



BELBaR

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Progress Report on the effects of the water chemistry, clay chemistry and water/clay interactions on erosion processes.

DELIVERABLE D2.1

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INTRODUCTION

The interest in studying bentonite erosion and the mechanisms of colloid generation from the compacted bentonite engineered barrier in a high level radioactive waste (HLRW) repository is twofold. First of all, colloids may affect RN transport in the repository. To understand and quantify the role of colloids produced from the bentonite on RN migration towards the geosphere is one of the issues of concern in safety assessment (SA). In fact, many uncertainties related to the role that these colloids may play in RN migration still exist (Missana et al., 2009). In particular, to establish if and how much bentonite colloids are able to affect RN transport from the near field to the far field of the repository, it is necessary to know under which conditions the compacted bentonite will produce colloidal particles, free to move into the contacting aqueous phase. Additionally, the evaluation of bentonite erosion is important for establishing its functionality at the long-term, which could be compromised if a significant clay loss occurs.

Colloid generation from powdered bentonite, under different chemical conditions, has been studied in the past (Kaufhold and Dohrmann, 2008; Birgersson et al, 2009). Much less studies performed with compacted bentonite have been published and, in most of the cases, the clay was not confined. For example, Garcia-Garcia et al. (2009) and Bessho and Degueudre (2009), studied the effects of ionic strength and clay type on colloid generation/sedimentation from compacted bentonite but allowing its free-swelling. Pusch (1999) studied the formation of clay particles (2-50 μm) from the MX-80 bentonite buffer and their release through apertures simulating fractures in granite.

From all these experiments, a general and good qualitative picture of the processes that affect the generation of colloids has been derived, but it is difficult to use these data for SA analyses, as they are not obtained under realistic (repository) conditions.

In the unconfined state, most of the mass of clay could be converted in “free” colloidal material if the conditions are favourable (i.e. in deionised water), therefore this type of experiments may lead to a significant overestimation of the quantity of colloids that actually could be generated in a repository. In a repository, the mean density of the compacted clay is not expected to change significantly after saturation and major loss of density will occur only in limited extrusion paths (fractures or microfractures).

Bentonite erosion studies in more realistic conditions, i.e. considering the compacted and confined clays were, so far, significantly scarcer. Missana et al. (2003) and Baik et al. (2007) studied the generation of bentonite colloid in different set-up simulating the bentonite / granite interface of a repository. More detailed and systematic studies of the parameters affecting colloid generation from the compacted and confined bentonite, under a wide range of physico-chemical conditions, are very recent (Alonso et al., 2007; Seher et al., 2009; Missana et al., 2011; Birgersson, 2009).

The problematic of colloids would be most crucial in dilute ground-waters and, in principle, would be less important in saline waters like, for example those existent in Äspö. However,

at the long term, after glaciation, glacial melt water could permeate the bedrock and dilute the salts of the present water, and this possibility must be taken into account.

OBJECTIVES

In the BELBaR Project, the objective of the Work Package 2 (WP 2, Bentonite Erosion), is to analyze bentonite erosion carried out in the conditions expected in a HLRW repository i.e. from highly compacted and confined bentonite, trying to identify the processes mostly affecting colloid generation under realistic conditions and, therefore, of potential interest to SA.

Any mechanism that can favor the formation of particles of colloidal size is of concern and two possible scenarios are considered: the *static* and the *dynamic*.

In the static system, the water interacts with the clay in a closed vessel (the water is not changed during all the experiment). In this case, the transformation of the gel to a sol is expected to be mainly a chemically – driven process, as it depends only on the combination of the water chemistry and clay properties. Under these conditions, diffusion would be the main transport process for the clay particles, eventually generated.

However, the worst scenario in a repository in crystalline rocks would be the presence of a hydraulically active fracture (the dynamic system), for this reason it is important to know if the water flow at the bentonite surface or gel-front may increase colloid detachment. In the dynamic system, erosion could be mechanically produced by drag forces, caused by the flow along the bentonite surface, exceeding the bond particle forces (Pusch, 1999). Under these conditions the advective transport will prevail.

In this report, the studies performed so far in WP2, to understand the effects of the water chemistry, clay chemistry and water/clay interactions on erosion process will be summarized.

EXPERIMENTAL CONTRIBUTION

1. CIEMAT (Tiziana Missana and Ursula Alonso)

CIEMAT, performed erosion studies using different experimental sets-up. The cells used in the first experiments can be seen in Figure 1. To determine the generation of colloids under static (no flow) conditions a tablet of approximately 4 grams of compacted bentonite (1.2 to 1.65 g/cm^3), was introduced in a stainless steel cylinder (Figure 1a) and located between two sintered stainless steel porous filters. The cell was closed by two open Delrin grids and immersed in the desired aqueous solution within a closed vessel (Figure 1b). The porous filters (Figure 1c) have a thickness of 3.1 mm, a mean pore size of $100 \text{ }\mu\text{m}$ and a porosity of approximately 40 %.

