Research paper

Size distribution analysis of colloid generated from compacted bentonite in low ionic strength aqueous solutions

Nairoby Albarran [a], Claude Degueldre [b], Tiziana Missana [a,*], Ursula Alonso [a], Miguel García-Gutiérrez [a], Trinidad López [a]

[a] CIEMAT/Departamento de Medioambiente, Avenida Complutense, 40. 28040, Madrid, Spain
[b] Paul Scherrer Institut/Laboratory for Waste Management, CH-5232 Villigen, Switzerland

ABSTRACT

An experimental methodology is presented, with the objective of investigating erosion and colloid generation from compacted bentonite, to evaluate its possible effects on radionuclide migration in a deep geological repository (DGR) in crystalline rock.

Bentonite erosion studies were performed using a natural bentonite and considering two possible scenarios existing in a DGR in crystalline rock: the first one, where the water hydrating the bentonite is stagnant (*static scenario*) and the second one where the water can flow at the bentonite surface, simulating the existence of a water conducting fracture (*dynamic scenario*).

In particular, the size of the generated colloids was analysed, as it is a very important parameter for transport and retention/filtration processes in crystalline rock and, ultimately, for colloid-driven radionuclide transport. The analysis of the size distribution of colloids, detected in erosion experiments, was carried out by the very sensitive single particle counting (SPC) technique.

As bentonite colloids are particularly stable and mobile in low ionic strength (I) solutions, these chemical conditions were considered of particular interest.

Results showed that the quantity of colloids generated from compacted bentonite depends on the chemistry of the water, and that the presence of calcium in the electrolyte inhibits the maximum generation of colloidal particles. The maximum concentration of bentonite colloid in solution corresponds to particles with a size around 50–100 nm.

The size distribution of bentonite colloids was similar in all the analysed cases, but the concentration of particles of smaller size (50–100 nm) was always higher in the absence of calcium, indicating the clear effect of this element on their aggregation.

Results also evidenced the importance of water/clay interactions: these can be of extreme importance for the evaluation of erosion and stability of colloids in a DGR at a long term.

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1. Introduction

Bentonite is a suitable backfill material in deep geological repositories (DGR) of high level radioactive waste (HLRW) emplaced in crystalline rock. Compacted bentonite acts as hydrological barrier, minimizing the flow of percolating groundwater and retarding the migration of radionuclides (RN), upon their accidental release from the waste container. Additionally, it withstands the mechanical stresses in the host rock and dissipates the heat generated in the waste container (Pusch, 1992; Pusch and Yong, 2006).

The contact between the compacted bentonite and the water coming from the geological emplacement produces clay hydration, swelling

and the formation of a surface gel that can penetrate into the fissures and pores of the rock (Grindrod et al., 1999).

Chemical or physical erosion processes on the clay surface gel might generate colloidal particles, free to move in groundwater. Colloids are particles smaller than 1 μm and potential contaminant carriers in groundwater (Marley et al., 1993; McCarthy and Zachara, 1989; Penrose et al., 1990). For this reason, it is important to study colloid generation mechanisms from compacted bentonite, as a previous step to establish their role on RN transport into the environment and to evaluate the associated risks in a DGR.

In the frame of the performance assessment (PA) of a DGR, to know if erosion processes at the clay surface may affect its functionality, as backfill barrier at the long term (Herbert et al., 2004; Pusch, 1999), is also an issue. In PA of radioactive waste repositories of some country, the colloid problem is partially included, but mostly in relation to colloid facilitated radionuclide transport. A PA applicable model of bentonite

* Corresponding author. Tel.: +34 913466140; fax: +34 913466542.
E-mail address: tiziana.missana@ciemat.es (T. Missana).

erosion (and its implications) is not yet available. For this reason, at present, great effort is being done to understand the main mechanisms involved in erosion and colloid generation from compacted bentonite (for example: in the EC project BELBaR, *Bentonite Erosion: effects on the Long Term performance of the engineered Barrier and Radionuclide Transport*, www.skb.es, and in the international project CFM, *Colloid Formation and Migration*, www.grimsel.com).

For this reason, detailed tests, under realistic conditions, are absolutely needed to develop and validate such models. Therefore, the quantification of colloids possibly generated from compacted bentonite and the knowledge of their properties are needed.

In particular, the particle size is a fundamental parameter related to filtration, retention and settling phenomena (James and Chrysikopoulos, 2003; Jen and Li, 2001) and, in consequence, on RN transport in fractured rock.

Particularly, low ionic strength (I ~ $1 \cdot 10^{-3}$ M) and neutral-alkaline conditions favour colloid stability and mobility (Missana et al., 2003) thus, these conditions are of special interest in colloid studies related to contaminant transport in waste repositories (Miller et al., 2000).

Previous studies on bentonite colloid generation, focussed attention on non-confined clay systems (Bessho and Degueldre, 2009; Degueldre et al., 2009; García-García et al., 2009; Kaufhold and Dohrmann, 2008; Lagaly and Ziesmer, 2003). Data on bentonite colloid generation obtained in more realistic conditions (compacted and confined bentonite) are still scarce (Alonso et al., 2007; Baik et al., 2007; Missana et al., 2003; Seher et al., 2008).

Alonso et al. (2007) studied bentonite colloid generation in compacted and confined clay focussing on the effects of clay density (1.2–1.6 g/cm³) and water chemistry on colloid generation. Preliminary results on bentonite colloid generation from compacted and confined bentonite in the presence of a water flow at the clay surface and their interpretation for repository risk assessment are more recent (Missana et al., 2011). Nevertheless, a more precise quantification of the bentonite erosion and the characterization of the generated colloids are still necessary.

The aim of this work is to quantify colloid generation from compacted and confined bentonite in low ionic strength aqueous solutions and, in particular, to analyse the size distribution of the generated colloids.

Bentonite erosion was studied under conditions as similar as possible as those expected in a radioactive waste geological repository for gathering information needed for the performance assessment of such repositories.

Three natural granitic waters from the underground laboratory Grimsel Test Site (GTS, Switzerland, www.grimsel.com), NaCl, CaCl₂ and a mixed Ca–Na electrolyte – all solutions with I of approximately $1 \cdot 10^{-3}$ M – were used for the experiments.

The bentonite used in this study (FEBEX bentonite) contains more than 90% of smectite. This clay has been used in the FEBEX experiment, a real-scale experiment simulating a DGR in crystalline medium, which is running at GTS since 1996. The FEBEX experiment allowed the evaluation of the thermo-hydro-mechanical and thermo-hydro-geochemical behaviour of compacted bentonite under repository conditions. Details on the FEBEX experiment can be found in Huertas et al. (2000).

At present, in the tunnel where the FEBEX experiment is emplaced, studies of bentonite colloid generation under realistic conditions are ongoing (Missana et al, 2011). The laboratory experimental conditions adopted in this study are representative of those existing in the FEBEX experiment; thus data obtained at a laboratory scale will be basic to interpret experimental data on colloid generation that are being collected *in-situ* since the year 2005 (Missana et al., 2009). However, it is important to stress again that these conditions are selected mainly because colloids are expected to be stable and mobile and then potentially relevant in RN transport.

