclides and low permeability. However, to guarantee the long-term safety of a repository, and for long-term performance assessment (PA) calculations, all mechanisms that could affect the RN migration rate within the barriers must be well defined and quantified.

The particular interest of this paper lies on the possible colloid contribution to the RN transport within the repository, considering an emplacement in a granite formation.

Why colloids may be relevant for RN transport? Colloids are particles suspended in a fluid, with diameters ranging from 1 nm to 1 μm, with high surface area and electrostatic charge (Hunter, 1986). The existence of colloidal phases may influence the radionuclide transport since due to their nature and dimensions they can be mobile. The formation of a stable dispersion requires sufficiently high surface charge that highly depends on the groundwater chemistry.

The initial interest of considering the colloid contribution, in the frame of a HLWR, came from the fact that many studies demonstrated that colloids may contribute to the transport of contaminants (Champ *et al.,* 1982; Eichholz *et al.,* 1982; McDowell-Boyer *et al.,* 1986; Buddemeier and Hunt, 1988; McCarthy and Zachara, 1989; Lieser *et al.,* 1990; Penrose *et al.,* 1990; Smith and Degueldre, 1993; Ryan and Elimelech, 1996; Kretzschmar *et al.,* 1999). For instance, the migration of Pu over a distance of kilometres far from nuclear test areas (Nevada Test Area, US) was attributed to colloid transport (Bud-

demeier and Hunt, 1988; Kersting *et al.,* 1999; Nuttal and Long, 1993). The association of RN released during the Chernobyl accident to colloidal material in surface water was also found (Matshunaga *et al.,* 2004).

In the repository scenario, several radiocolloids can be considered. On one hand, the RN themselves can exist in colloidal form (*eigencolloids or intrinsic colloids*). On the other hand, colloids of different nature, that can be generated in the barriers or natural groundwater colloids present in the systems, in certain conditions can adsorb radionuclides, forming what is known as *pseudo-colloids*.

To evaluate the colloid contribution to the RN transport, several conditions need to be considered (Miller *et al.,* 1994), mainly their existence, stability and mobility in the studied medium.

Firstly, it is necessary to know which colloids may be present in the repository. In this work, we focus only on inorganic colloids, even though biocolloids and organic matter may deserve equal attention. If a RN release from the waste form occurred, the first colloids to be considered are those possibly formed at the canister/bentonite interface, as colloidal precipitated radionuclide oxyhydroxides, secondary phase colloids formed during dissolution of vitrified waste (Bates *et al.,* 1992), or iron oxide colloids result of the water - canister interaction (Geckeis *et al.,* 1998). However, and despite there are not too much studies on colloid diffusion within media of low porosity as the compacted clay barrier, it is generally considered that the bentonite would act as a filter for these colloids (Kurosawa and Ueta, 2001; Wold and Eriksen, 2003).

Therefore, the colloids that should be next taken into account are those existing (groundwater colloids) or generated at the bentonite / host rock interface, as intrinsic colloids or bentonite colloids. At this interface, groundwater contacting the bentonite favours the swelling of the clay, promoting both the clay intrusion into the host-rock pores and micro-fractures and the formation of colloidal phases (Pusch, 1999). Since these clay particles have high sorption capability for many radionuclides, under certain circumstances, they could influence the RN migration, provided they are mobile (McCarthy and Degueldre, 1993).

To assess the relevance of colloids for the RN migration at the bentonite / granite interface of a HLWR, several processes need to be studied, as sketched in figure 1.
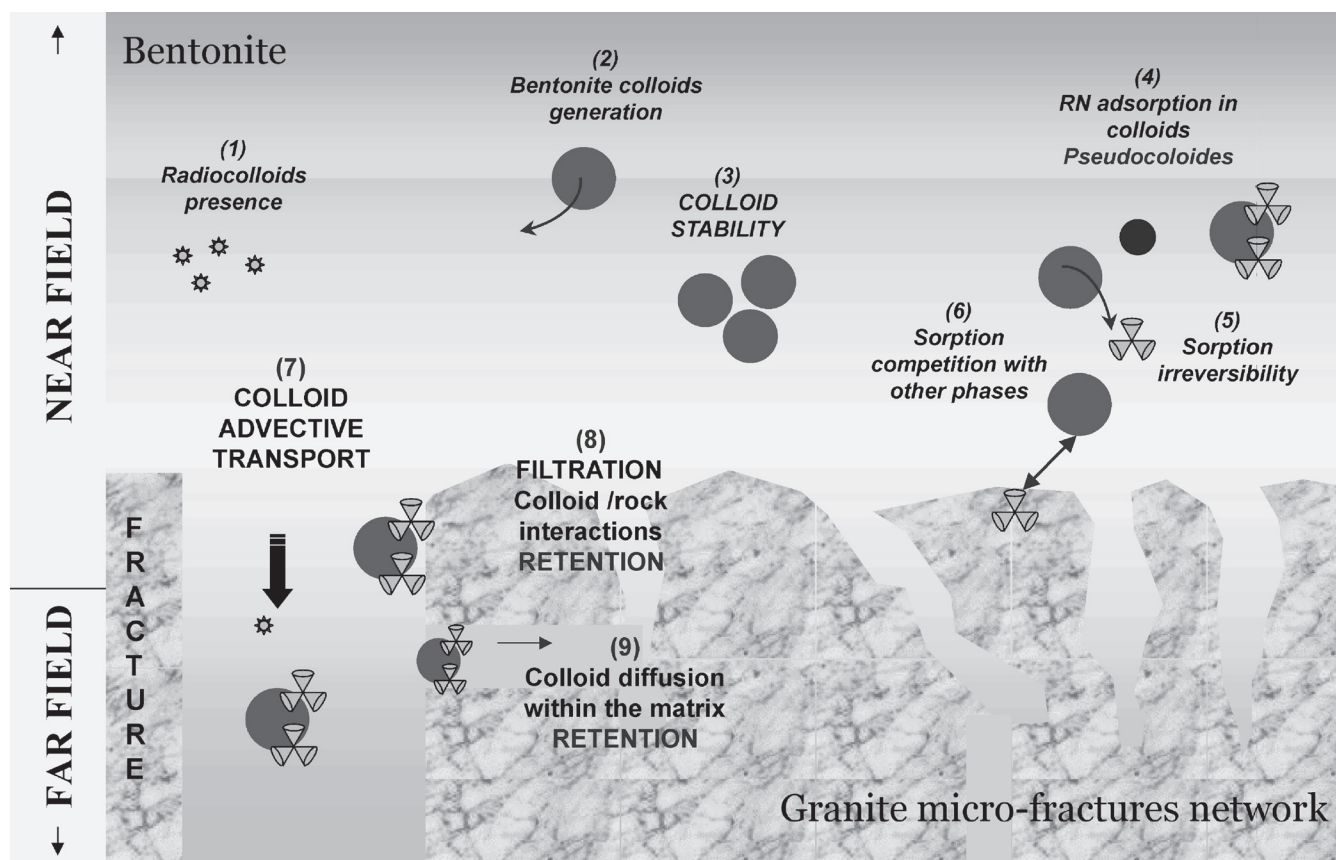
Fig. 1.- Schematic diagram of the colloid processes necessary to inspect at the bentonite/granite interface in order to assess their importance for radionuclide migration.

Fig. 1.- Esquema de los procesos que es necesario conocer para predecir el destino de los coloides en la interfaz bentonita/granito y determinar su influencia en el transporte de radionucleidos.

Firstly, the colloids have to exist at relevant concentration levels: Those colloids may be natural groundwater colloids, precipitated dispersed RN in colloidal form (*eigencolloids or intrinsic colloids*) (1) or generated bentonite colloids (2). Assuming the colloids are stable (3), they can adsorb RNs (4): *pseudo- colloids*. In that sense, the irreversibility of the RN binding to colloids (5) and the competition of colloids and rock surfaces in terms of RN sorption (6) are related key-points necessary to evaluate for the assessment of the 'colloid problem' (Cvetkovic *et al.,* 2004; Honeyman, 2001). A final prerequisite for considering the colloid relevance is that the colloids have to be mobile within the rock. In the case of fractured rocks, advective transport is expected to be the main transport mechanism for colloids (7). As sketched in figure 1, several filtration mechanisms as surface retention (8) or matrix diffusion (9) are counteracting processes.

Comprehensive reviews concerning colloid-mediated contaminant transport in groundwater systems can be found in the literature (Ryan and Elimelech, 1996; Kretzschmar *et al.,* 1999; Honeyman, 2001; Moridis *et al.,* 2003), where it was always pointed out that many open questions still exist, as for instance the evaluation of colloid-contaminant kinetic interactions and colloid filtration mechanisms within the medium. As general research needs, the acquisition of experimental data sets to validate theoretical models, the up scaling from laboratory to real scale and the need of accounting for the medium heterogeneities were pointed out. Concerning to the fate of colloids at the bentonite / host rock interface of a repository, a specific and detailed studied in a rather complex system is required to predict the long-term behaviour (van der Lee *et al.*, 1994). The aim of this paper is to review the studies carried out during the last years to elucidate the colloid contribution to the RN migration, paying special attention to bentonite colloids. In particular, we would like to highlight the main associated uncertainties, pointing out the main achievements and open questions, mentioning the present projects and possible further research strategies. It is that obvious that the application of innovative analytical techniques in laboratory and field investigations is required to quantify all processes that influence colloid-borne RN migration and to complete the fundamental understanding needed to facilitate the transfer of information to performance assessment (PA).