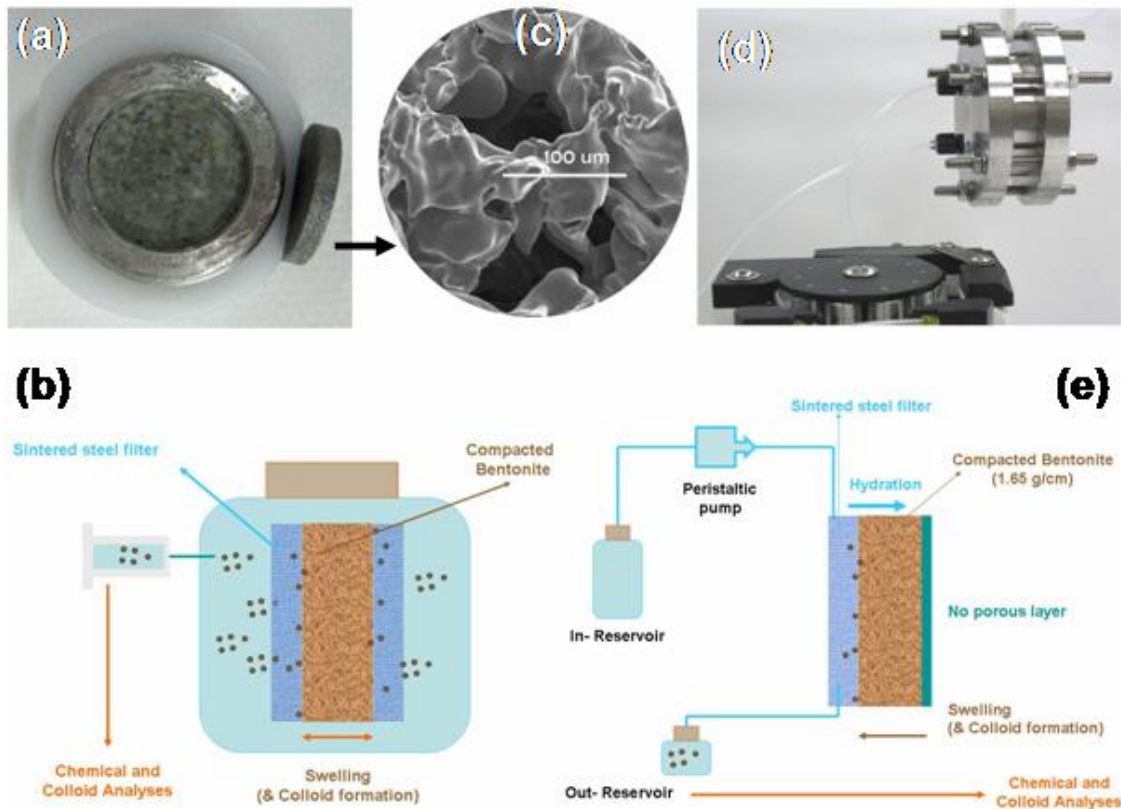


Figure 1: Experimental cells and schematic of the generation tests for static (a and b) or dynamic (d and e) experiments. In (c) a SEM image of the sintered steel porous filter shows large pores.

The filters allow the water to hydrate the bentonite and, at the same time, provide an open space for the extrusion of the gel formed, as well as for colloid formation and transport towards the aqueous phase. Provided the porosity of the filters is similar, the filters pore size does not affect appreciably neither the final concentration nor the size of the colloids generated, as shown by Seher et al. (2009) who compared pore sizes of 100, 10 and 2 μm . The experiments under static conditions were performed with *as-received*, Na- and Ca-homoionized clays.

A periodical sampling of the aqueous solution was carried out to analyze the concentration and size of colloids (eventually) formed. One small aliquot of the aqueous solution (approximately 1 mL) was extracted with a syringe after gently shaking the vessel to homogenize the suspension. This allows determining the total mass of clay colloids detached. At the end of the experiment the chemistry of the final solution left was always analyzed, to check by geochemical modeling if dissolution and ionic exchange process occurred.

To determine the generation of colloids under dynamic (flow) conditions and to study the contribution of a water flow on bentonite erosion a different set-up was used. Approximately 46 grams of bentonite compacted to a desired density in cylindrical pellets (5

cm of diameter and 1.24 cm of thickness) are installed in the experimental cell. The cell used for erosion experiments with flow, is similar to that used in through-diffusion experiments (Garcia-Gutierrez et al., 2001), but with one of the two sides closed (Figure 1d).

A large reservoir (in-reservoir) contained the initial aqueous solution that entered into the cell through Teflon tubing. The solution was forced through the sintered steel filter with a peristaltic pump and periodically collected after the contact with the bentonite surface, for colloids and chemical analysis (Figure 1e). The water eluted was collected in polyethylene tubes of 20-60 mL for colloid analysis.

The analysis of colloids was performed by Photon Correlation Spectroscopy (PCS) using a Malvern 4700 system equipped with a Spectra - Physics 4W argon laser ($\lambda = 514$ nm) and the photomultiplier located at a scattering angle of 90° . PCS was used to determine the size and concentration of colloids in the aqueous solutions as a function of time.

Another set up used more recently for erosion experiments under dynamic conditions consisted on a methacrylate cell, simulating a conductive fracture, shown in Figure 2. In these experiments, apart from the chemical conditions (of water and clay), the velocity of the water at the bentonite surface can be changed and also the dimensions of the artificial fracture.

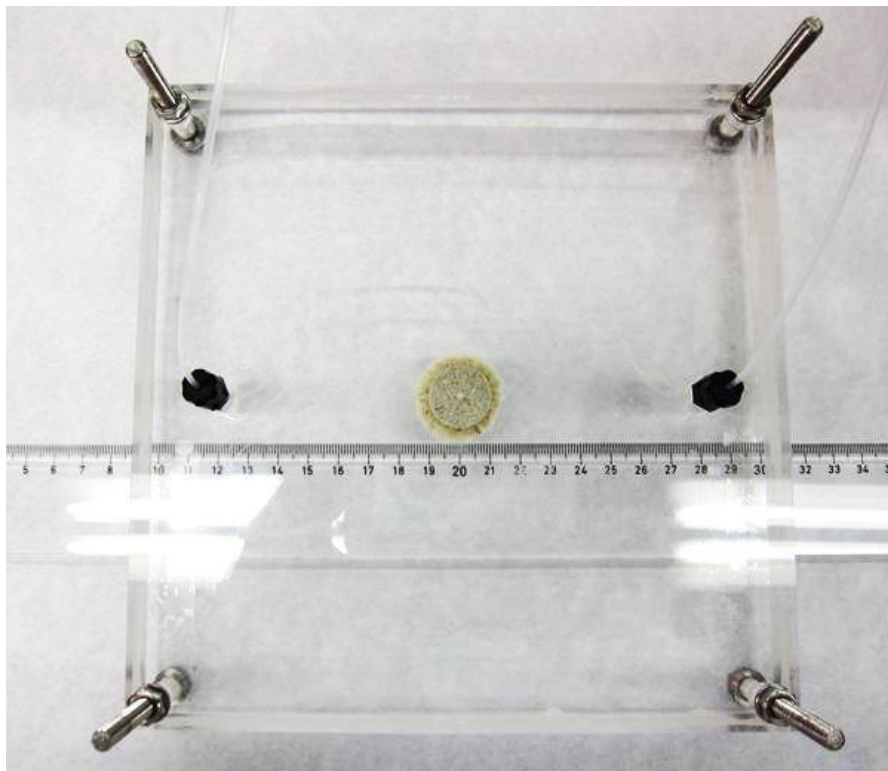


Figure 2: Experimental methacrylate cell simulating a fracture.

The effects of different parameters (density of the clay, the exchange complex of the clay and chemistry of the contacting water) were studied in static experiments.

The analysis of the water in which the compacted bentonite was submerged, in static experiments, indicated that the higher the compaction density the higher the concentration of bentonite colloids found in solution. In general, the increase of clay particles in solution is initially rapid, but an equilibrium concentration is finally reached; this was observed in more than 30 experiments, even with duration larger than one year.