Generation studies were carried out considering two possible scenarios for colloid generation in a repository: 1) the *static* system, in which the water hydrating the bentonite is fairly immobile and colloids generated moves towards the aqueous phase by diffusion and 2) the *dynamic* system, in which the presence of water flow, coming from a fracture with major hydraulic conductivity, in contact with surface clay imposes a shear force. The shear force might be an additional force causing the erosion of the clay surface gel. In the dynamic system, the transport of colloid generated occurs mainly by advection.

In a first stage of the experiments, mean colloid concentration and average particle size were determined by photon correlation spectrometry (PCS). PCS is a dynamic light scattering technique which measures the scattered light intensity produced by colloidal particles subject to Brownian motion (Chu, 1974; Holthoff et al., 1996). Nevertheless, as particular emphasis was given to the analysis of the colloid size distribution, the single particle counting (SPC) technique was also used. SPC is based on the principle of light scattering by single particles to determine concentration and size distribution. More details on SPC can be found in Degueldre et al. (1996b) and Rossé and Loizeau (2003). An important feature of this technique is that, in contrast to techniques like PCS, it allows the measurement of natural, highly polydispersed and diluted water samples. SPC was previously used to analyse the concentration and size of natural colloid in natural waters (Atteia and Kozel, 1997; Degueldre et al., 1996a,b; Walther et al., 2006). The application of the SPC technique is very important for size distribution studies because it is much more sensitive than PCS, and it allows detecting difference upon varying experimental conditions, not otherwise observable.

2. Materials and methods

2.1. Bentonite

The FEBEX bentonite comes from the Cortijo de Archidona deposit in Almeria (Spain). It is a Ca–Mg bentonite, composed of smectite (92 ± 3%), quartz (2 ± 1%), plagioclase (3 ± 1%), cristobalite (2 ± 1%) and other accessory minerals (<1%). It presents traces of soluble salts as halite (NaCl), calcite (CaSO₄) and/or dolomite (CaMg(CO₃)₂) which dissolve in contact with aqueous solutions.

In particular, the chloride (Cl⁻) inventory in the *as-received* FEBEX clay is 2.19 ± 0.40 mmol/100 g (Fernández et al., 2004). The cationic exchange capacity (CEC) of the FEBEX clay is 102.0 ± 0.4 meq/100 g and the exchange complex is as follows: Ca²⁺ (42 ± 3 meq/100 g); Mg⁺ (32 ± 2 meq/100 g); Na⁺ (25 ± 2 meq/100 g) and K⁺ (2.5 ± 0.3 meq/100 g) (Fernández et al., 2004; Huertas et al., 2000).

For the experiments, FEBEX bentonite was used *as-received* with a grain size <1.18 mm and humidity of approximately 14%.

2.2. Aqueous solutions

The experiments were carried out using three natural granitic waters and other electrolytes with different chemical composition and calcium content, but similar ionic strength (I).

Two granitic waters came from a tunnel at GTS where the FEBEX experiment is installed (FEBEX tunnel). Nineteen boreholes were drilled radial to the FEBEX experiment to monitor the chemistry of the surrounding water (Buil et al., 2010; Gómez et al., 2007). In particular, the water coming from interval 3 of the SJ5 borehole (SJ5-3) was selected as representative of undisturbed granitic groundwater.

In the frame of the European FUNMIG project (Buckau et al., 2009), chemical effects of the bentonite in contact with granite waters (Buil et al., 2010) and the possible *in-situ* generation of bentonite colloids (Missana et al., 2009) were started to be analysed. With this purpose, two boreholes (FUN1 and FUN2), parallel to the FEBEX tunnel and relatively near to the bentonite barrier (20 and 60 cm respectively), were drilled. Detailed geophysical and geological characteristics of boreholes drilled in the FEBEX tunnel can be found elsewhere (Carbonell et al., 2006; Pérez-Estaún et al., 2006). Precisely, the second granite water selected for generation studies came from interval 3 of the FUN2 borehole (FUN2–3), not yet affected by the presence of the bentonite clay. Finally,

the third water granitic (GW) comes from the GTS in a region outside the FEBEX tunnel (BOADUS borehole). All waters sampled at the GTS have low electric conductivity (60–130 μS/cm) and neutral-alkaline pH (Buil et al., 2010; Duro et al., 2000; Möri et al., 2003).

Additionally, NaCl, CaCl$_2$ and a mixed Ca–Na electrolyte (Mixed), all with I = 10^{-3} M, were used. Table 1 shows the pH, I, and initial concentration of the main ions of all the aqueous solutions used for bentonite colloid generation experiments.

2.3. Generation experiments

Fig. 1 shows the set-up of colloid generation tests. All colloid generation experiments were carried out at room temperature and in an anoxic glove box to avoid the oxidation of granitic waters and to minimize dust contamination of the samples.

Fig. 1a and b shows the set-up used for the experiments under static conditions (Alonso et al., 2007). A pellet of approximately 4.80 g of FEBEX bentonite compacted with a pneumatic press (SPX Power Team-230) at a dry density of 1.60 or 1.65 g/cm^3, was introduced into a stainless steel cylinder. A porous steel filter was located by each side of the clay. These filters have a diameter of 20 mm, thickness of 3.1 mm, a pore size of 100 μm and porosity of approximately 40%. The cells were closed with two open Delrin grids, allowing the contact between the clay surfaces and the aqueous solution through the porous filter (Fig. 1a). The surface clay exposed to the hydration, S, when both bentonite faces are exposed to water, is approximately 3.56 cm^2.

Finally, the cell was submerged in 200 mL of aqueous solution in a polystyrene closed vessel (Fig. 1b). The aqueous solution hydrates the bentonite through the porous filters producing the swelling of the clay, the formation of a gel layer on the clay surface, and its extrusion into the open spaces of filter (pores). The erosion process of this gel layer leads to the formation/generation of colloidal particles free to move towards the aqueous solution.

The sampling of the water in contact with the clay was periodically carried out to detect and quantify the colloidal particles generated. To quantify the total mass eroded from clay, the closed vessel was gently shaken before extracting approximately 2 mL of the sample. The chemistry of aqueous solutions was analysed at the end of the experiments to study clay/solution interactions.

Under static conditions, data from seven cells were analysed. With the bentonite compacted at a dry density of 1.60 g/cm^3, the generation process was analysed with NaCl, CaCl$_2$ and GW. With the bentonite compacted at a dry density of 1.65 g/cm^3 NaCl, Mixed, SJ5-3 and FUN2–3 aqueous solutions were used. The set of experiments performed with FEBEX bentonite compacted at a dry density of 1.65 g/cm^3 will be referred to as the "Grimsel case" because these conditions represent those of the FEBEX experiment at GTS.

Fig. 1c shows the set-up used for generation experiments under dynamic conditions (Missana et al., 2011). For colloid generation under dynamic conditions, a pellet of approximately 48 g of the FEBEX bentonite compacted at a density of 1.65 g/cm^3 was introduced in a stainless steel cell (Fig. 1c, García-Gutiérrez et al., 2006) with a diameter of 5 cm and located between a porous stainless steel filter of 10 μm pore size (thickness of 0.33 cm) and a layer of no porous material. In this

configuration, the total surface clay in contact with the aqueous solution, S, was approximately 19.63 cm^2.