Following the outline of mechanisms that affect the colloid-mediated radionuclide transport, presented in figure 1, the paper is structured in five sections that include (1) colloid existence and generation at the bentonite/granite interface, (2) colloid stability, (3) radionuclide sorption onto colloids; sorption irreversibility and sorption competition with other phases, (4) the colloid mobility within a granitic medium and (5) the main colloid retention mechanisms.

2. Main achievements and open questions

2.1. Colloid presence and generation at the near/far field interface of a HLWR

2.2.1. Natural colloids in a crystalline environment

In a first step to assess the relevance of colloids to the transport behaviour of radionuclides, studies aim to analyse and to quantify colloid populations in deep granite waters. Because of the low concentration of natural colloids present in groundwaters, these studies are basically subjected to the resolution of analytical techniques available. In the beginnings, the studies were performed by filtration or ultracentrifugation techniques, or Photon Correlation Spectroscopy (PCS) (Koppel, 1972; Ledin *et al.,* 1994). As example of natural colloids evaluation, at the underground laboratory in the granitic massif of the Grimsel Test Site, in Switzerland (GTS) (Degueldre *et al.,* 1989a; Degueldre *et al.,* 1989b; Degueldre *et al.,* 1996), different studies demonstrated that the colloidal concentration found in fairly stationary conditions were rather low (0.2 mg/L) and their formation was attributed to mechanical processes due to erosion caused by the water flow or small tectonic movements. Re-suspension from fissures or fractures was observed as well (Degueldre *et al.,* 1989a). Also in Spain, a study performed at the El Berrocal granite massif demonstrated the existence of natural colloids at very low concentration (< 0.1 mg/L), even if the low salinity of the groundwater represented a very favourable medium for colloids (Gómez *et al.,* 1992; Turrero *et al.,* 1995; Turrero, 2002).

As a general conclusion, it can be said that 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. Therefore, 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 (Swanton, 1995).

2.2.2. Intrinsic colloids

The analysis of intrinsic colloids in the water is in many cases hampered by their small size (<1-2 nm) and their low concentration. The investigation of such colloids and the elucidation of their geochemical behaviour and colloid-formation mechanisms in general call for extremely sensitive analytical tools. Many studies have, however, demonstrated that the aqueous speciation of tetravalent actinides is very often dominated by colloids (Olofsson *et al.,* 1982; Lieser *et al.,* 1986; Kim and Kanellakopulos, 1989; Nagasaki *et al.,* 1998). Such behaviour can be rationalized by the low solubility of tetravalent actinide hydroxides and their tendency to form polymers. Recently, innovative techniques have been developed to study the radionuclide colloids in groundwater at even trace concentration. The Laser-Induced Breakdown Detection (LIBD) exhibits a very high sensitivity for the detection of colloids, being it many magnitudes superior to that of light scattering methods, particularly in the particle size range < 50 nm (Walther *et al.,* 2002). Other techniques such as Flow Field-Flow Fractionation (FIF-FF) combined with different detection modes (Geckeis *et al.,* 2003; Gimbert *et al.,* 2003) or the Single Particle Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) (Degueldre and Favarger, 2003), have been also successfully applied. 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 to sample vial surfaces, redox reactions by e.g. oxygen access to the sample, etc. can decrease or strong increase the colloid population in the sample. 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. Devices like a mobile LIBD arrangement are described and have been recently applied in field studies (Hauser *et al.,* 2002; Hauser *et al.,* 2003).

2.2.3. Bentonite colloids

The bentonite barrier is considered a potential source of colloids. Bentonite colloid generation at a HLWR, was investigated at 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.,* 2003a). The main results of these experiments were the demonstration of the detachment of solid particles (> 1 μm) and colloids (< 1 μm) 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 approximately, according to Photon Correlation Spectroscopy (PCS) measurements, as can be seen in the SEM image in figure 2 (Missana *et al.,* 2003a). Colloid concentration was found to mainly depend on the flow conditions but appears to be widely independent on the chemical variations (e.g. water salinity). Such finding suggests that the colloid generation was mainly induced by 'mechanical' erosion at the clay surface. However, 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. Nevertheless, the quantification of the colloidal source term in a repository containing a bentonite barrier deserves further investigation also in larger-scale test under 'realistic' in-situ conditions. In that sense, further efforts are needed to evaluate the different processes that could lead to a bentonite colloid generation depending on geochemistry and hydrodynamics. High groundwater flow produces mechanical forces that favour the detachment of colloidal particles (Ryan and Gschwend, 1994). Flow rates in a repository, however, are believed to be low so that such processes are considered as less relevant, and it has been reported that, 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 waters of low salinity (Pusch, 1985).

Thus, the quantification of the colloid generation rates under low groundwater flow and the elucidation of geochemical processes at the bentonite/host rock boundary under in-situ conditions are open questions related to the bentonite colloid generation, that are absolutely fundamental to assess the colloid relevance on radionuclide migration.

2.2. Colloid stability

The potential relevance of colloids for radionuclide transport is highly dependent on their stability in different chemical environments. The theoretical analysis of the interaction between two colloidal particles was first developed by Derjaguin, Landau, Wervey and Overbeek, in what is commonly kwon as the DLVO theory (Derjaguin and Landau, 1941; Wervey and Overbeek, 1948). This 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 competition of these two forces will determine the colloid stabil-
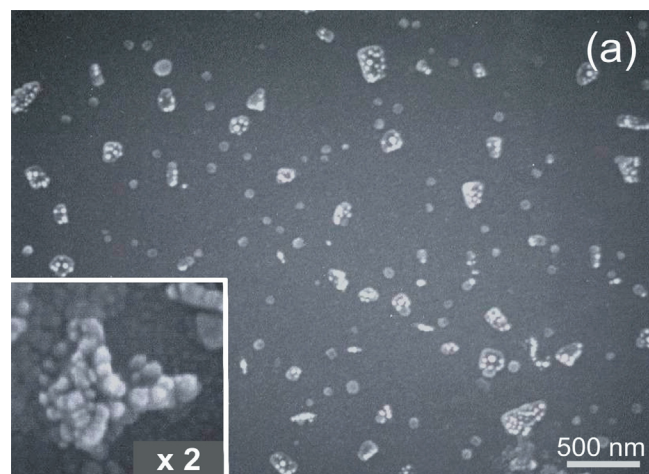

Fig. 2.- SEM image of bentonite colloids generated at the granite/ bentonite interface in dynamic experiments. In the inset, a detail of the structure of bentonite colloids can be appreciated.

Fig. 2.- Imagen de microscopía SEM de los coloides de bentonita generados en la interfaz bentonita /granito en experimentos dinámicos. En el insertado de la figura se presenta la estructura en detalle de estos coloides.

ity. Obviously the colloids will remain stable, avoiding coagulation, if the repulsive term exceeds the attractive interaction. The DLVO theory is generally applied to describe colloid stability and agglomeration rates. But, however, it was also demonstrated that the application of DLVO models to heterogeneous natural systems has its limitations. For instance, it was observed that the prediction of bentonite colloid stability by a simple DLVO approach deviates from experimental findings (Missana and Adell, 2000). An experimental study on the coagulation kinetics of natural bentonite colloids performed 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 (pH$\geq$8) the edge sites are negatively charged and thus impose a high colloidal stability to clay dispersions. Also, it was shown that high bivalent cation concentration would decrease bentonite colloids stability, in agreement with observations found for other natural colloids (Degueldre *et al.*, 1996; Degueldre *et al.*, 2000). In general, low salinity waters ($\sim 1\cdot 10^{-3}$ M) favours bentonite colloids stability (Missana *et al.*, 2003a). It was observed that the bentonite colloids remained stable in waters of low salinity over long periods. However, 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. In addition, in groundwaters probed at the Äspö hard rock laboratory, it was found that at ionic strength values > 0.2 mol/L, natural colloid concentrations can drop to very low values (< 25 µg/L) (Hauser *et al.*, 2003).