Figure 3 shows different examples of results obtained in these experiments, made using low ionic strength waters. Figure3(a) shows the mass of clay colloids generated from bentonite compacted at a density of 1.60 g/cm^3 in contact with NaCl, CaCl_2 and GW with ionic strength (IS), $\text{IS} = 1 \cdot 10^{-3} \text{ M}$. Data obtained with deionized water and $1 \cdot 10^{-2} \text{ M}$ NaCl (Alonso et al., 2007) are included for comparison; Figure2(b) shows the results obtained with bentonite compacted at 1.65 g/cm^3 in contact with NaCl and a mixed Ca-Na electrolytes with $\text{IS} = 1 \cdot 10^{-3} \text{ M}$ and natural granitic waters FUN2-3 and SJ5-3, from the Grimsel Test Site (Switzerland).

The fact that steady-state conditions are reached is a relevant point, because it means that the maximum quantity of colloids generated, will depend on the initial conditions of the system (chemistry of the water, clay, compaction density, etc...), but that the bentonite loss in a static system will not be continuous. The values of colloids mass generated in the experiments presented in Figure 3 are summarized in Table 1.

The size of the extrusion paths (joints or fractures) must have a primary importance on the quantity of colloids found in solution. This hypothesis was verified using experimental cells, with the same mass of bentonite, in which one of the two porous filters (Figure 1b) was substituted by a non-porous layer.

It was previously observed that, when the extrusion area was halved, the concentration of colloid in solution was approximately the half as well. Besides, the presence of colloids in solution will be limited to the surface available for colloid transport from the clay surface to the liquid phase and not to the surface available for clay hydration. If filters with a pore size much smaller than $1 \text{ }\mu\text{m}$ were used, we could observe the same clay hydration, the same water/clay interactions but we would not be able to observe any particle in the contacting solution.

This result indicates the need of normalizing the mass of colloids found in solution to the bentonite surface available for erosion; the advantage of this normalization is that it allows comparing results from different experimental set-up and initial conditions.

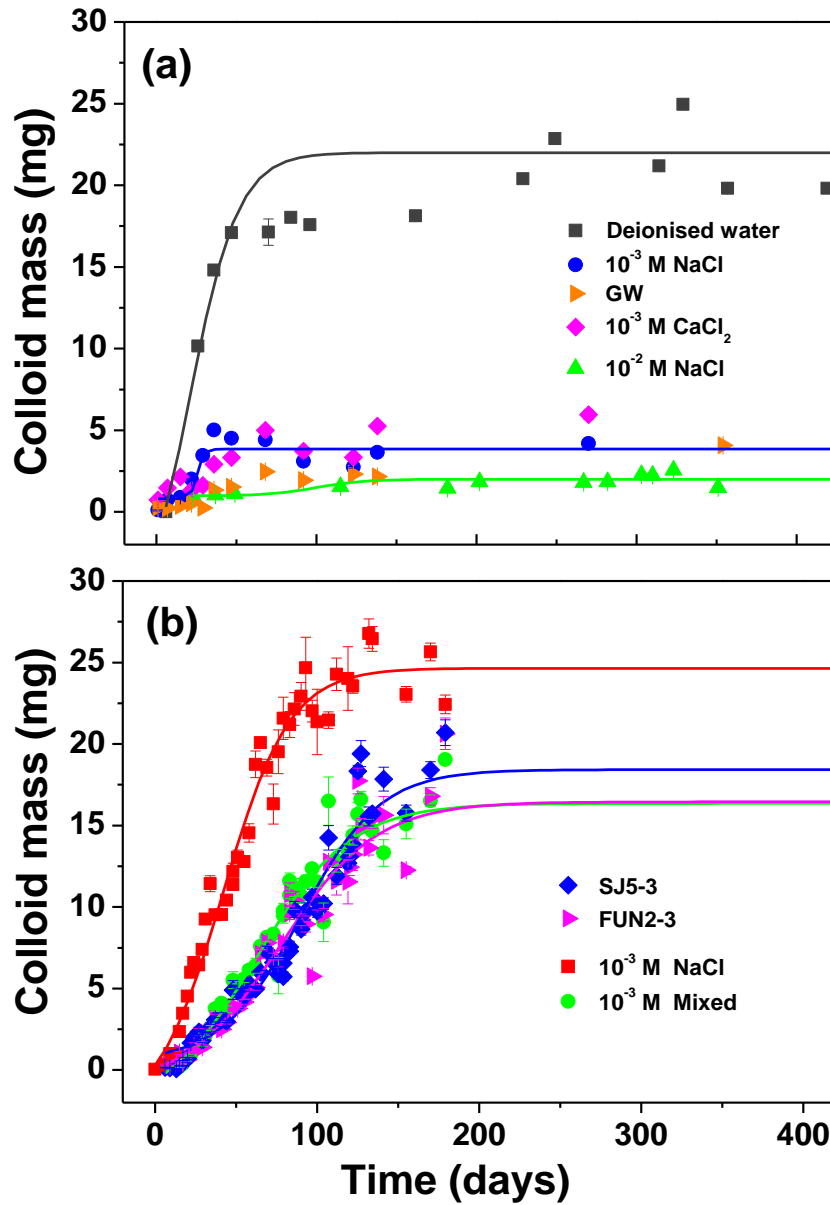


Figure 3. Mass of colloids generated from bentonite under static conditions. (a) bentonite compacted at a density of 1.60 g/cm³ in contact with NaCl, CaCl₂ and GW with IS = 1·10⁻³ M. Data obtained with deionized water and 1·10⁻² M NaCl (Alonso et al., 2007) are included for comparison; (b) bentonite compacted at 1.65 g/cm³ in contact with NaCl and Mixed electrolytes with IS = 1·10⁻³ M and natural granitic waters FUN2-3 and SJ5-3, from the Grimsel Test Site.

Table 1: Summary of results of bentonite colloid generation experiments (Figure 1) under static conditions. All these experiments are made with similar IS ($I=1\cdot10^{-3}M$)

Compaction clay density P_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	Grimsel Water	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 (Ca-Na)	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

The ionic strength and the exchange complex of the clay are other important factors that affect bentonite erosion and the release of bentonite colloids. Figure 4a shows the quantity of bentonite colloids generated from the as-received bentonite compacted at a density of $1.6 g/cm^3$ in contact with solutions of increasing ionic strength (deionized water, Grimsel groundwater, $1\cdot10^{-3} M CaCl_2$ and $1\cdot10^{-2} M NaCl$). The quantity of colloids generated decreases abruptly when the ionic strength of the solution increases.

Figure 4b shows colloids generated in deionized water using either the as-received FEBEX bentonite or the bentonite homoionized in Ca or in Na. The quantity of colloids generated from the Ca-bentonite was always near or below the PCS experimental detection limit even in low or very low ionic strength solutions. Thus 100 % Ca-bentonites are not expected to be source of colloidal material, due to the high attractive inter-particle forces caused by ion correlation (Kjellander et al, 1988).