The electrolyte was injected with peristaltic pump (Gilson, Minipuls MP3) through polyethylene capillary tubes into the stainless steel filter. The electrolyte contacted with the clay surface and eluted from the filter was periodically collected in polyethylene tubes for colloid quantification and chemical analyses.

In the dynamic set-up, three bentonite cells in contact with NaCl, CaCl$_2$ and Mixed electrolytes (Table 1) were analysed. Two water flow rates (20 and 595 mL/day) corresponding to water velocities of approximately $3 \cdot 10^{-7}$ and $1 \cdot 10^{-5}$ m/s were evaluated.

2.4. Colloid and chemical analyses

The first analysis of the concentration and mean size of the particles generated in the different aqueous solutions was carried out by photon correlation spectroscopy (PCS) with a Malvern 4700 system equipped with a Spectra Physic argon laser (λ = 514 nm, 1 W) and the photomultiplier located at a scattering angle of 90°.

To determine the mass of bentonite colloid in solution by PCS, calibration curves were needed, that were generated measuring the response of photomultiplier (cps, counts per second) at different and known concentrations of bentonite colloids in suspension. The optimal conditions for measurements are those in which the relation cps vs. colloid concentration is linear. Stable bentonite colloid dispersions for calibration (in $5 \cdot 10^{-4}$ M NaClO$_4$), with a mean size of 250–300 nm, were prepared in the laboratory. The stability of these dispersions was often checked to guarantee the precision of PCS analyses. The PCS's detection limits for bentonite colloid is approximately 1 mg/L.

The analysis of colloid size distribution was carried out by the single particle counting (SPC) technique. SPC analyses were done both on samples from experiments under static conditions (obtained at the steady-state) and on samples from experiments under dynamic conditions (obtained at different times, upon different volumes of eluted water).

Single particle counter is designed to measure particle concentration in ultrapure water systems. Therefore samples have to be diluted prior to analysis. The SPC measurements were performed with HSLIS-M50 and HVLIS C200 particles counter from PMS (Particle Measuring System, Inc.) and a photodetector (micro laser particle spectrometer, μLPS). This combination of single-particle monitors and spectrometer allows the counting of 13 size classes from 50 to 5000 nm.

HSLIS-M50 has four channels to detect particles with size between 50 and 200 nm in the size range of 50–100 nm, 100–150 nm, 150–200 nm and 200 nm.

HVLIS C200 has eight channels and measures particles between 200 and 5000 nm, in the size range of 200–300 nm, 300–400 nm, 400–500 nm, 500–700 nm, 700–1000 nm, 1000–1500 nm, 150–2000 nm, and 2000–5000 nm.

The sample is injected, with a high precision volumetric pump (DESAGA KP 200) into the ultrapure water (Milli-Q from Millipore) main stream, at water flow rate of 500 mL/min. The sample is subsequently divided in two lines at water flow rate of 100 and 400 mL/min to be analysed by the HSLIS-M50 and HVLIS C200, respectively.

Colloid concentration recorded for a particle size range is normalized as a function of the size class. Thus, the normalized concentrations corresponding to the original sample solution in the experimental batch are expressed in mL^{-1} · nm^{-1}.

The chemical analyses on the aqueous solutions in contact with the clay were performed to determine major ions as Na$^+$, Ca^{2+}, Cl$^-$, and Mg$^+$, amongst others. These analyses allowed evidencing changes in solutions due to raw bentonite/aqueous solution interactions (dissolution of trace minerals and cationic exchange process).

The concentration of aluminium was determined to verify the bentonite colloid concentration in the aqueous solution with appropriate calibration curves (Missana et al., 2008).

Table 1
Characteristics of the aqueous solutions used in bentonite colloid generation experiments: pH, ionic strength (I), and initial concentration of main ions.

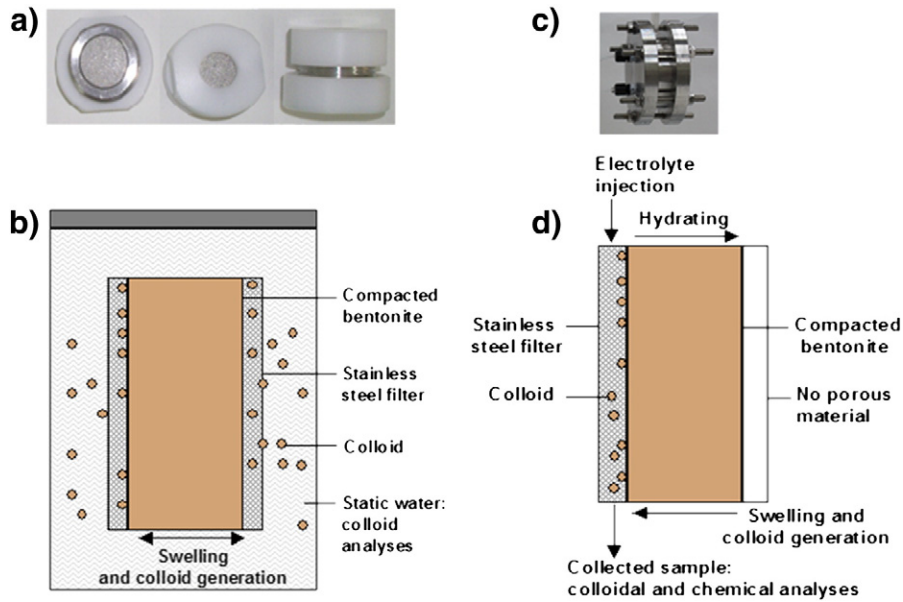| Aqueous solution	pH	I (M)	Na$^+$ (mg/L)	Ca^{2+} (mg/L)	Cl$^-$ (mg/L)
GW	7.90	9.50 10^{-4}	9.2	8.2	0.9
SJ5-3	9.20	1.02 10^{-3}	9.2	7.8	0.3
FUN2–3	8.13	9.80 10^{-4}	11.0	7.1	0.9
NaCl	6.50	1.00 10^{-3}	23.0	<0.5	35.0
CaCl$_2$	6.50	1.00 10^{-3}	<0.5	11.0	22.0
Mixed	6.50	1.00 10^{-3}	9.3	6.9	27.0

Fig. 1. Experimental set-up for bentonite colloid generation experiments under (a, b) *static* and (c, d) *dynamic* conditions.

In experiments under static conditions, the chemical analyses of contact waters were carried out once, at the steady-state, whereas in the case of the dynamic experiment the analyses were done periodically.

Finally, the composition of particles detected was analysed by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) with a JEOL JSM-6400. For microscopic analyses the samples were filtered by Millipore membranes of 0.1 μm, 0.05 μm or ultra-filtration membranes YM30, Amicon XM50 and the solid deposited in the filter was analysed.

3. Results

3.1. Bentonite colloid generation under static conditions

Fig. 2 shows the evolution of mass of the particles generated from FEBEX bentonite obtained by PCS measurements. Fig. 2a shows the experiments carried out with the bentonite compacted at a dry density of 1.60 g/cm^3 in NaCl, CaCl$_2$ (10^{-3} M) and GW. Data, from Alonso et al. (2007), obtained in deionized water and NaCl 10^{-2} M, are included for comparison. Fig. 2b shows the experiments carried out with the bentonite compacted at 1.65 g/cm^3 in NaCl, Mixed electrolyte, FUN2–3 and SJ5-3, which represent the *Grimsel case*.