Further, temperature effects in the repository case may affect colloid stability. In the near field of a nuclear repository, the temperature can rise up to 150 ºC. 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 Brownian motion, variations in surface charge and influences from the temperature dependent electrolyte behaviour (Mohtadi and Rao, 1973; Luckham and Rossi, 1999). As example, the hydrodynamic diameter (nm) of hematite colloids measured by PCS as a function of the temperature is shown in figure 3. It can be appreciated that, as expected, an increasing of the temperature promotes the colloid aggregation. This agglomeration will significantly affect settling rates and transport (retention). Quantification, however, 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 closure of a HLWR. Taking as an example the 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 ºC at the waste form surface (simulated by an electrical heater), over 85 ºC at the canister/bentonite barrier to about 30 ºC at the bentonite/granite interface (Huertas *et al.,* 2000). In the course of time, these temperature gradients can significantly influence not only many proprieties of the bentonite barrier but also the colloid stability and should be accounted for the evaluation of the colloid contribution to RN transport in the *near field*.

2.3. Radionuclide sorption onto colloids

Putting intrinsic colloids aside, strong RN sorption onto colloids is a necessary condition for the existence of colloid-mediated RN migration. Radionuclide sorption to solids can be quantified by the so-called batch experiments that determine the distribution coefficients K_d, i.e. the distribution ratio of the radionuclide between solid and liquid phase. As an example for the different behaviours of several RNs, the distribution coefficients (K_d in mL/g) obtained at different contact times for the sorption of several elements onto bentonite colloids are presented in Table 1 (Missana *et al.,* 2003b; Geckeis *et al.,* 2004; Missana *et al.,* 2004). The K_d approach gives an idea of the degree of sorption, but does not provide information on the sorption mechanism and it is argued to be conservative. If slow or irreversible sorption were to occur, it 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 RN sorption on the solid surface. However, slow or irreversible sorption on colloids may increase releases if colloids are sufficiently mobile. Indeed, some elements exhibit a significant sorption / desorption hysteresis. This was observed for the cesium sorption onto smectite and therefore cannot be considered totally reversible within the laboratory time scale (Missana *et al.,* 2004). Sorption reactions, where the 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.

Therefore, laboratory experiments are absolutely needed to elucidate the underlying sorption mechanisms. A quantitative description of solid-liquid interface reactions based on surface complexation models (e.g. in Bradbury and Baeyens, 1993; Bradbury and Baeyens, 2002), can only be applied if sorption mechanisms are fully understood and the sorption reaction can be described by dynamic equilibrium complexation constants. Without the validation of underlying sorption reaction mechanisms, the development of surface complexation models is al-
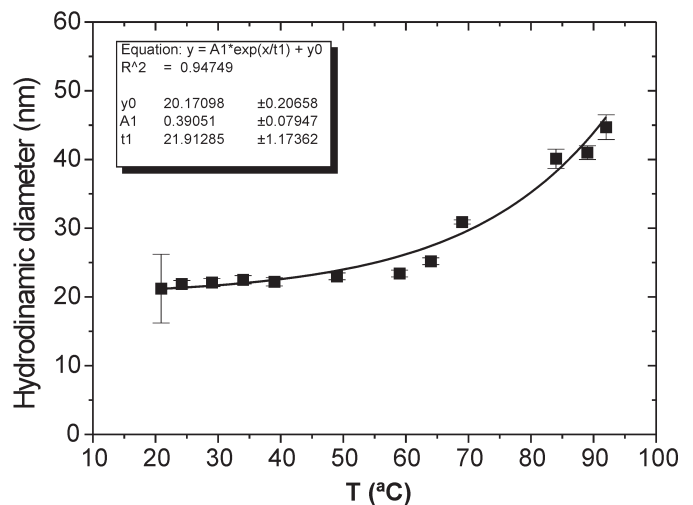

Fig. 3.- Hydrodynamic diameter of hematite colloids as a function of temperature measured by Photon Correlation Spectroscopy (PCS).
Fig. 3.- Medida de Espectrometría de Correlación Fotónica (PCS) del diámetro hidrodinámico de coloides de hematites en función de la temperatura.

CONTACT TIME

	1 week	2 weeks	4 weeks	12 weeks	18 weeks
^{137} Cs (I) (1.10·10^{-7} M)	8746 ± 900 (mL/g)	6422 ± 600 (mL/g)	6849 ± 250 (mL/g)	8492 ± 250 (mL/g)	not determined
^{233} U (VI) (4.04·10^{-7} M)	824 ± 50 (mL/g)	1050 ± 50 (mL/g)	1420 ± 50 (mL/g)	1508 ± 50 (mL/g)	1628 ± 50 (mL/g)
^{99} Tc (VII) (5.33·10^{-7} M)	0 (mL/g)	0 (mL/g)	0 (mL/g)	6.5 ± 2 (mL/g)	46±15(mL/g)
^{75} Se (IV) (1.36·10^{-7} M)	7.0 ± 3 (mL/g)	14 ± 1 (mL/g)	11 ± 3 (mL/g)	45 ± 9 (mL/g)	27 ± 9 (mL/g)
^{99} Tc (IV) (4.5·10^{-9} M)	361.18±50 (mL/g)	482.27±50 (mL/g)	470.40±70 (mL/g)	446.81±50 (mL/g)	n.d.

Table 1.- Distribution coefficients (K$_d$ in mL/g) obtained at different contact times for the sorption of several elements onto bentonite colloids.

Tabla 1.- Coeficientes de distribución (K$_d$ en mL/g)) obtenidos a distintos tiempos de contacto para la sorción de diversos elementos en coloides de bentonita.

ways hampered by uncertainties in the postulation of the relevant surface species. In addition, surface complexation models do not account for sorption/desorption kinetics, which is a main issue of concern.

Thus, the study of the underlying RN sorption mechanisms onto colloids requires the identification of the sorbing species and bonds. Techniques such us the Nuclear Magnetic Resonance (NMR) spectroscopy and X-Ray Photoelectron Spectroscopy (XPS) are sometimes applied to identify the different sorption mechanisms (Weiss *et al.*, 1990; Kim *et al.*, 1996). 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 ad outer-sphere species (Sylwester *et al.*, 2000; Dähn *et al.*, 2002; Nakano *et al.*, 2003). Time Resolved Laser Fluorescence Spectroscopy (TRLFS) is also applied to study the uptake mechanisms (Stumpf and Fanghänel, 2002; Panak *et al.*, 2003; Wang *et al.*, 2005) of trivalent actinides and lanthanides. Some studies revealed the formation of new solid phases at the surface, incorporating the radionuclides (e.g. Stumpf and Fanghänel, 2002). Such processes might be responsible for experimentally observed 'hysteresis' effects of sorption / desorption reactions. But still, the sorption behaviour of many radionuclides is not yet fully understood, and the underlying mechanisms for the experimentally observed partly very slow sorption and desorption kinetics are unknown.

Nonetheless, the distribution of radionuclide ions between the mobile colloidal and immobile rock phases obviously determines their mobility and thus has to be deeply investigated and quantified. For instance, in batch experiments containing dispersed colloids a strong decrease of sorption to granite and minerals being present as secondary phases in a granite fracture was observed for notably the tri- and tetravalent actinide ions and to a minor extend also for uranium in the oxidation state VI and cesium (Missana *et al.*, 2003b; Geckeis *et al.*, 2004). To quantify the radionuclide/rock surface interactions, accounting for the rock heterogeneities is as well a fundamental issue that is discussed in this volume in a separated paper (Missana *et al.*, this volume).

2.4. Colloid mobility

As a final criterion for the assessment of colloid relevance to radionuclide migration remains the question regarding colloid mobility in a natural system.

In crystalline rocks, the colloid transport is expected to mainly take place by advection in conductive fractures. Colloid transport is significantly different to that of a solute since, due to their surface charge, colloids suffer interactions with the rock surfaces. Because of that, the colloid transport is difficult to describe and there are many aspects to be considered, as water flow, geochemical conditions, colloid size distribution, and also the nature of the surfaces of the surrounding rock and of the colloids, which interactively determine whether colloids are retained or not within the rock (Saiers *et al.,* 1994; Yan *et al.,* 1995).

The colloid mobility in a fracture has been scarcely investigated in transport experiments (i.e. Vilks *et al.,* 2003). But in particular, the bentonite colloid transport within

a granite fracture was recently investigated by complementary laboratory (Missana *et al.,* 2002; Missana *et al.,* 2003a; Schäfer *et al.,* 2004) and in-situ studies within the Colloid and Radionuclide Retardation Experiment (CRR project) (Hauser *et al.,* 2002; Möri *et al.,* 2003; Geckeis *et al.,* 2004). The influence of the bentonite colloids on the RN transport within a granite fracture was studied under in-situ conditions in the Grimsel Test Site (GTS) underground laboratory applying an hydraulic dipole (injection flow: 10 mL/min; extraction flow: 150 mL/min), and compared with the RN transport of some elements in absence of those bentonite colloids. In accompanying laboratory-column studies, a granite core from the GTS, 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 unretarded, compared to the water flow, other colloids eluted retarded and a colloid fraction was filtered in the medium. The different behaviors 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 was satisfactory, accounting for different parameters (Möri *et al.,* 2003; Kosakowski, 2004; Kosakowski and Smith, 2004; Möri, 2004). But however, it was pointed out that the underlying mechanisms that lead to colloid retardation and filtration are still not understood. An adequate description of colloid-mediated transport within natural media requires the identification and quantification of colloid retention mechanism accounting both the colloid and medium main characteristics.