On the other hand, the quantity of colloid generated from the as-received clay was not very different from that generated from the Na-homoionized clay. The quantity of Na in the exchange complex of the as-received FEBEX bentonite ($\sim 25\%$) is therefore enough to favor almost the maximum possible generation of colloids, at least under favorable conditions in terms of water chemistry. A relatively small amount of Na in the exchange complex may thus significantly increase the dispersivity of the clay as Na adsorbed at the surface dominates the surface properties (Shainberg and Kaiserman, 1969).

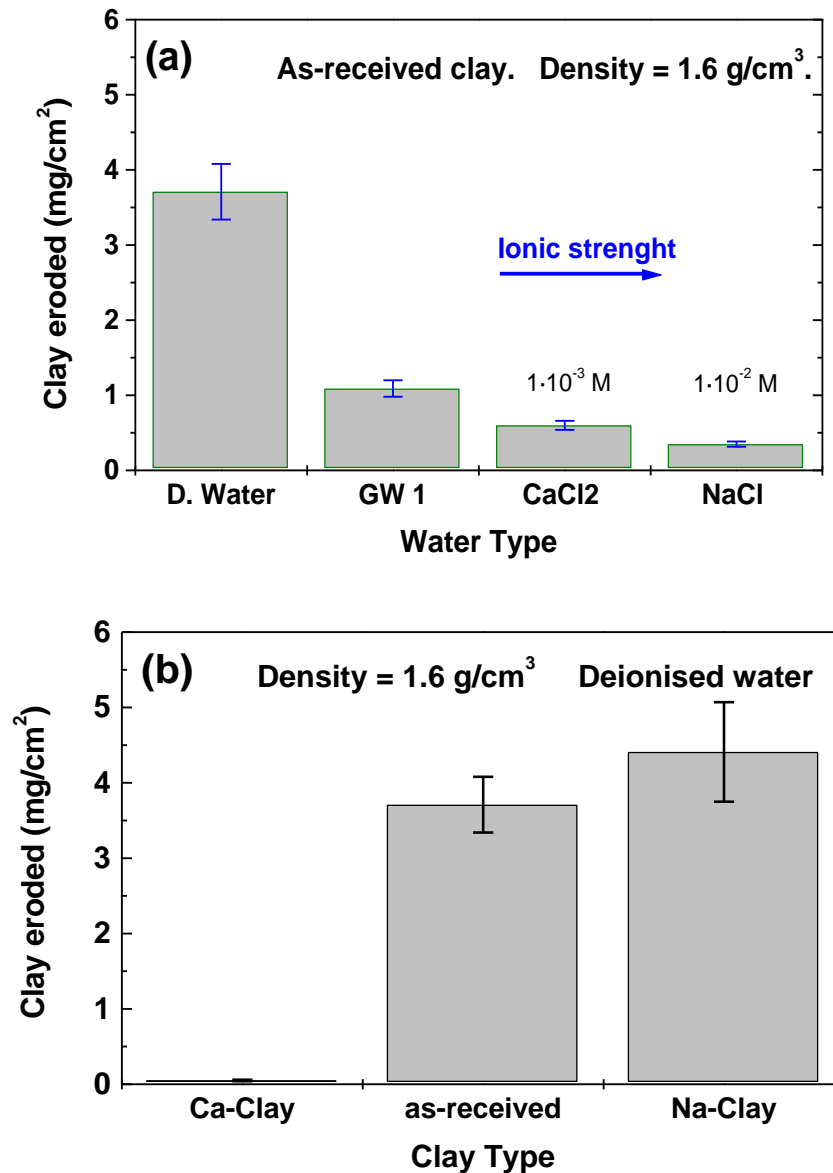


Figure 4: (a) Mass of clay eroded from the as received bentonite compacted at a density of 1.6 g/cm³ in solutions at different ionic strengths, See Table 1; (b) Bentonite colloids generated from different clays compacted at a density of 1.6 g/cm³ in deionized water

Ionic strength is not the only parameter affecting the formation and stability of colloids. Divalent ions as Ca are more effective than monovalent ions as coagulants (Shultz-Hardy rule), for this reason is important to analyze the chemical properties of the solution. Furthermore, the presence of Na (or Ca) in the exchange complex of clay minerals is known to be a very important parameter determining the dispersion capacity of soils (Sparks, 2003). The results obtained in low ionic strength solutions, also indicate some effect of the presence of Ca in the aqueous solution. In a range of approximately one order of magnitude for Ca concentration ($1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ M) the effect on the quantity of colloid generated (in

mg/cm²) was not very important although the sizes of colloids in the presence of Ca were always larger. The fact that, under these experimental conditions, the presence of Ca seems not to be very relevant is most probably due to cation exchange effects.

Ca is incorporated in the clay and the aqueous solution is therefore depleted in Ca; this effect has been clearly observed and discussed both in the static and in dynamic generation experiments (Missana et al., 2011). Major effects on colloid generation are expected only when the surface of the gel becomes saturated in calcium, i.e. when the concentration of Na in the exchange complex of the clay at the gel front has decreased under the critical value limiting its dispersion (Sparks, 2003), as already mentioned. This can occur only in an open system i.e. when fresh water with Ca content is continuously provided. An example of this behavior is provided in Figure 5.

In the experiments under dynamic conditions, the evolution of the concentration of the main ions Cl⁻, Ca²⁺ Na⁺ and in the water eluted from the generation cell was periodically measured. The evolution of the concentration of Cl⁻ (Fig. 5a), Ca²⁺ (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) Ca²⁺ concentration is still lower than that of the incoming electrolyte and Na⁺ concentration is higher.

For example, in the cell hydrated with CaCl₂ the Ca²⁺ concentration in the incoming electrolyte (Fig. 5b) is approximately 11 mg/L and, in the eluted water at the end of the experiments, Ca²⁺ 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 solution by means of 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 in the frame of PA of a radioactive waste repository.

Ionic exchange processes indicate that parameters as the liquid/solid ratio as well as kinetic aspects must be taken into account in the description of erosion processes

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 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.