At the beginning of the experiment, the mass of the particle generated increased almost linearly, but after a certain time (approximately 50 days or 150 days, in the case of the clay compacted at 1.60 or 1.65 g/cm^3 respectively), no further increase of particles in solution was observed, indicating that the system reached a steady-state. Therefore a maximum quantity of colloids can be generated in each case, depending on the initial conditions.

Table 2 summarizes the characteristic of all the experiments (compaction density, contact water type and days of experimentation) and the main results obtained: the colloid mass at the steady-state with its standard deviation, the mean size of particle measured by PCS and the colloid mass normalised to the surface clay exposed to hydration (Colloid/S). Normalization of data allows comparing results obtained with different set-ups and initial conditions.

As shown in Table 2, PCS measurements indicated that, the mean size of the particle generated from the bentonite is in the colloidal range (<1 μm) in all the experiments, therefore "colloid generation" is proven.

Colloids with a slightly larger mean size (500–600 nm) are generated in aqueous solution with calcium. According to Schulze–Hardy rule, the

coagulant properties of bivalent ions, as Ca^{2+}, which additionally is capable to bind two clay layers *via* Ca-bridging, are more effective than that of monovalent ones (Na$^+$) (Lagaly, 2006). Particle mean size, measured at
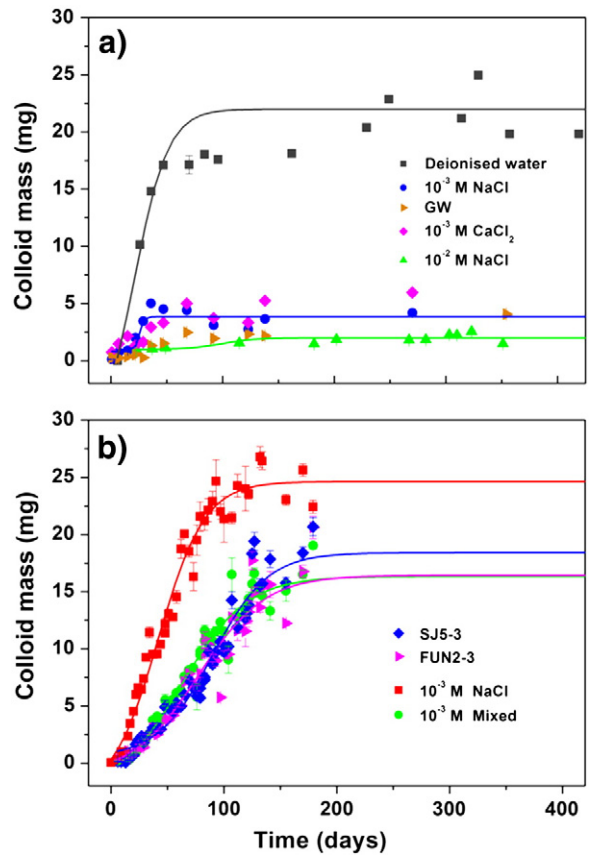

Fig. 2. Mass of colloids generated from bentonite under static conditions. (a) bentonite compacted at a density of 1.60 g/cm^3 in contact with NaCl, CaCl$_2$ and GW with I = 1 · 10^{-3} M. Data obtained with deionized water and NaCl 1 · 10^{-2} M (Alonso et al., 2007) are included for comparison; (b) bentonite compacted at 1.65 g/cm^3 in contact with NaCl and Mixed electrolyte with I = 1 · 10^{-3} M and natural granitic waters FUN2–3 and SJ5-3.

Table 2
Summary of results of bentonite colloid generation experiments under static conditions.

Compaction clay density ρ_d (g/cm^3)	Aqueous solution	Experimental time (days)	Colloid mass at the equilibrium by PCS (mg)	Mean size by PCS (nm)	Colloid/S mg/cm^2
1.60	GW	354	3.8 ± 1.0	329 ± 59	1.1 ± 0.3
	NaCl	354	3.4 ± 0.6	318 ± 77	1.0 ± 0.2
	CaCl$_2$	270	4.0 ± 1.7	515 ± 56	1.1 ± 0.5
1.65	NaCl	179	24.0 ± 4.0	456 ± 19	6.8 ± 1.1
	Mixed	179	15.1 ± 1.7	494 ± 98	4.3 ± 0.5
	FUN2-3	179	14.5 ± 2.7	519 ± 93	4.1 ± 0.8
	SJ5-3	179	17.3 ± 3.0	481 ± 69	4.9 ± 0.9

different times was constant within the experimental error, indicating that colloids are stable, at least within the experimental time-frame.

Independently of the electrolyte chemistry, the quantity of particles generated is significantly higher for clay density of 1.65 g/cm^3 (almost one order of magnitude), compared to that obtained for lower density (1.60 g/cm^3). This confirms previous studies performed by Alonso et al. (2007), which showed a clear increase of bentonite colloid in solution when the compaction density of the clay increased.

At a fixed compaction density, the mass of eroded colloids strongly depended on the electrolyte I, as can be clearly seen in Fig. 2a. In deionized water ($I < 10^{-5}$ M), the mass of colloid in solution was the highest (24.0 ± 4.0 mg, Table 2), whereas the lowest quantity of colloids was generated in $1 \cdot 10^{-2}$ M NaCl.

On the other hand, at a fixed I, (Fig. 2b, $I = 1 \cdot 10^{-3}$ M) the quantity of generated colloids was influenced by the presence of calcium. The maximum value, almost 7 mg/cm^2, was observed in the NaCl electrolyte; the three waters SJ5-3, FUN2–3 and Mixed, which all have a similar calcium content, showed similar values (4–5 mg/cm^2), lower than that observed in the electrolyte without calcium.

In order to corroborate the value of bentonite colloid concentration, determined by PCS, the aluminium content in the final aqueous solutions was analysed. Table 3 presents the comparison between the values of bentonite colloid concentration obtained by PCS and those obtained considering the Al concentration (ICP-MS analyses), for the *Grimsel case*. Both techniques gave similar values.

3.2. Bentonite colloid generation under dynamic conditions

Fig. 3 shows the results of the experiments performed under dynamic conditions with FEBEX bentonite compacted at 1.65 g/cm^3. Three different electrolytes were used (NaCl, CaCl$_2$, Mixed, all with $I = 1 \cdot 10^{-3}$ M). In Fig. 3, the evolution of the accumulated mass of colloid generated is plotted as a function of the eluted volume. The water flow rate used was 20 mL/day.

As a continuous income of fresh water is provided, the dilution of the generated colloids makes difficult the analysis of data by PCS. Under dynamic conditions, the concentration of particles observed in each sample was small, sometimes near to the detection limit, thus errors on estimated concentration can be around a 15–20%. The plot of data in an accumulated form helps enhancing the small differences observed.

After the hydration stage (initial region approximately 250 mL of eluted volume) colloids started to be generated. The trend of

the accumulated curve was nearly linear at constant water flow rate, at least in the relatively short time-frame of these experiments. The initial linearity of the process allowed determining the generation rates for each electrolyte at the water flow rate of 20 mL/day. Table 4 summarizes the main results obtained in the different tests.