2.5. Colloid filtration mechanisms

In general, all processes that contribute to eliminate colloids from the aqueous phase are comprised in the term "filtration" (Yao *et al.,* 1971; Rajagopalan and Tien, 1976) that can be due to physical-chemical interactions or to mechanical processes (dead-end pores, cavities, etc.) (Kretzschmar *et al.,* 1999). Colloid matrix diffusion is not considered as filtration mechanism (Cumbie and McKay, 1999), but it is theoretically included in many transport models, as responsible of the observed colloid retention (Smith and Degueldre, 1993; Oswald and Ibaraki, 2001).

A straightforward modeling, should include all relevant processes, as colloid attachment to reactive sites at the rock surface, physical filtration of larger particles due to small matrix pores, or matrix diffusion (Chrysikopoulos,

1998; James and Chrysikopoulos, 1999). In general it is not easy to weigh up these different mechanisms involved in colloid retardation/retention from advective experiments. Colloid retention at the fracture walls is mostly theoretically described by introducing an empirical filtration factor in the transport equation, which accounts for any mechanism (i.e. Kessler and Hunt, 1994; Logan *et al.,* 1995; Moreno *et al.,* 1998; Cvetkovic *et al.,* 2004). This underlines the necessity for gaining a deeper understanding of the colloid filtration mechanisms and the need of determining experimentally filtration parameters.

2.5.1. Colloid diffusion within the rock matrix

Recently, a methodology based on the ion nuclear beam technique Rutherford Backscattering Spectrometry (RBS) (Chu *et al.,* 1978; Ryan, 2004) was applied to assess whether bentonite colloids are able to diffuse within the rock (Alonso *et al.,* 2003a; Alonso *et al.,* 2003b; Patelli *et al.*, 2005). The proposed methodology allowed experimentally obtaining, for the first time, bentonite colloid (of about 250 nm) diffusion within a low permeability medium. The apparent diffusion coefficients calculated with this methodology, $D \approx 7.5 \cdot 10^{-17}$ m^2/s, were clearly slower than those measured for Eu in solution (10^{-14} m^2/s) (Alonso *et al.,* 2005).

In a further work, similar diffusion coefficients (10^{-18} m^2/s) were obtained for the diffusion of model gold colloids of different sizes (2 nm to 250 nm) within granite (Alonso *et al.,* 2002). Moreover, it was observed that the colloid access to the granite is restricted.

In figure 4A the gold concentration that acceded to the granite samples, for the different colloid sizes as function of time is presented. It can be appreciated that the Au access initially increases with time, but later tends to a saturation value that is also dependant on the colloid diameter. This indicates that the solid surface (void pores) accessible to the transport decreases as particles accumulates thus hindering the access of other colloids and restricting the diffusion. Taking from figure 4A, the time in which saturation occurs (96% of the total concentration), defined as *clogging time* is plotted in figure 4B as function of the colloid size. It can be seen that this clogging time presents 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 that can accede to the granite, in the experimental conditions (123 nm). Evidently, a diffusion coefficient of such magnitude, and the observed colloid limited access, discards colloid diffusion as the main responsible for colloid filtration. However, the possibility of introducing experimental values in theoretical
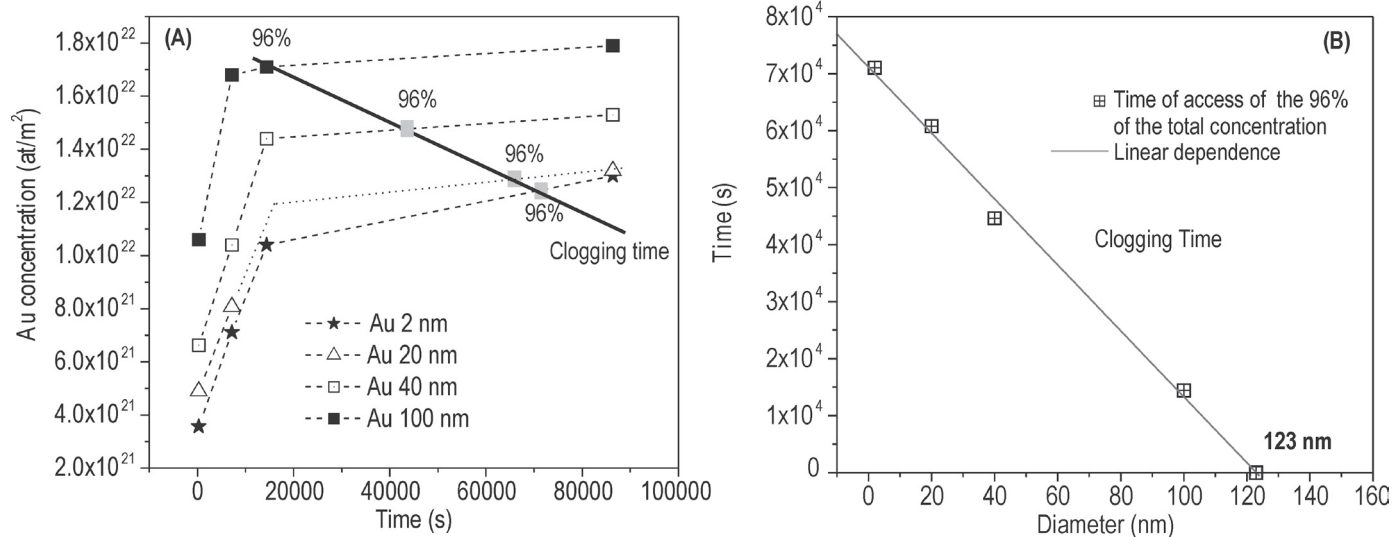
Fig. 4.- (A) Au concentration found inside the granite after the contact with Au colloids suspensions of different sizes, (★) 2 nm, (∇) 20 nm, (□) 40 nm and (■) 100 nm, as a function of the contact time. (B) *Clogging time* as function of the colloid diameter.

Fig. 4.- (A) Concentración de Au medida dentro del granito después del contacto con coloides de Au de distintos tamaños (★) 2 nm, (∇) 20 nm, (□) 40 nm and (■) 100 nm, en función del tiempo de contacto. (B) Representación del *tiempo de atasco* en función del diámetro de coloide.

transport codes can help to identify and quantify other filtration mechanisms.

2.5.2. Colloid/rock surface interactions

The quantification of the colloid / rock interactions are fundamental to determine colloid retention (Elimelech, 1991; Ryde *et al.,* 1991). Considering the high heterogeneity that exhibits the granite surface, due to the presence of different minerals, and to the pores size distribution or roughness (Saiers *et al.,* 1994), the evaluation of the surface area available for colloid retention is a fundamental parameter, however, almost no experimental determination exists (Toran and Palumbo, 1992) and most of the available data is based on theoretical models (Grindrod, 1993; Ibaraki and Sudicky, 1995a; Ibaraki and Sudicky, 1995b).

The colloid interactions with the rock surface 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. In figure 5, the ζ - potentials measured for the granite and minerals such as biotite, muscovite, feldspar and a mixture of quartz and plagioclase, as function of the pH are plotted. It can be seen that whereas the granite has, in average, a negative surface charge in the all 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 pH < 6. This is an important fact since, considering the colloid sizes (< 1 μm), a single particle will not be affect-

ed by the average rock surface charge but by the specific charge of a certain mineral (Song and Elimelech, 1993; Song *et al.,* 1994).