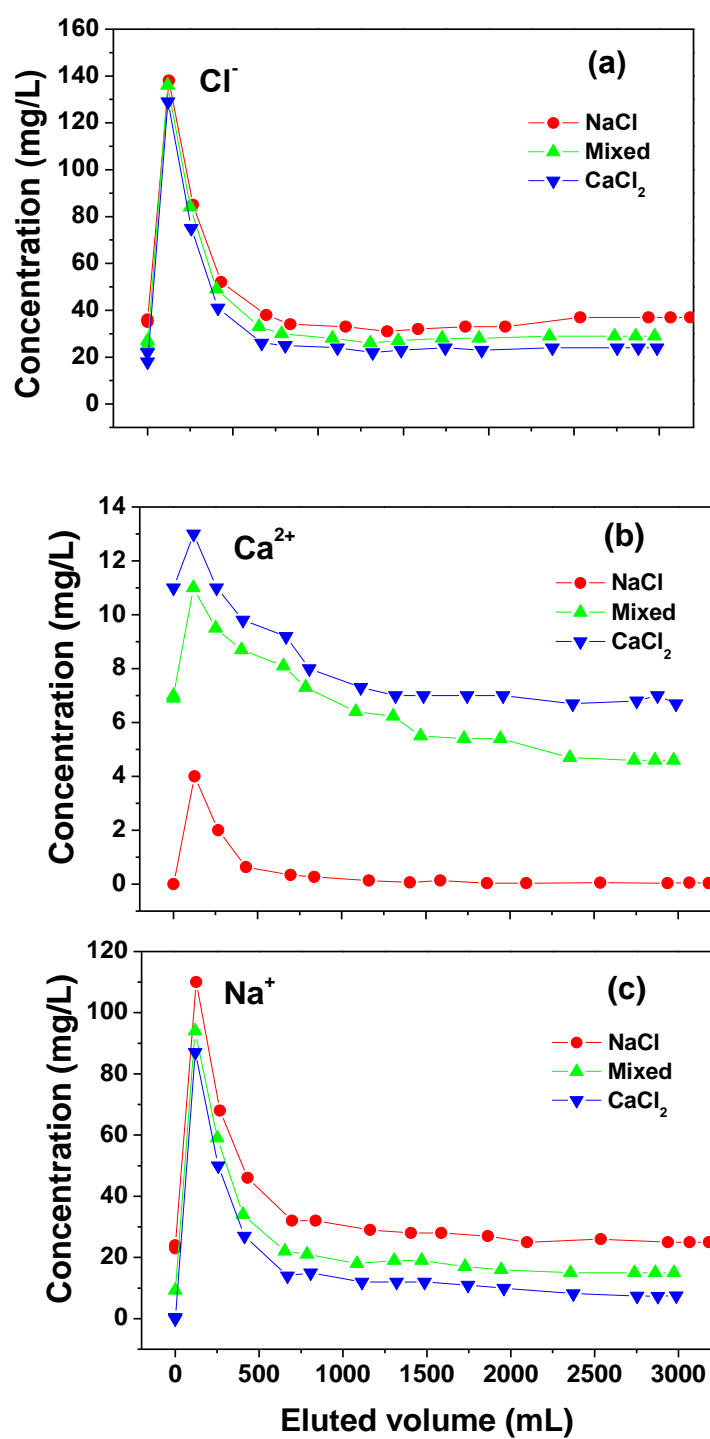


Figure 5. Evolution of the concentration of a) Cl⁻ ; b) Ca²⁺ and c) Na⁺ in NaCl, Mixed and CaCl₂ electrolytes (IS=1·10⁻³ M) eluted in bentonite colloid generation experiments under dynamic conditions.

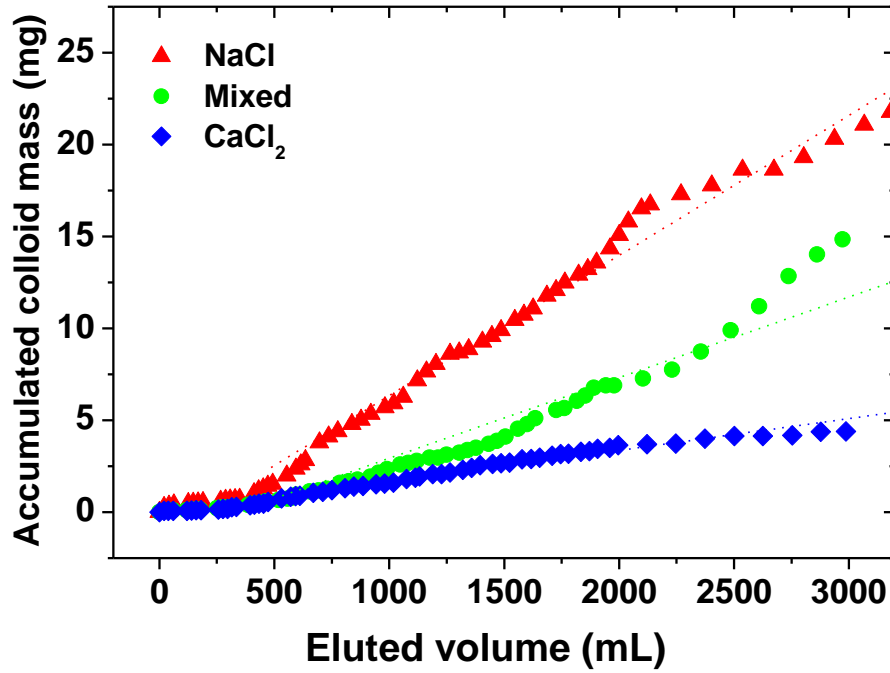


Figure 6. Accumulated mass of colloids generated under dynamic conditions in NaCl, Mixed and CaCl₂ (IS = $1 \cdot 10^{-3}$ M) at water flow rate of 20 mL/d.

The effects of the chemistry of the water can be clearly observed also in dynamic experiments (Figure 1d). In these experiments, the FEBEX clay was used as-received and compacted to a dry density of 1.65 g/cm³. Three different solutions (NaCl, CaCl₂ and CaCl₂/NaCl mixed electrolyte) at the same ionic strength ($I = 1 \cdot 10^{-3}$ mol/dm³) were used.

Figure 6 shows an example of the results obtained in dynamic experiments performed with a water flow rate of 20 ± 1 mL/day. The graph represents the accumulated colloid mass during the experiments.

At a fixed ionic strength, the presence of Ca in the fresh solutions inhibited the erosion process and the generation of bentonite colloids. As a clear increasing or decreasing trend in colloid generation was not observed, the bentonite colloid concentration was considered a constant, for a constant water flow rate, under this time frame of the experiment. However, new experiments showed that this initial rate is decreasing with time and that in certain cases generation even stops.

Table 2 shows these initial bentonite erosion rates, which can be used as “conservative” values for PA calculations.

The values estimated by these experiments are significantly lower than those estimated by a modeling approach by Liu and Neretkiens (2006) even in the worst case.

Table 2: 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)	Erosion rate (mg/d)	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

Also in preliminary dynamic experiments, carried out in the cells shown in Figure 2, the effects of the chemistry of the water used can be observed. These tests were carried out with the as-received FEBEX bentonite, using a water flow rate of 8 mL/h and a fracture thickness of 0.18 mm. Two different tests were carried out, one hydrating the bentonite with NaClO₄ 5·10⁻⁴ M, and the other with 1·10⁻³ M Ca(NO₃)₂. The mass of colloids generated as a function of the eluted volume is shown in Figure 7.