The mean size of particles measured by PCS was always in the colloidal range, but the very low concentrations present in the samples made difficult the measurement of colloid size by PCS, above all in Mixed and CaCl$_2$ electrolytes.
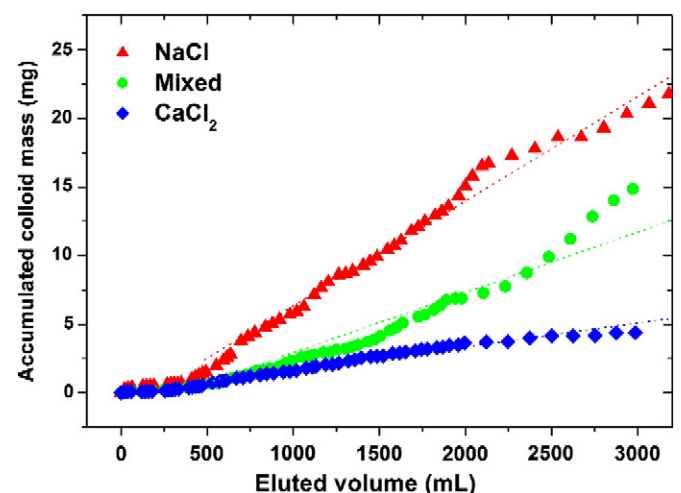
The generation rates of colloids in waters of similar ionic strength ($I = 1 \cdot 10^{-3}$ M) clearly decreased as the presence of calcium increased (from 0.14 mg/day in NaCl to 0.03 mg/day in CaCl$_2$). This is an indication that, also under dynamic conditions, the initial chemical composition of the water is an important factor.

After the elution of approximately 3 L of solution, the flow rate was increased from 20 mL/day to 595 mL/day (nearly 30 times) to evaluate if such a change would produce changes in generation process in relation to colloid quantity and/or size. Neither the colloid concentration nor the size measured by PCS showed significant differences at higher water flow rate but, as mentioned before, a further dilution of the samples made even more difficult PCS measurements.

Therefore the measurements by SPC, in different samples at both flow rates acquired special importance.

3.3. EDX analyses

Fig. 4 shows (a) SEM images and (b) EDX spectra of colloids generated from FEBEX bentonite in FUN2-3 water under static conditions (left) and in $1 \cdot 10^{-3}$ M NaCl under dynamic conditions (right). The objective of SEM analyses was not to analyse the structure of colloids, as

Table 3
Comparison of colloid concentration measured by PCS and ICP-MS (aluminium). Generation experiments under static conditions (Grimsel case).

Compaction clay density ρ_d (g/cm^3)	Aqueous solution	Results by PCS (mg/L)	Results by ICP-MS (mg/L)
1.65	NaCl	24.0 ± 4.0	22.0 ± 2.2
	Mixed	15.1 ± 1.7	13.3 ± 1.3
	FUN2-3	14.5 ± 2.7	14.7 ± 1.5
	SJ5-3	17.3 ± 3.0	14.7 ± 1.5

Fig. 3. Accumulated mass of colloids generated under dynamic conditions in NaCl, Mixed and CaCl$_2$ ($I = 1 \cdot 10^{-3}$ M) with a water flow rate of 20 mL/d.

Table 4
Summary of results of bentonite colloid generation experiments under dynamic conditions.

Compaction clay density ρ_d (g/cm^3)	Aqueous solution	Mean particle size by PCS (nm)	Generation rate (mg/day)	Generation rate normalized to surface exposed (mg/y · cm^2)
1.65	NaCl	390 ± 60	0.14	2.6
	Mixed	560 ± 180	0.06	1.1
	CaCl$_2$	>700	0.03	0.5

they are in the aqueous solution, but rather to analyse the composition of the sample *cake* formed on the filters and verify if it is formed by smectite. Microscopic analyses of smectite can be found, for example, in Pusch and Yong (2006).

Table 5 shows the semi-quantitative composition obtained from EDX on the filters in which the colloids generated were deposited, compared with the one obtained from the FEBEX powdered clay. The composition of the particles, in all the experiments performed, is quite similar to that obtained in the FEBEX clay. Furthermore, other minerals different than smectite were not detected.

3.4. Bentonite/aqueous solutions interactions

To evidence the bentonite/aqueous solution interaction, chemical analyses were performed. In the experiments under static conditions, the chemical analyses were performed only at the steady-state conditions. Table 6 shows the differences between the final and initial concentrations of the main ions Na$^+$, Ca^{2+} and Cl$^-$ in the different aqueous solutions.

The soluble salts present in the *as-received* FEBEX bentonite (Section 2.1) dissolve in contact with water leading to an increase of the salinity. The main salts are halite, gypsum and calcite, therefore an increase of Cl$^-$, Na$^+$ and Ca^{2+} is expected.

The total dissolution of halite (NaCl) (2.19 ± 0.4 mmol/100 g, Section 2.1) in 200 mL of electrolyte would contribute to an increase

of the Cl$^-$ and Na$^+$ concentration of 18.8 ± 4.8 mg/L and 12.1 ± 3.1 mg/L, respectively.

As shown in Table 6, the excess of the ion Cl$^-$ reasonably corresponds to that expected upon halite dissolution. However, the increase of Na$^+$ concentration is much higher than the expected in all waters. On the other hand, Ca^{2+} concentration decreases in spite of the possible dissolution of gypsum or calcite.

Therefore, chemical analyses demonstrate that bentonite adsorbs calcium (by ionic exchange) thus causing a depletion of calcium in solution. At the end of the experiments all aqueous solutions, independently of their initial calcium content, present similar calcium concentration (approximately 1 mg/L, 3.50 · 10^{-5} M).

In the experiments under dynamic conditions, the evolution of the concentration of the main ions Cl$^-$, Ca^{2+} Na$^+$ and in the water eluted from the generation cell was periodically measured and the results are presented in Fig. 5.

The evolution of the concentration of Cl$^-$ (Fig. 5a), Ca^{2+} (Fig. 5b) and Na$^+$(Fig. 5c) in the three electrolytes shows a single major peak, corresponding to the dissolution of halite (for Na and Cl), gypsum and calcite (for Ca) present in the bentonite.