This heterogeneity effect on colloid/rock surface interactions has been theoretically studied (Grindrod, 1993; Velegol and Thwar, 2001) and recently experimentally studied by the μ-Particle Induced X-Ray Emission (μPIXE) technique (Johansson and Campbell, 1988). Studies were performed by contacting granite sheets to colloid solutions under various chemical conditions to analyse the sorbed colloids at the granite surface. The μPIXE allows not only detecting the colloids but also the mineral phases responsible for the colloid attachment (Alonso *et al.,* 2004). Results showed that the measured colloid/rock surface interactions could be explained by repulsive/attractive interactions between charged colloid and surface-charged minerals, when "favourable" areas, in terms of an electrostatic interaction, exist. For example, the case of granite areas studies after the contact with Eu-traced bentonite colloid at pH 5 is presented in figure 6. The distribution maps of the Si, Al, Fe, Ce, K, Ti, and the signals from different X-ray emission lines for Eu (Kα, and Lα) content measured on two different 2*2 mm² granite area after 7 days of contact with the Eu-traced bentonite colloids are presented. Please note that Eu 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 the Eu acts as bentonite colloid indicator. In figure 6, the Eu (and therefore the bentonite colloids) presents a clear

relationship with the Fe presence, usually related to minerals as biotite or other micas. This is in agreement with an expected attractive electrostatic interaction between positively charged minerals and negatively charged colloids in these conditions (pH = 5). Surprisingly, even in the case where both the colloids and rock surface should electrostatically repel each other, colloid deposition was as well detected. This can be observed in figure 7, where (at pH 9) the Eu-traced bentonite colloids are on the surface, not specifically related to any mineral, even though both the whole granite surface and the colloids presented a negative charge, unfavourable for an attractive interaction according to zeta potential measurements (Fig. 5). Similar observations have been reported by other authors as well (Elimelech and O'Melia, 1990; Swanton, 1995) that concluded that classical models failed to predict colloid retention under 'unfavourable' conditions. Therefore other mechanisms are responsible of the colloid deposition in the "electrically unfavourable" case. It is worth mentioning that the values calculated for the deposition velocities, just accounting gravitation effects, could neither explain the observed deposition, and it is reported that in general particle repulsion reduces sedimentation by blocking effects (Song and Elimelech, 1993; Song *et al.,* 1994; Liu *et al.,* 1995). It is possible that the geochemical conditions favoured the colloid aggregation, increasing the sedimentation rate by the *filter rippening* phenomenon (Yao *et al.,* 1971), but also chemical effects, like surface (co)precipitation, may enhance the colloid/

rock interactions when favourable electrostatic interactions do not exist, so that this geochemical contribution should be studied and quantified more in detail.

The kinetics of the attachment/detachment of colloids to mineral surfaces and the nature and potential reversibility of this interaction are of crucial relevance for the understanding of the processes affecting radionuclide mobility. For instance, complementary studies on colloid / rock interactions with different techniques such as Atomic Force Microscopy AFM (Hodges, 2002), X-ray based techniques could additionally help to quantify the mechanisms that lead to colloid filtration in the rock, fundamental to understand the colloid-mediated RN transport. As final remark, applicable to all the above mentioned mechanism, both the transferability from laboratory experiments and up-scaling to real-site, are related issues that need to be evaluated as well, for assessing the relevance of colloid-mediated transport.

3. Conclusions

To evaluate the colloid-mediated radionuclide transport at the bentonite /granite interface of a HLWR it is necessary to quantify all processes that may play a relevant role. During the last decades great progresses were made to quantify the colloid contribution to radionuclide migration not only in a theoretical way but also by conducting experimental studies in the laboratory and at an in-situ scale. Many techniques and innovative approaches are being applied to deal with this rather complex issue, but further efforts are needed to give a clear answer to the question of colloid relevance in a repository system. At this point, the logic evolution will be to proceed via two pathways in parallel: 1) To elucidate the underlying mechanisms of colloid-radionuclide and colloid-rock interaction and 2) To perform radionuclide and colloid migration studies under relevant conditions. The combination of mechanistic information, acquainted in laboratory experiments with the outcome of migration studies will help to improve existing geochemical transport models and in turn, to allow the assessment of the colloid relevance for radionuclide migration in a nuclear waste repository.

By analysing the already existing knowledge one can conclude that three main uncertainties exist, preventing the quantification of the colloidal processes at the bentonite/granite interface:

-The question towards a quantification of colloid generation under realistic repository conditions. The possibility of establishing a 'colloid-source term' has to be discussed.
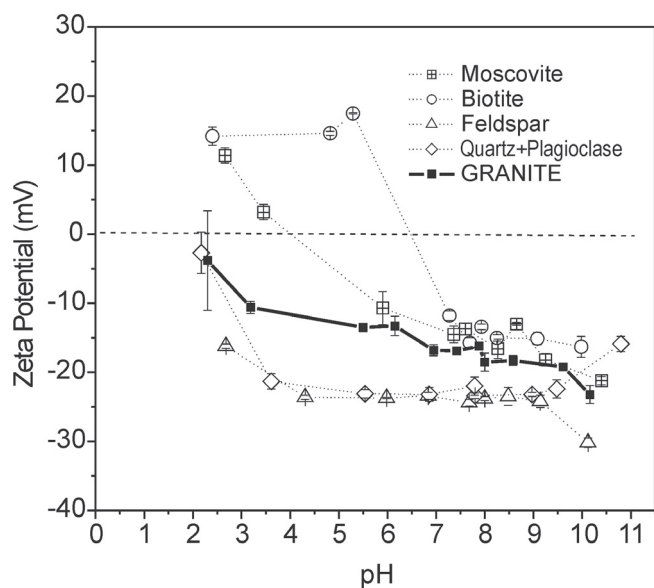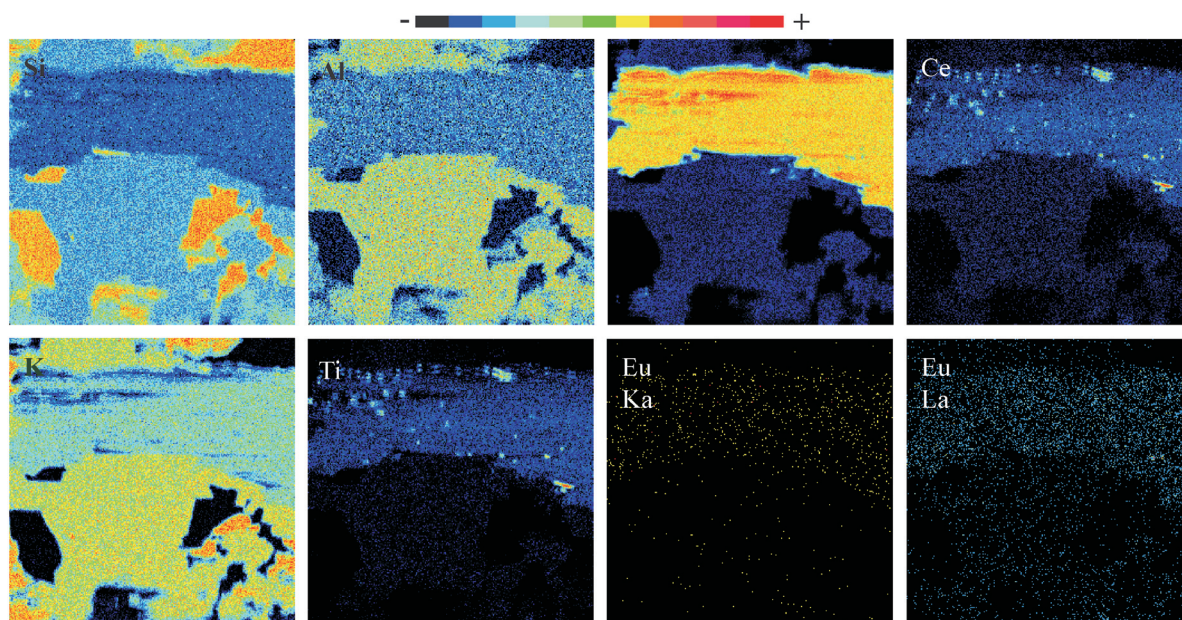

Fig. 5.- ζ-potential as function of the pH measured for granite and for different minerals composing it (muscovite, biotite, feldspar and a mixture of quartz-plagioclase).

Fig. 5.- Potenciales ζ medidos en función del pH, separadamente para el granito y los minerales mayoritarios que lo componen (moscovita, biotita, feldespato y una mezcla de cuarzo y plagioclasa).

Fig. 6.- Distribution maps of the Si, Al, Fe, Ce, K, Ti, Eu (Kα) Eu (Lα) content measured by µPIXE on a 2*2 mm² granite area after 7 days contact with the Eu-labelled bentonite colloids.

Fig. 6.- Mapas de distribución de Si, Al, Fe, Ce, K, Ti, Eu (Kα) Eu (Lα) medidos mediante µPIXE en un área de granito de 2*2 mm² después de 7 días de contacto con coloides de bentonita trazados con Eu.
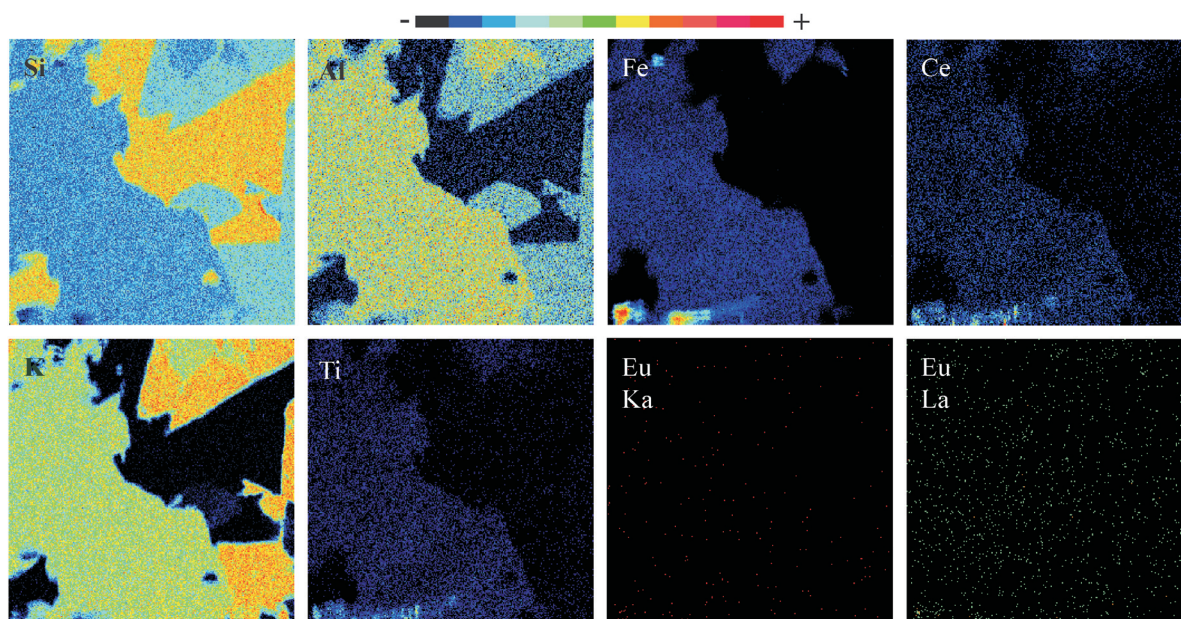