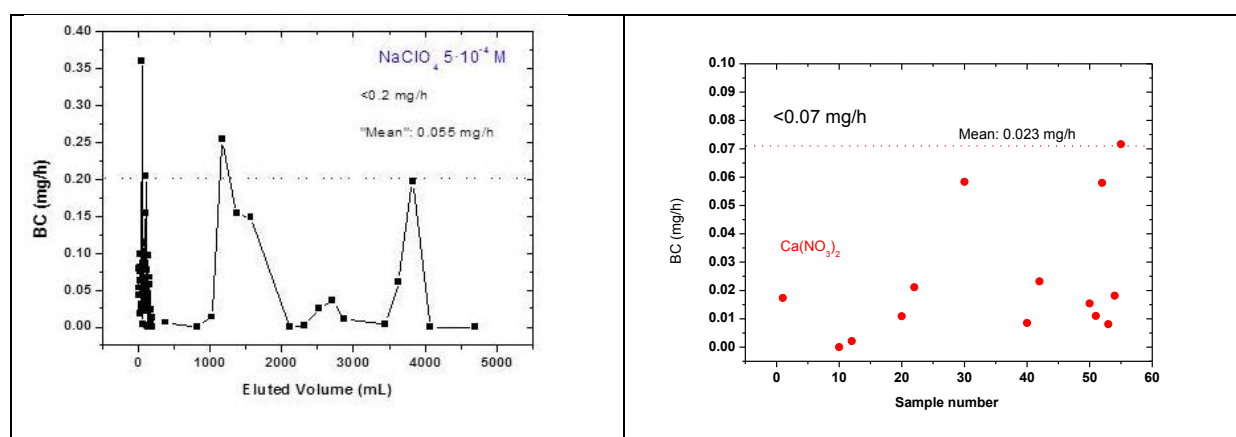


Figure 7. Mass of particle eroded as a function of the eluted volume: (left) NaClO₄ and (right) Ca(NO₃)₂. Water flow rate of 8 mL/h (7E-05 m/s).

In the cell hydrated with NaClO₄, a mean erosion rate of 0.056 mg/h (4.8E-04 Kg/y) was measured, and all the measured values were lower than 1.7E-03 Kg/y (upper limit). In the cell hydrated with Ca(NO₃)₂, a mean erosion rate of 0.023 mg/h (2E-04 Kg/y) was measured, and all the measured values were lower than 6.1E-04 Kg/y (upper limit).

The quantity of colloids generated from compacted FEBEX bentonite, under similar geometrical and water flow conditions, depends on the contacting electrolyte; the quantity

of extruded material is similar (Figure 8), but the presence of Ca in the electrolyte decreases the erosion; the gel is more easily depleted in absence of Ca;

Schatz et al (2012), in similar experiments, analyzed the effects of the ionic strength of the solution. They observed no erosion for sodium montmorillonite against solutions from 10 to 0.5 g/L NaCl, and also in 50/50 Ca/Na montmorillonite at 0.5 g/L NaCl. Erosion is not seen up to 8/4 mM in Na and Na/Ca clays.

The values obtained in this dynamic configuration, are in the same order of magnitude than that measured with the first experimental sets-up (Figure 1). Also in these experiments, simulating the fracture, it seems that the initial erosion rate tends to slow down. To verify this hypothesis, longer experiments are planned.

The effects of the chemistry of the water can be observed observing the characteristics of the gel that extrudes in the fracture. The extrusion depth of the gel is similar in both cases, but the gel hydrated with NaClO_4 appears “less compact”, in agreement with a mayor formation (and mobilization) of colloidal particles, as can be seen in Figure 8.

The swelling pressure is the first driving force for colloid generation determining the thickness of the gel layer, extruding in fractures and potentially subject to erosion. The presence of colloids in solution will be limited to the surface available for colloid transport (fracture) and not to the surface available for clay hydration.

Results (also quantitatively) are basically in agreement with previous tests. (Missana et al, 2011);

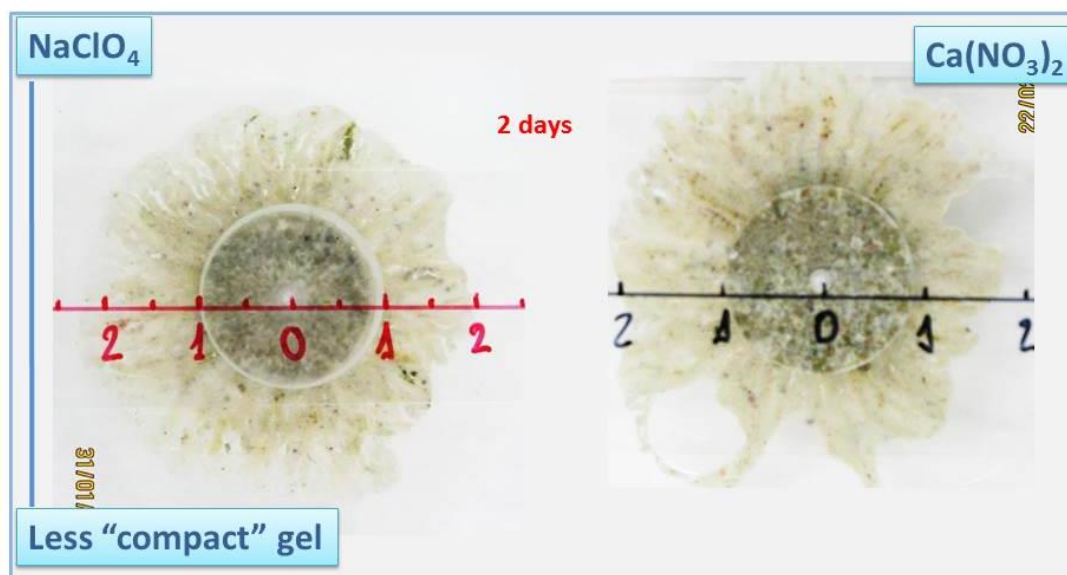


Figure 8. Comparison of the gel extruded in the fracture upon hydration with different electrolytes.

CONCLUSIONS

Formation of clay particles from compacted and confined bentonite has been analyzed by different experimental.

The swelling pressure seems to be the first driving force causing the gel intruding the fracture/pores of the rock; thus the density of the clay determines the thickness of the extruded gel layer, potentially subject to erosion. The presence of colloids in solution will be limited to the surface available for colloid transport from the clay surface to the liquid phase and not to the surface available for clay hydration.