The concentration of the conservative ion Cl$^-$ in the eluted water (Fig. 5a) returned equal to that of the inlet water after approximately 750 mL (35 days). On the other hand, after 3 L of eluted water (150 days) Ca^{2+} concentration is still lower than that of the incoming electrolyte and Na$^+$ concentration is higher.
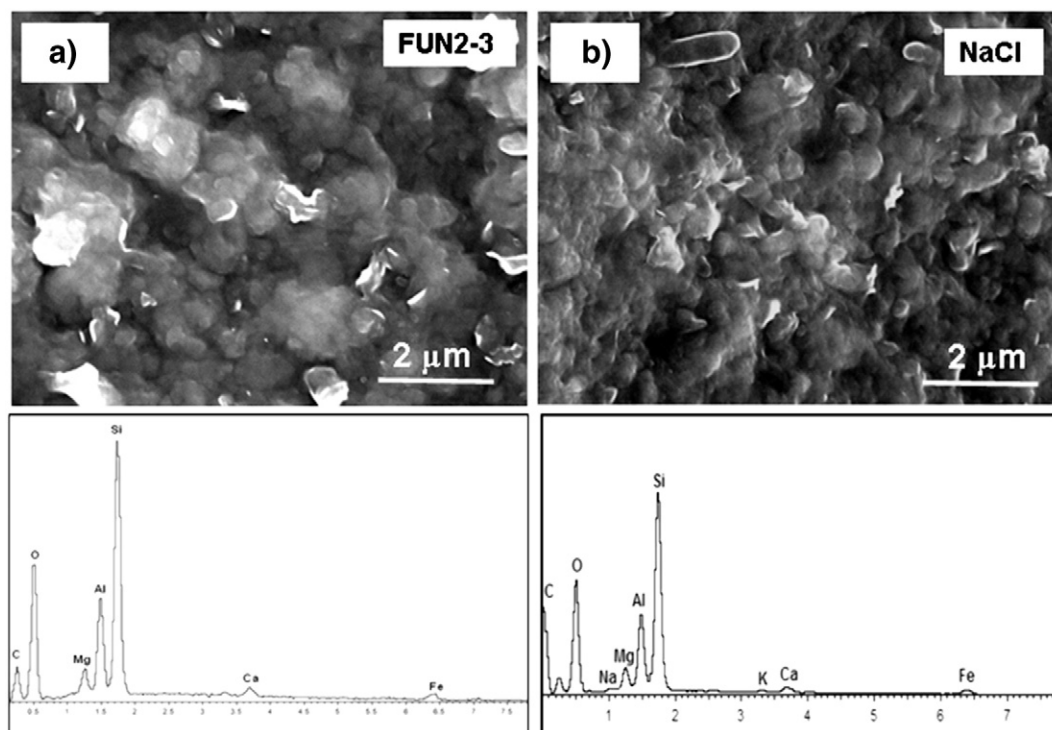
Fig. 4. (a) SEM image and (b) EDX spectrum of colloidal particles obtained in generation experiments with: FUN2–3 water under static conditions (left), and with 1 · 10^{-3} M NaCl under dynamic conditions (right). See EDX analysis in Table 5.

Table 5
Comparison of EDX analyses of colloids generated in two different experiments with FEBEX bentonite powder.

Composition (%)	Colloids in FUN2–3 under static conditions	Colloids in NaCl under dynamic conditions	FEBEX powder
SiO₂	68.64	61.76	70.00
Al₂O₃	18.75	18.23	17.90
MgO	5.56	4.42	5.35
FeO	4.04	2.89	4.50
CaO	1.85	1.60	1.40

For example, in the cell hydrated with $CaCl_2$ the Ca^{2+} concentration in the incoming electrolyte (Fig. 5b) is approximately 11 mg/L and, in the eluted water at the end of the experiments, Ca^{2+} concentration is approximately 7 mg/L. The concentration of Na^+ (Fig. 5c) in the eluted water is 7.50 mg/L compared with initial concentration less than 0.5 mg/L.

These results clearly show that bentonite adsorbs the calcium present in aqueous solutions by ionic exchange. This is a significant aspect to be accounted for the interpretation of the data and the relevance of these results at a long term, especially for radioactive waste repository PA.

The existence of ionic exchange processes makes it important that parameters as the liquid/solid ratio and kinetic aspects must be taken into account in the description of erosion processes. For example, in the experiments under static conditions, the increase of the ionic strength produced by the salt dissolution would depend on the liquid/solid ratio.

Geochemical modelling is fundamental to understand the conditions existing at the rock/bentonite interface, and to design experiments to reproduce chemical conditions as realistic as possible. Of particular interest is evaluating the effect of the ionic exchange at a long term. Under dynamic conditions, where the contribution of calcium is continuous (even if it is small) the saturation of the bentonite surface in calcium could occur. It has been shown that calcium bentonite does not produce colloids (Kaufhold and Dohrmann, 2008; Lagaly, 1989; Missana et al., 2011), thus generation rates are expected to slow down and even stop at a certain time. This also evidences the importance of performing long-term tests.

3.5. Colloid size distribution analyses

3.5.1. Colloids generated under static conditions

Fig. 6 shows the normalized size distribution measured by SPC (particles · mL⁻¹ · nm⁻¹) of the particles generated from the FEBEX bentonite at a density of 1.65 g/cm³ in NaCl, Mixed ($I = 1 \cdot 10^{-3}$ M) FUN2–3 and SJ5-3 (Grimsel case).
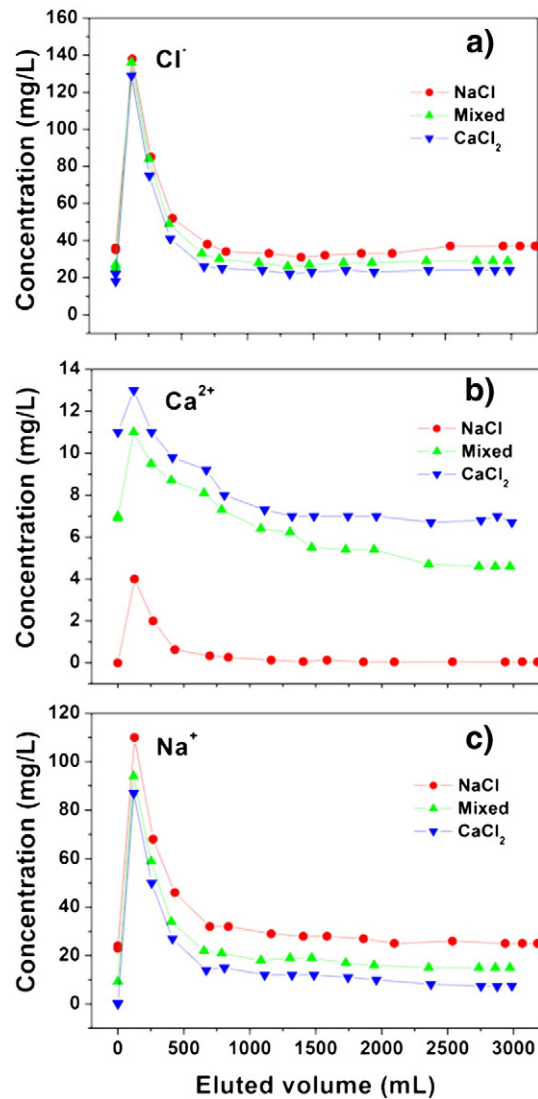
The highest concentration is observed for particles with a size range of approximately 50–100 nm, then the concentration decreases as the size of the particle increases. The *quasi*-linear behaviour observed in the log–log plot of Fig. 6, suggests that the size distribution can be described by the Pareto's law (Lerman, 1979).

In all the electrolytes, the size distribution is very similar; however the quantity of particles with size lower than 200 nm is slightly higher

Fig. 5. Concentration of a) Cl⁻; b) Ca^{2+} and c) Na^+ eluted during bentonite colloid generation experiments under dynamic conditions ($I = 1 \cdot 10^{-3}$ M) with NaCl, Mixed and $CaCl_2$ electrolytes.

in NaCl, whereas higher quantity of particle larger than 200 nm is observed when calcium is present (Mixed, FUN-2, SJ5-3).

Results confirm that even low calcium concentration slightly inhibits the generation of colloids and favour their aggregation. Nevertheless, the size distributions observed for colloids generated under static conditions, in all the considered electrolytes (with similar I) is not very different. Considering that ionic exchange processes exist, which lead to a very similar calcium content in the water at the equilibrium, this is not a very surprising effect.