Fig. 7.- Distribution maps of the Si, Al, Fe, Ce, K, Ti, Eu (Kα) Eu (Lα) content measured by µPIXE on a 2*2 mm² granite area after 7 days contact with the Eu-labelled bentonite colloids

Fig. 7.- Mapas de distribución de Si, Al, Fe, Ce, K, Ti, Eu (Kα) Eu (Lα) medidos mediante µPIXE en un área de granito de 2*2 mm² después de 7 días de contacto con coloides de bentonita trazados con Eu.

-Mechanisms of RN sorption onto bentonite colloids and rock surfaces at enhanced contact times are not yet clear. Possible phase transformations at the colloid and rock surfaces may lead to very strong fixation and very slow desorption rates. Such processes may impede the application of common sorption model approaches as surface complexation or ion exchange models to describe and predict the partitioning of radionuclides between solution colloid and rock surface.

-Quantification of the main colloid filtration mechanisms acting in a natural system. It is notably important to understand colloid-filtration under 'unfavorable' con-

ditions, i.e. under conditions where colloid repulsion from rock surfaces is predicted by classical model approaches.

To deal with these uncertainties a close collaboration between modelling and experimental groups is necessary, to define the models requirements and to adequately approach the experimental work, both by laboratory and in-situ tests.

It has to be mentioned that at present, there are several projects running that aim to elucidate the colloid transport mechanisms, which indeed demonstrates the particular interest in eliminating the uncertainties related to the 'colloid problem' in the vicinity of a HLRW. Just to mention, the CFM (Colloid Formation and Migration) project aims to the analysis of colloid generation and migration at the bentonite-groundwater interface at the underground laboratory at the Grimsel Test Site (GTS, Switzerland), as close as possible under realistic conditions. This project is the logical continuation of the successful CRR (Colloid and Radionuclide Retardation experiment) project performed as well at the GTS (Möri *et al.,* 2003). Both experiments are carried out by a number of international research groups under the coordination of The Swiss Cooperative for Radioactive Waste Management (NAGRA).

Within the EU project FUNMIG (Fundamental Processes of RN Migration) started in January 2005, the colloid issue will be studied within different work packages. In this project, field evidences of bentonite colloid generation at the FEBEX site (Huertas *et al.,* 2000) will be investigated, and the mechanism related to colloid-borne migration will be addressed. The FEBEX project was developed to demonstrate the feasibility of a compacted bentonite barrier, studying their thermo-hydro-mechanical (THM) behaviour. In terms of colloids, after already 7 years of continuous activity is likely, that the bentonite barrier could have produced bentonite colloids in the vicinity of the gallery, that can be mobilised along the hydraulic field by advection.

Acknowledgements

References

Alonso, U. (2003): *Influencia de los coloides en el transporte de contaminantes en la interfaz campo cercano/ campo lejano de un almacenamiento de residuos radiactivos de alta actividad.* Ph.D. Thesis. Facultad de Ciencias Físicas, Universidad Complutense, Madrid: 238 p.

Alonso, U., Missana, T., Patelli, A., Ravagnan, J., Rigato, V. (2004): Experimental study of colloid interactions with rock surfaces. J.M. Hanchar, S. Stroes-Gascoyne, L. Browning (eds.): *Scientific Basis For Nuclear Waste Management XXVIII*. MRS Symposium Procedures 824. Material Research Society, San Francisco, USA.

Alonso, U., Missana, T., Patelli, A., Rigato, V., and Ravganan, J. (2002): Size effects on colloids diffusion in granite microfractures. *Geochimica et Cosmochimica Acta,* 66: 15.

Alonso, U., Missana, T., Patelli, A., Rigato, V., Ravagnan., J. (2003a): RBS and mPIXE analysis of uranium diffusion from the bentonite to the rock matrix in a deep geological waste disposal. *Nuclear Instruments and Methods in Physics Research B*, 207(2): 195-204.

Alonso, U., Missana, T., Patelli, A., Rigato, V., Rivas, P. (2003b): Study of the contaminant transport into granite micro-factures using nuclear ion beam techniques. *Journal of Contaminant Hydrology*, 61(1-4): 95-105.

Alonso, U., Missana, T., Patelli, A., Rigato, V. (2005): Bentonite colloid diffusion through the host rock of a deep geological repository. Presented at the *2nd Internationl Meeting on Clays in Natural & Engineered Barriers for Radioactive Waste Confinement* (ANDRA, Tours 14-18 March).

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

Bradbury, M.H., Baeyens, B. (1993): A general application of surface Complexation to Modelling radionuclide Sorption in Natural Systems. *Journal of Colloid and Interface Science*, 158: 364-371.

Bradbury, M.H., Baeyens, B.. (2002): Sorption of Eu on Na- and Ca--montmorillonites: Experimental investigations and modelling with cation exchange and surface complexation. *Geochimica et Cosmochimica Acta*, 66(13): 2325-2334.

Buddemeier, R.W., Hunt, J.R. (1988): Transport of colloidal contaminants in groundwater: Radionuclide migration at the Nevada Test Site. *Applied Geochemistry*, 3: 535-548.

Cumbie, D.H., McKay, L.D. (1999): Influence of diameter on particle transport in a fractured shale saprolite. *Journal of Contaminant Hydrology*, 37: 139-157.

Cvetkovic, V., Painter, S., Turner, D., Pickett, D., Bertetti, P. (2004): Parameter and model sensitivities for colloid-facilited radionuclide transport on field scale. *Water Resources Research*, 40(6): W06504.

Champ, D.R., Merritt, W.F., Young, J.L. (1982): Potential for the rapid transport of plutonium in groundwater as demonstrated by core column studies. In: E.W. Lutze (ed.): *Scientific Basis for Radioactive Waste Management V*, MRS Symposium Procedures 11, Elsevier: 745-754.

Chrysikopoulos, C.V. (1998): Transport of colloids in saturaded fracture. In E.B. Ahiabadi (ed): *Advances in fracture mechanics: Fracture of Rock*, Chap. 10, p. 297-330. Computational Mechanics Publications, WIT press, Southamptom, U.K.

Dähn, R., Scheidegger, A.M., Manceau, A., Schlegel, M.L., Baeyens, B., Bradbury, M.H., Morales, M. (2002): Neoformation of Ni phyllosilicate upon Ni uptake on montmorillonite: A kinetics study by powder and polarized extended X-ray absorption fine structure spectroscopy. *Geochimica et Cosmochimica Acta*, 66(13): 2335-2347.

Degueldre, C., Baeyens, B., Goerlich, W., Riga, J., Verbsit, J., Stadelmann, P. (1989a): Colloids in water from a subsurface fracture in granitic trock, Grimsel Test Site, Switzerland. *Geochimica et Cosmochimica Acta*, 53: 603-610.

Degueldre, C., Favarger, P.Y. (2003): Colloid analysis by single particle inductevely coupled plasma-mass spectroscopy: a feasibility study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 217: 137-142.

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

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

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

Derjaguin, B., Landau, L.D. (1941): Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes. *Acta Physhicochimica USSR*, 14: 633-662 .

Eichholz, G.G., Wahlig, B.G., Powell, G.F., Craft, T.F. (1982): Subsurface migration of radioactive waste materials by particulate transport. *Nuclear Technology*, 58: 511-520.

Elimelech, M. (1991): Kinetics of capture of colloidal particles in packed beds under attractive double layer interactions. *Journal of Colloids and Interface Science*, 146: 337-352.

Elimelech, M., O'Melia, C.R. (1990): Effect of particle size on collision efficiency in the deposition of Brownian particles with electrostatic energy barriers. *Langmuir*, 6: 1153-1163.