In a closed system, a concentration of colloids in equilibrium with the clay surface is reached and dispersion is not continuous. The colloid concentration at the equilibrium depends on various factors such as clay type, ionic strength and/or Ca content and on the bentonite/water chemical interactions. Chemical conditions are of major importance in all the cases.

Ca-bentonite forms colloids in quantities very near or lower than to the detection limit of our techniques, even in chemical conditions which are favorable for colloid generation. However, a percentage of Na around 20-30 (as that present in FEBEX bentonite) is enough to obtain a generation of colloids similar to that observed for the Na-bentonite.

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

EXPERIMENTAL CONTRIBUTION

B+TECH (Tim Schatz)

Background

This report summarizes research conducted at B+Tech during the first 15 months of the BELBaR Project. The work described below is related to BELBaR deliverable D2.1 “Report on the effects of water chemistry and clay chemistry on erosion processes” and covers factors other than flow velocity, fracture geometry and accessory minerals (which are described in BELBaR deliverable D2.2 “Progress report on erosion processes under flowing water conditions”) affecting erosion.

The work at B+Tech is conducted mainly using small-scale, flow-through, artificial fracture systems in which swelling clay material can extrude/erode into a well-defined, intersecting fracture (see Figure 9). These experiments are performed in order to simulate the potential extrusion/erosion behavior of bentonite buffer material at a transmissive fracture interface. Using such systems the effect of solution chemistry (salt concentration and composition), material composition (sodium montmorillonite and admixtures with calcium montmorillonite, natural bentonites), flow velocity, fracture geometry (aperture, down-slope) and the role of accessory minerals on erosion processes can be analyzed.

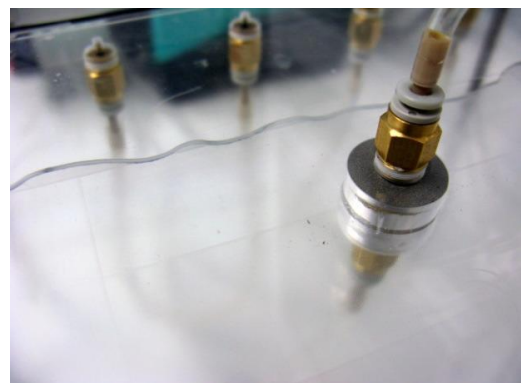
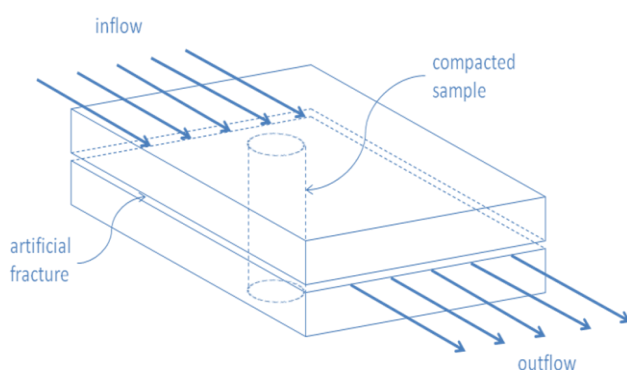


Figure 9. Schematic representation of the flow-through, artificial fracture test system design basis (left) and photographic image of a flow front approaching a compacted sample through a 1 mm aperture fracture (right).

Response to solution chemistry and material composition

The aim of this work is to examine the extrusion/erosion behavior of bentonite buffer material into an intersecting, transmissive fracture environment over a range of solution chemistry (salt concentration and composition) and material composition (sodium

montmorillonite and admixtures with calcium montmorillonite) conditions [Schatz et al. 2012].

Artificial fracture testing permits clear distinctions to be made (both visually and analytically) between those tests for which erosive mass loss is observed and those for which it isn't (see Figure 10.)

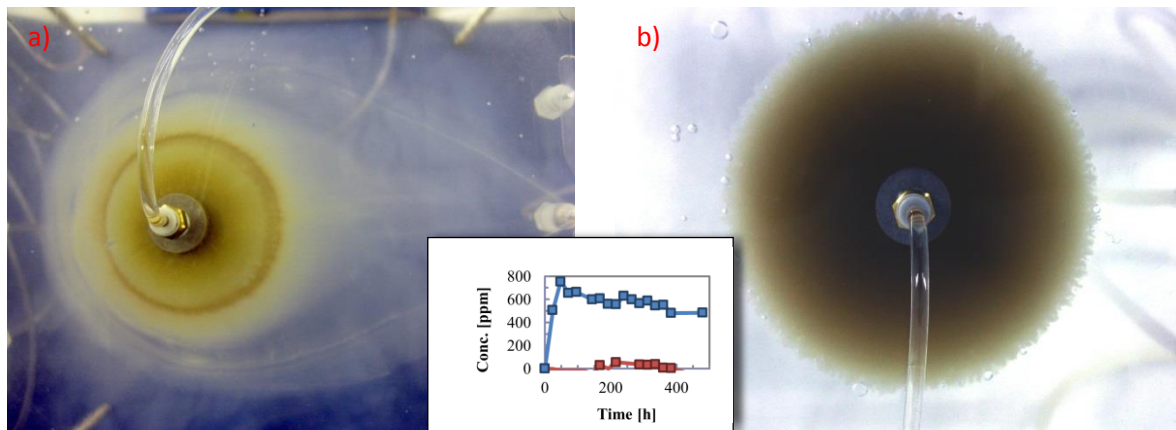


Figure 10. Overhead photographic images of artificial fracture tests at 336 h showing a) 50/50 calcium/sodium montmorillonite against deionized water flowing at 0.47 ml/min and b) sodium montmorillonite against 1 g/L NaCl flowing at 2.68 ml/min. Note the erosive flow in image a but not image b. Inset plot shows effluent solids concentration data over time for the same tests. The blue-filled squares represent data for test presented in image a and the red-filled squares represent data for the test presented in image b. The scatter of effluent data for the test at 1 g/L around the zero concentration level corresponds quite well with the variability in background solids content and the eroding solids concentration is considered to be, effectively, zero.

Overall, no erosion was observed for sodium montmorillonite against solution compositions from 10 g/L to 0.5 g/L NaCl. Most reports in the literature indicate that a concentration of 0.5 g/L NaCl (8.6 mM) is below, in some cases well below, the (experimentally observed) critical coagulation concentration (CCC) for the colloidal sodium montmorillonite/sodium chloride system. Of course the reported CCC values were all obtained under batch conditions whereas the artificial fracture test results correspond to spatially confined, dynamic conditions which are of more relevance to the erosion scenario. Insofar as CCC values are often used to describe a limiting boundary condition for colloid generation and stability and, by extension, a concentration limit below which erosion may take place, the discrepancy between reported CCC values (higher concentrations) and observed erosion limits (lower concentrations) is potentially quite important.