Table 6
Difference between the initial and final concentrations in aqueous solutions of major ions: Cl⁻, Ca^{2+} and Na^+. Generation experiments under static conditions.

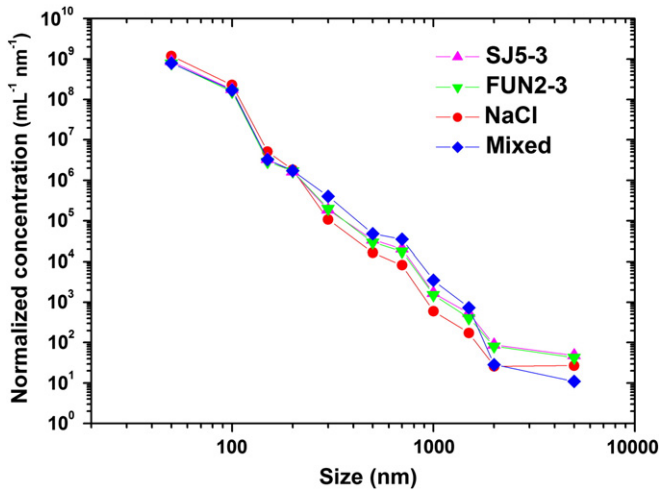| Compaction clay density ρ_d (g/cm³)	Aqueous solution	Difference in ion concentration (Δ = (final conc. − initial conc.) ± 2) (mg/L)		
		Cl⁻	Na⁺	Ca²⁺
1.60	GW	12.1	46.8	−7.5
1.65	NaCl	19.0	39.0	1.0
	Mixed	17.0	42.7	−5.9
	FUN2-3	13.1	37.0	−6.2
	SJ5-3	13.7	38.8	−6.4

Fig. 6. Normalized size distribution of colloids generated from the bentonite compacted at 1.65 g/cm^3 in NaCl, Mixed (I = 1 · 10^{-3} M), SJ5-3 and FUN2–3 (*Grimsel case*). Generation experiments under static conditions.

3.5.2. Colloids generated under dynamic conditions

In the case of colloids generated under dynamic conditions, it is interesting to evaluate the size distribution as a function of the chemistry of the incoming water but also as a function of the velocity of the water at the bentonite surface.

In dynamic experiments, periodical sampling was performed and the concentration and colloid size were measured by PCS. For SPC analyses different samples obtained at the main flow rate (20 mL/d) were selected (S1, S2 and S3) corresponding to the eluted volume of 1.8, 2.0 and 2.6 L. At the highest flow rate analysed (595 mL/d) two additional samples S4 and S5 were selected, corresponding to an eluted water volume of 4.3 and 6 L, respectively.

Fig. 7 shows the comparison of normalized size distribution obtained in the three contact electrolytes at water flow rates of 20 mL/day (Fig. 7a, sample S2) and 595 mL/day (Fig. 7b, sample S5). Also under dynamic conditions, particle size distributions follow the Pareto's law.

At the low flow rate, the concentration of particle smaller than 300 nm is higher in the NaCl electrolyte, whereas the size distribution of larger particles is quite similar in the three electrolytes. A plateau of concentration in the range between 100 and 200 nm is observed (not seen in the size distribution of colloids generated under static conditions) indicating the shear force imposed by the water flow rate used probably increases tearing off particles in this size range.

Fig. 7b clearly shows that the increase of the water flow rate (30 times) produces a decrease in the colloid mass (approximately 1 order of magnitude) due to the sample dilution. Additionally, the increase of the water flow decreases the differences induced by the chemistry of the electrolyte, even when the concentration of particles produced in NaCl is always slightly higher. If the relative percentage of particles of different size is considered, the increase of the flow rate seems causing a small increase of particles with larger size.

4. Discussion

Results demonstrated that, in low ionic strength aqueous solutions, erosion occurs and colloids are generated from the compacted clay both under static and dynamic conditions. Furthermore, the quantity of colloids generated can be quantified.

Considering the conditions in which the *in-situ* FEBEX experiment is running (*Grimsel case*) under static conditions, bentonite erosion would not exceed 5 mg/cm^2 (Table 2); in the presence of a conductive fracture at the bentonite surface and considering the data obtained with a water flow rate of 10^{-7} m/s (20 mL/d), the mass eroded would be
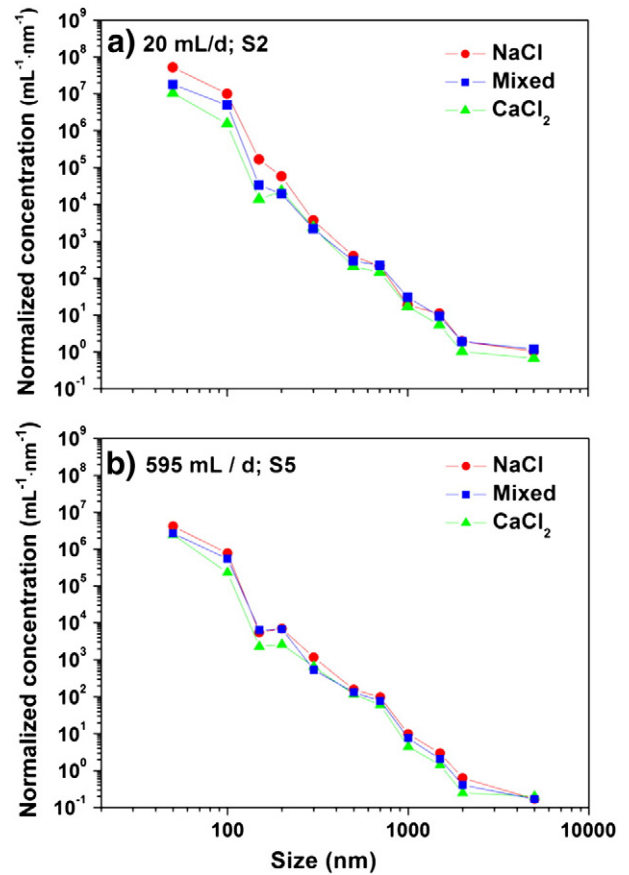

Fig. 7. Normalized size distribution of colloids in NaCl, Mixed and CaCl$_2$ (IS = 1 · 10^{-3} M) at water flow rates of (a) 20 mL/d (S2) and (b) 595 mL/d (S5). Experiments under dynamic conditions.

1.1 mg/y·cm^2 (Table 4). As mentioned in Missana et al. (2011), in real cases, surface area should be referred to the area accessible to bentonite extrusion (fractures width).

To play a role in RN transport, once generated, colloids must be mobile. Filtration processes in fractures, which would decrease the mobile colloid fraction, strictly depend on colloids size. Previous studies on mechanism affecting colloid transport in fractured rock showed that small particles are mainly affected by Brownian diffusion whereas for larger ones settling phenomena can be more relevant (Albarran, 2011; Baek and Pitt, 1996; Becker et al., 1999; Zvikelsky and Weisbrod, 2006). Ripening effects (increasing rate of colloid attachment due to already attached particles acting as collector) might increase the retention of larger particles (Bradford and Bettahar, 2006; Camesano et al., 1999).