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

Geckeis, H., Ngo Mahn, T., Bouby, M., Kim, J.I. (2003): Aquatic colloids relevant to radionuclide migration: characterization by size fractionation and ICP-mass spectrometric detection. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 217: 101-108.

Geckeis, H., Schäfer, T., Hauser, W., Rabung, T., Missana, T., Degueldre, C., Möri, A., Eikenberg, J., Fierz, T., Alexander, W.R. (2004): Results of the Colloid and Radionuclide Retention experiment (CRR) at the Grimsel Test Site (GTS), Switzerland - Impact of reaction kinetics and speciation on radionuclide migration. *Radiochimica Acta*, 92(9-11): 1-10.

Gimbert, L.J., Andrew, K.N., Haygarth, P.M., Worsfold, P.J. (2003): Environmental applications of flow field-flow fractionation (FIFFF). *Trends in Analytical Chemistry*, 22(10): 615-633.

Gómez, P., Turrero, M.J., Moulin, V., Magonthier, M. (1992): Characterization of natural colloids in groundwaters of El Berrocal, Spain. *Proceedings of the 7th International Symposium on Water-Rock Interaction-WRI-7*, USA: 797-800.

Grindrod, P. (1993): The impact of colloids on the migration and dispersal of radionuclides within fractured rock. *Journal of Contaminant Hydrology*, 13: 167-181.

Hauser, W., Geckeis, H., Kim, J.I., Fierz, T. (2002): A mobile laser-induced breackdown detection system and its application for teh in-situ monitoring of colloid migration. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 203: 37-45.

Hauser, W., Götz, R., Geckeis, H., Kienzler, B. (2003): In-situ colloid detection in granite groundwater along the Äspö hard rock laboratory access tunnel. In: Laaksoharju, M. (ed.): *Äspö Hard Rock Laboratory: Status report of the colloid investigation conducted at the Äspö HRL during the years 2000-2003*. Swedish Nuclear Fuel and Waste Management Co. (SKB).

Hodges, C.S. (2002): Measuring forces with the AFM: polymeric surfaces in liquids. *Advances in Colloid Interface Science*, 99: 13-75.

Honeyman, B.D. (2001): The role of colloids in Radionuclide Retention by and Transport Through Geological Media. *Workshop on Radionuclide Retention in Geological Media*. Geotrap Project., p. 91-99. Nuclear Energy Agency, OECD, Sweden.

Huertas, F., Fuentes-Santillana, J.L., Jullien, F., Rivas, P., Linares, J., Fariña, P., Ghoreychi, M., Jockwer, N., Kickmaier, W., Martínez, M.A., Samper, J., Alonso, E., Elorza, F.J. (2000): *Full scale engineered barriers experiment for a deep geological repository for high-level radioactive waste in crystalline host rock*. EC Final REPORT EUR 19147.

Hunter, R.J. (1986): *Foundations of colloid Science I*. Clarendon Press, Oxford: 541 p.

Ibaraki, M., Sudicky, E.A. (1995a): Colloid-facilitated contaminant transport in discretely fractured porous media. 1. Numerical formulation and sensitivity analysis. *Water Resources Research*, 31: 2945-2960.

Ibaraki, M., Sudicky, E.A. (1995b): Colloid-facilitated transport in discretely fractured porous media. 2. Fracture network examples. *Water Resources Research*, 31: 2961-2969.

James, S.C., Chrysikopoulos, C.V. (1999): Transport of polydispersed colloid suspensions in a single fracture. *Water Resources Research*, 35(3): 707-718.

Johansson, S.A.E., Campbell, J.L.E. (1988): *PIXE, a novel technique for elemental analysis*. John Wiley& Sons, Ltd.

Kersting, A.B., Efurt, D.W., Finnegan, D.L., Rokop, D.J., Smith, D.K., Thompson, J.L. (1999): Migration of Plutonium in groundwater at the Nevada Test Site. *Nature*, 397: 56-59.

Kessler, J.H., Hunt, J.R. (1994): Dissolved and colloidal contaminant transport in a partially clogged fracture. *Water Resources Research*, 30: 1195-1206.

Kim, J.I., Kanellakopulos, B. (1989): Solubility products of Plutonium (IV) oxide and hydroxide. *Radiochimica Acta*, 48, 145-150.

Kim, Y., Kirkpatrick, R. J., Cygan, R.T. (1996): 133Cs NMR study of cesium on the surfaces of kaolinite and illite. *Geochimica et Cosmochimica Acta*, 60(21): 4059-4074.

Koppel, D.E. (1972): Analysis of macromolecular polidispersivity in intensity correlation spectroscopy: The method of cumulants. *The Journal of Chemistry Physical*, 57: 4815.

Kosakowski, G. (2004a): Anomalous transport of colloids and solutes in a shear zone. *Journal of Contaminant Hydrology*, 72(1-4): 23-46.

Kosakowski, G., Smith, P. (2004): *Grimsel Test Site – Investigation Phase V: Modelling the Transport of Solutes and Colloids in a Water-Conducting Shear Zone in the Grimsel Test Site*. NAGRA Technical Report NTB-04-01, Wettingen, Switzerland, 66 p.

Kretzschmar, R., Borkovec, M., Grolimund, D., Elimelech, M. (1999): Mobile subsurface colloids and their role in contaminant transport. *Advances in Agronomy*, 66: 121-194.

Kurosawa, S., Ueta, S. (2001): Effect of colloids on radionuclide migration for performance assessment of HLW disposal in Japan. *Pure and Applied Chemistry*, 73(12): 2027-2037.

Ledin, A.S., Karlsson, A., Duker, A., Allard, B. (1994): Measurements in situ of concentration and size distribution of colloidal matter in deep groundwater by photon correlation spectroscopy. *Water Resource Research*, 28: 1539-1545.

Lieser, K.H., Ament, A., Hill, R., Singh, R.N., Stingl, U., Thybusch, B. (1990): Colloids in groundwater and their influence on migration of trace elements and radionuclides. *Radiochimica Acta*, 49: 83-100.

Lieser, K.H., Gleitsmann, B., Peschke, S., Steinkopff, T. (1986): Colloid formation and sorption of radionuclides in natural systems. *Radiochimica Acta*, 40(1): 39-47.

Liu, D., Johnson, P.R., Elimelech, M. (1995): Colloid deposition dynamics in flow through porous media: Role of electrolyte concentration. *Environmental Science and Technology*, 29: 2963-2973.

Logan, B.E., Jewett, D.G., Arnold, R.G., Bouwer, E.J., O'Melia, C.R. (1995): Clarification of bed filtration models. *Journal of Environmental Engineering*, 121(12): 869-863.

Luckham, P.F., Rossi, S. (1999): The colloidal and rheological propierties of bentonite suspensions. *Advances in Colloid and Interface Science*, 82: 43-92.

Matshunaga, T., Nagao, S., Ueno, T., Takeda, S., Amano, H., Tkachenko, Y. (2004): Association of dissolved radionuclides released by teh Chernoyl accident with colloidal materials in surface water. *Applied Geochemistry*, 19: 1581-1599.

McCarthy, J.F., Degueldre, C. (1993): Sampling and characterization of colloids and particles in groundwater for studying their role in the subsurface transport of contaminants. In: J. Buffle, H. Van Leeuwen (eds.): *Environmental Particles*, vol. 2. Lewis Publishers, Chelsea, Chapter 6: 247-315.

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

McDowell-Boyer, L.M., Hunt, J.R., Sitar, N. (1986): Particle transport through porous media. *Water Resources Research*, 22: 1901-1921.

Miller, W., Alexander, R., Chaoman, N., McKinley, J., Smellie, J. (1994): Natural analogue studies in the geological disposal of radioactive waste. *Studies in Environmental Science*. Monograph 57. Elsevier.

Missana, T., Adell, A. (2000): On the Applicability of DLVO Theory to the Prediction of Clay Colloids Stability. *Journal of Colloid and Interface Science*, 230: 150-156.

Missana, T., Alonso, U., Turrero, M.J. (2003a): Generation and stability of bentonite colloids at the bentonite /granite interface of a deep geological radioactive waste repository. *Journal of Contaminant Hydrology*, 61: 17-31.

Missana, T., García-Gutiérrez, M., Alonso, U. (2004): Kinetics and irreversibility of cesium and uranium sorption onto bentonite colloids in a deep granitic environment. *Applied Clay Science*, 26(1-4): 137-150.

Missana, T., Gutierrez, M.G., Alonso, U., Quiñones, J. (2002): Migration of bentonite colloids in a granite fracture. *Geochimica et Cosmochimica Acta*, 15(S1): 515.

Missana, T., Gutiérrez, M.G., Turrero, M.J., Alonso, U., Mingarro, M. (2003b): *The role of colloids in the radionuclide transport in a deep geological repository: participation of CIEMAT in the CRR Project*. ENRESA Tecnical Publication, ENRESA, Madrid, 198 p.

Missana, T., García-Gutiérrez, M., Alonso, U., Mingarro, M. (2006): On radionuclide retention mechanism in fractured geological media. *Journal of Iberian Geology*, 32(1): 55.77.

Mohtadi, M.F., Rao, P.N. (1973): Effect of temperature on flocculation of aqueous dispersions. *Water Research*, 7: 747-767.

Moreno, L., Tsang, T.W., Tsang, C.F., Hale, F.V., Neretnieks, I. (1998): A stochastic model and its relation to some field observations. *Water Resources Research*, 24(12): 2033-2048.

Möri, A., Alexander, W.R., Geckeis, H., Hauser, W., Schäfer, T., Eikenberg, J., Fierz, T., Degueldre, C., Missana, T. (2003): The colloid and radionuclide retardation experiment at the Grimsel Test Site: influence of bentonite colloids on radionuclide migration in fractured rock. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 217: 33-47.

Möri, A, Editor (2004): *Grimsel Test Site – Investigation Phase V: The CRR final project report series I: Description of the Field Phase – Methodologies and Raw data*. NAGRA Technical Report NTB-03-01, Wettingen, Switzerland, 100 p.

Moridis, G.J., Hu, Q., Wu, Y.S., Bodvarsson, G.S. (2003): Preliminary 3-D site-sacle studies of radioactive colloid transport in teh unsaturated zone at Yucca Mountain, Nevada. *Journal of Contaminant Hydrology*, 60: 251-286.

Nagasaki, S., Tanaka, S., Suzuki, A. (1998): Geochemical Behaviour of Actinides in High-Level Radiactive Wate disposal. *Progress in Nuclear Energy*, 32(1/2): 141-161.

Nakano, N., Kawuamura, K., Ichikawa, Y. (2003): Local structural information of Cs in smectite hydrates by means of an EXAFS study and molecular dynamics simulations. *Applied Clay Science*, 23(1-4): 15-23.

Nuttal, H.E., Long, R.L. (1993): Mobility of radioactive colloidal particles in groundwater. R*adioactive Waste Management and the Nuclear Fuel Cycle*, 17(3-4): 237-251.

Olofsson, U., Allard, B., Torstenfelt, B., Anderson, K. (1982): Properties and mobilities of actinide colloids in geologic systems. In: *Scientific Basis for Radioactive Waste Management V*: 755-764. Elsevier.

Oswald, J.G., Ibaraki, M. (2001): Migration of colloids in discretely fractured porous media: effect of colloidal matrix diffusion. *Journal of Contaminant Hydrology*, 52: 213-244.

Panak, P.J., Kim, M.A., Jun, J.I., Kim, J.I. (2003): Interaction of actinides with aluminosilicate colloids in statu nascendi. Part II: spectroscopic speciation of colloid-borne actinides(III). *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 227(1-3): 93-103.

Patelli, A., Alonso, U., Rigato, V., Missana, T., Restello, S. (2005): Validation of the RBS analysis for colloid migration through a rough granite surface. *Nuclear Instruments and Methods B*. (In press).

Penrose, W.R., Polzer, W.L., Essington, E.H., Nelson, D.M., Orlandini, K.A. (1990): Mobility of Plutonium and Americium through a shallow aquifer in a semiarid region. *Environmental Science and Technology*, 24: 228-234.

Pusch, R. (1985): *Final Report of the Buffer Mass Test – Volume III: Chemical and Physical Stability of the Buffer Materials*; Stripa Project Technical Report 85-14, SKB, Stockholm, Sweden.

Pusch, R. (1999): *Clay colloid formation and release from MX-80 buffer*. SKB Technical Report TR 99-31.

Rajagopalan, R., Tien, C. (1976): Trajectory analysis of deep-bed filtration with the sphere-in-cell porous media. *American Institute of Chemical Engineers Journal*, 22: 523-533.

Ryan, C.G. (2004): Ion beam microanalysis in geoscience research. *Nuclear Instruments and Methods in Physics Research B*, 219-220: 534-549.

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

Ryan, J.N., Gschwend, P.M. (1994): Effects of ionic strength and flow rate on colloid release: Relating kinetics to inter-surface potential energy. *Journal of Colloid and Interface Science*, 164: 21-34.

Ryde, N., Kallay, N., Matijevic, E. (1991): Particle adhesion in model systems. Part 14: Experimental evaluation of multilayer deposition. *Journal of the Chemical Society - Faraday Transactions*, 87: 1377-1381.

Saiers, J.E., Hornberger, G.M., Harvey, C. (1994): Colloidal silica transport through structured, heterogeneous porous media. *Journal of Contaminant Hydrology*, 163: 271-288.

Schäfer, T., Geckeis, H., Bouby, M., Fanghaenel, T. (2004): U, Th, Eu and colloid mobility in a granite fracture under near-natural flow conditions. In: W.S.I. (eds), Water-Rock Interaction., 703-707. Taylor & Francis Group, London.

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

Song, L., Elimelech, M. (1993): Dynamics of colloid deposition in porous media: Modelling the role of retained particles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 73: 49-63.

Song, L., Johnson, P.R., Elimelech, M. (1994): Kinetics of colloid deposition onto heterogeneously charged surfaces in porous media. *Environmental Science and Technology*, 28: 1164-1171.

Stumpf, T., Fanghänel, T. (2002): A Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) Study of teh interaction of trivalent Actinides (Cm(III) with calcite. *Journal of Colloid and Interface Science*, 249: 119-122.

Swanton, S.W. (1995): Modeling colloid transport in groundwater; The prediction of colloid stability and retention behavior. *Advances in Colloid and Interface Science*, 54: 129-208.

Sylwester, E.R., Hudson, E.A., Allen, P.G. (2000): The structure of uranium (VI) sorption complexes on silica, alumina, and montmorillonite. *Geochimica et Cosmochimica Acta*, 64(14): 2431-2438.

Toran, L., Palumbo, A.V. (1992): Colloid transport through fractured and unfractured laboratory sand columns. *Journal of Contaminant Hydrology*, 9: 289-303.

Turrero, M.J. (2002): *Hidrogeoquímica y coloides inorgánicos del plutón granítico de El Berrocal (Sierra de Gredos, Sistema Central)*. Tesis Doctoral. Universidad Complutense, Madrid.

Turrero, M.J., Gómez, P., Pérez del Villar, L., Moulin, V., Magontier, M.C., Menager, M.T. (1995): Relation between colloid composition and the environments of their formation: application to El Berrocal site (Spain). *Applied Geochemistry*, 10: 119-131.

Van der Lee J., Ledoux E., de Marsily G., de Cayeux M.D., van de Weerd H., Fraters B., Dodds J., Rodier E., Sardin M., Hernandez A. (1994): A bibliographical review of colloid transport through the geosphere. *Nuclear Science and Technology Nr. EUR 15481* EN, Commission Européenne, Bruxelles, Belgique.

Velegol, D., Thwar, P.K. (2001): Analytical Model for the Effect of Surface Charge Nonuniformity on Colloidal Interactions. *Langmuir*, 17(24): 7687 - 7693.

Vilks, P., Cramer, J.J., Jensen, M., Miller, N.H., Miller, H.G., Stanchell, F.W. (2003): In situ diffusion experiment in granite: Phase 1. *Journal of Contaminant Hydrology*, 61: 191-202.

Walther, C., Bitea, C., Hauser, W., Kim, J.I., Scherbaum, F.J. (2002): Laser induced breakdown detection for teh assessment of colloid mediated radionuclide migration. *Nuclear Instruments and Methods in Physics Research B*, 195: 374-388.

Wang, Z., Zachara, J.M., Gassman, P., Liu, C., Qafoku, O., Yantasse, W., Catalano, J.G. (2005): Fluorescence spectroscopy of U(VI)-silicates and U(VI)-contaminated Hanford sediment. *Geochimica et Cosmochimica Acta*, 69(6): 1391-1403.

Weiss Jr, Ch. A., Kirkpatrick, R. J., Altaner, S. P. (1990): The structural environments of cations adsorbed onto clays: 133Cs variable-temperature MAS NMR spectroscopic study of hectorite. *Geochimica et Cosmochimica Acta*, 54(6): 1655-1669.

Wervey, E. J. W., Overbeek, J. Th. G. (1948): *Theory of stability of liophobic colloids*. Elsevier, Amsterdam: 642 p.

Wold, S., Eriksen, T.E. (2003): Diffusion of lignosulfonate colloids in compacted bentonite. *Applied Clay Science*, 23(1-4): 43-50.

Yan, Y., Borkovec, M., Sticher, H. (1995): Deposition and release of colloidal particles in porous media. *Progress in Colloid and Polymer Science*, 98: 132-135.

Yao, K.M., Habibian, M.T., O'Melia, C.R. (1971): Water and waste water filtration: Concepts and applications. *Environmental Science and Technology*, 5: 1105-112.