Therefore, depending on their size, the particle can suffer distinct types of interaction with the rock and different fates in groundwater. All these effects were specifically analysed for bentonite colloid transport in crystalline rocks in another study (Albarran et al, 2013).

In the present study, the fraction of particle in each size interval, in different experimental tests, could be established. In particular, the analysis of the size distribution indicated that colloids generated from the compacted bentonite, in all the low I electrolytes, show the maximum concentration of particles in the range of 50–100 nm, and that the size distribution followed a Pareto's law (Lerman, 1979):

$$\frac{d[N]}{dD} = A \cdot D^{-b} \tag{2}$$

where A and b are constants (in size intervals), D (nm) is the size and $[N]$ (mL^{-1}) is the cumulative colloid concentration for size D. When $b > 1$,

and for sizes ranging from $D_{(m)}$ the minimum size analysed to $D_{(M)}$ the maximum size considered, *e.g.* 1000 nm, the cumulative size distribution is given by:

$$[N] = \frac{A}{b-1} \cdot \left\{ D_{(m)}^{(1-b)} - D_{(M)}^{(1-b)} \right\} \tag{3}$$

The integrated colloid concentration (E. 3) can be determined from a minimum value of $D_{(m)}$ (*i.e.* detection limits of instrument) to a maximum size for which colloids are not found in significant concentration.

The general validity of Pareto's law is subject to the number of small particles in a sample is orders of magnitude higher than large ones (Buffle and Leppard, 1995).

The constant value b determines the stability of colloid population and can be estimated as the *slope* of the representation of logarithm of the normalized distribution size *vs.* logarithm of their size, as those presented in Figs. 6 and 7.

For colloids or particles produced by erosion b is 4 (Lerman, 1979). However, in natural media, nucleation and aggregation may modify both A and b values. A value of $b = 4$ (or higher) indicates that aggregation does not take place but $b < 4$ indicates that aggregation may have occurred (Degueldre et al., 1996b).

Table 7 shows the Pareto's law parameters obtained in generation experiments calculated for the size range of 50–2000 nm (Figs. 6 and 7), where the data hold a normal distribution.

Previous studies showed that particles in groundwater present b values in the range 2–6 (Degueldre et al., 2000; van Beek et al., 2010) and the value is strictly related to the chemical conditions of the system (pH, dissolved organic carbon). In the experiments presented in this study, the highest values of parameter b of the Pareto's law, obtained by the fit of the experimental curves (Figs. 6 and 7) were observed for the colloid generated under static and dynamic conditions in NaCl (4.85 and 4.55, respectively).

The analysis of the system stability by means of the Pareto's law showed that both under dynamic and static conditions aggregation processes are not likely to occur ($b > 4$).

In the presence of calcium (Mixed, FUN2–3 and SJ5-3) b took values in the range 4.15–4.36 indicating that, at this low ionic strength, colloids are still stable.

The presence of bivalent ions as calcium inhibits the initial stages of gel/colloid formation and, in general, the quantity of colloid generated in presence of calcium is lower in any experimental configuration analysed in this study. However, at the low ionic strength analysed in this work, this effect is small.

Previous studies showed that the colloid generation from FEBEX bentonite homoionized in calcium is negligible (Missana et al., 2011), therefore if a continuous income of calcium is provided, and this could be the case of a DGR, the bentonite generation behaviour could drastically change at the long term. Thus it is very important to analyse these interactions at a longer time-frame with long-term tests.

Under dynamic conditions the presence of a water flow at the bentonite surface imposes a shear force on surface clay. The shear force τ_f

(N/m^2) is related to the flow velocity by Stoke's law by means of this equation (Pusch, 1983):

$$\tau_f = 6\pi\eta Dv \tag{1}$$

where η is the viscosity of the water, D is the particle diameter, η is the viscosity of the groundwater, and v is the water flow velocity. In principle, higher water flow rates may contribute to physical erosion process.

This relation clearly shows that the shear force should be more important for larger particles and higher velocities. Baik et al. (2007) stated that velocity in the range of 10^{-5}–10^{-7} m/s is enough to promote erosion from compacted bentonite generating particles with size between 500 and 1400 nm. Kurosawa et al (1999) indicated that higher velocities (10^{-5}–10^{-4} m/s) are necessary.

At water velocities evaluated in this work (10^{-7} and 10^{-5} m/s) colloid generation was observed. In dynamic experiments, the dilution of the samples, makes difficult the analysis with techniques not as sensitive as SPC, very important in this study.

At the low water flow rate used (20 mL/day), the importance of the electrolyte was mainly observed in the generation of particles of smallest size (<300 nm), which clearly presented higher concentrations in the absence of calcium. This effect was not as clear for larger particles because, if the shear force increases with the size of the particle, the mechanical effect may predominate over the chemical one.

At high flow rate (595 mL/day) the size distribution was very similar in all the electrolytes (even if in the absence of calcium the concentration of particles was always slightly higher); probably due to the preferential tearing off of larger particles due to the shear force.

5. Conclusions

Bentonite erosion and colloid generation studies from FEBEX compacted bentonite were performed under conditions as similar as possible as those expected in a radioactive waste geological repository, for gathering information needed for the safety assessment of such repositories. The study provides a lot of experimental data, under realistic conditions, not available before and provides methodologies adequate to the scope, considering that in such a complex systems chemical and hydrodynamic factors can compete.

Experiments were carried out considering chemical conditions favourable for colloid stability and mobility ($I = 1 \cdot 10^{-3}$ M). Colloid generation rates which can be the main interesting parameters for PA applications have been determined in the present work under these conditions. These generation rates correspond to the initial stages of the erosion process and should be verified with long-term tests if chemical changes due, for example, to ionic exchanges are expected.

The analysis of particle size distribution showed that both in dynamic and static conditions the highest concentration of particles was always within the size range of 50–100 nm. In the absence of calcium, the highest concentration of smaller particles was observed both under dynamic and static condition. The particle size distributions could be described by Pareto's law.

The chemistry played a very important role in generation processes in all the cases and cannot be ruled out. However, under dynamic experiments, less dependence of size distribution on the chemistry was observed as the water flow rate increased. This is most probably due to the fact that a raising shear force causes the erosion of larger particles.

The presented results also evidence the importance of water/clay interactions, which should be then explicitly considered in erosion models. Ionic exchange processes must be taken into account to evaluate the colloid generation and the chemistry of the system. Longer tests and geochemical modelling are needed to better understand the effects of cationic exchange in the system at the long term.

Table 7
Paretos's law parameters obtained in the size range of 50–2000 nm from SPC tests.

Generation conditions	Aqueous solution	A	b
Static	NaCl	$2.95 \pm 0.55 \times 10^{17}$	4.85 ± 0.19
	Mixed	$2.82 \pm 0.64 \times 10^{16}$	4.36 ± 0.20
	FUN2–3	$2.29 \pm 0.48 \times 10^{16}$	4.36 ± 0.18
	SJ5-3	$2.19 \pm 0.50 \times 10^{16}$	4.34 ± 0.19
Dynamic	NaCl	$3.20 \pm 0.63 \times 10^{15}$	4.55 ± 0.25
	CaCl$_2$	$6.80 \pm 0.61 \times 10^{13}$	4.15 ± 0.13
	Mixed	$1.30 \pm 0.60 \times 10^{14}$	4.23 ± 0.05

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