No erosion was observed for 50/50 calcium/sodium montmorillonite against 0.5 g/L NaCl either. Although it has been demonstrated that a CCC value for clay/water systems

containing both mono and divalent counterions cannot be defined in terms of a single, aqueous cation concentration due to ion exchange, [Birgersson et al. 2009], erosion tests on such mixed electrolyte systems can be used to establish stability limits. Moreover, as indicated above, batch CCC values in and of themselves may have limited relevance to actual erosion stability limits in transmissive fracture environments.

Below the electrolyte concentrations indicated above, measureable erosion was observed in artificial fracture tests. For most of these tests erosion was observed to begin almost immediately upon contact between the compacted material and the dilute solution and continue throughout. The sole exception to this characteristic was 50/50 calcium/sodium montmorillonite against a flowing 4 mM NaCl solution where erosive conditions first developed only after a much longer period of time.

The average mass loss rates for the systems with observed erosion, expressed in terms of flow velocity, are displayed in Figure 11.

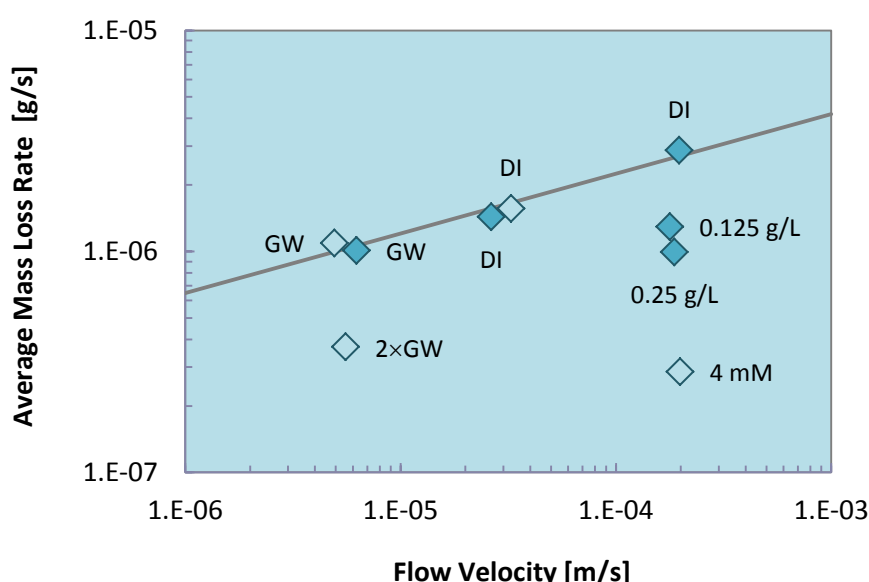


Figure 11. Average mass loss rates from artificial fracture experiments expressed in terms of flow velocity. Filled symbols correspond to sodium montmorillonite samples and open symbols correspond to 50/50 calcium/sodium montmorillonite samples. Data points are labelled with contact solution compositions. Limiting line (grey) though the data points for the most highly eroding systems represents power-law fit to the data.

The average mass loss rates for the tests with the highest levels of observed erosion, appear to be equivalently correlated to flow velocity. Interestingly, 50/50 calcium/sodium montmorillonite against flowing deionised water erodes with the same functionality as does sodium montmorillonite against flowing deionised water. In other words, no effect on erosion due to material composition (at the levels examined here) was observed at zero

ionic strength. Similarly, sodium montmorillonite and 50/50 calcium/sodium montmorillonite against flowing Grimsel groundwater simulant erode with the same functionality as they do against flowing deionised water. As such, no effect on erosion due to solution composition was observed up to the ionic strength of Grimsel groundwater on the time scale of these tests.

On the other hand, a number of tests for which erosion was also observed, are not equivalently associated. The erosive mass loss for 50/50 calcium/sodium montmorillonite against 4 mM NaCl, 50/50 calcium/sodium montmorillonite against double strength Grimsel groundwater simulant, sodium montmorillonite against 0.125 g/L NaCl and sodium montmorillonite against 0.250 g/L NaCl was attenuated by nearly factors of 10, 3, 2, and 3, respectively, relative to the correlated behavior of the most highly eroding tests. This attenuation can be attributed solely to solution composition effects, i.e., increased ionic strength, regarding the tests at 0.125 and 0.250 g/L NaCl and to solution and material composition effects, possibly in combination, regarding the other two tests. The difference in erosive mass loss the test with 50/50 calcium/sodium montmorillonite against 4 mM NaCl solution and the test with sodium montmorillonite against 0.250 g/L (4.3 mM) NaCl solution indicates that both material and solution composition can significantly affect erosion rates.

A comparison of the effluent data for all of the eroding tests shows distinct differences in erosion behavior due to small increases in electrolyte concentration (see Figure 12).

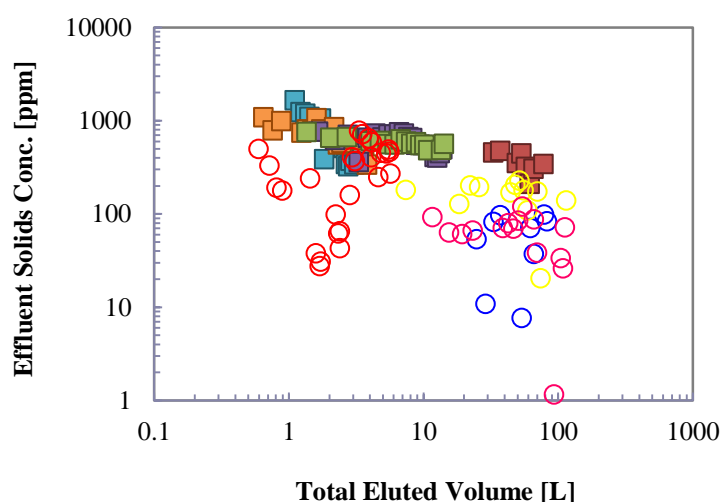


Figure 12. Effluent solids concentrations as a function of total eluted volume for erosive artificial fracture tests. The filled squares correspond to tests performed against most dilute solutions, i.e., $IS \leq 1.1$ mM, and the open circles correspond to tests performed against marginally less dilute solutions, i.e., $2.2 \text{ mM} \leq IS \leq 4.3 \text{ mM}$.

The tests performed against the most dilute solution conditions ($IS \leq 1.1 \text{ mM}$) display somewhat equivalent behavior whereas the tests performed against marginally less dilute solutions ($2.2 \text{ mM} \leq IS \leq 4.3 \text{ mM}$) display significant scatter. A possible explanation for this attenuated erosion may be due to structure formation and evolution of the eroding material. Evidence for this possibility is displayed in Figure 13.

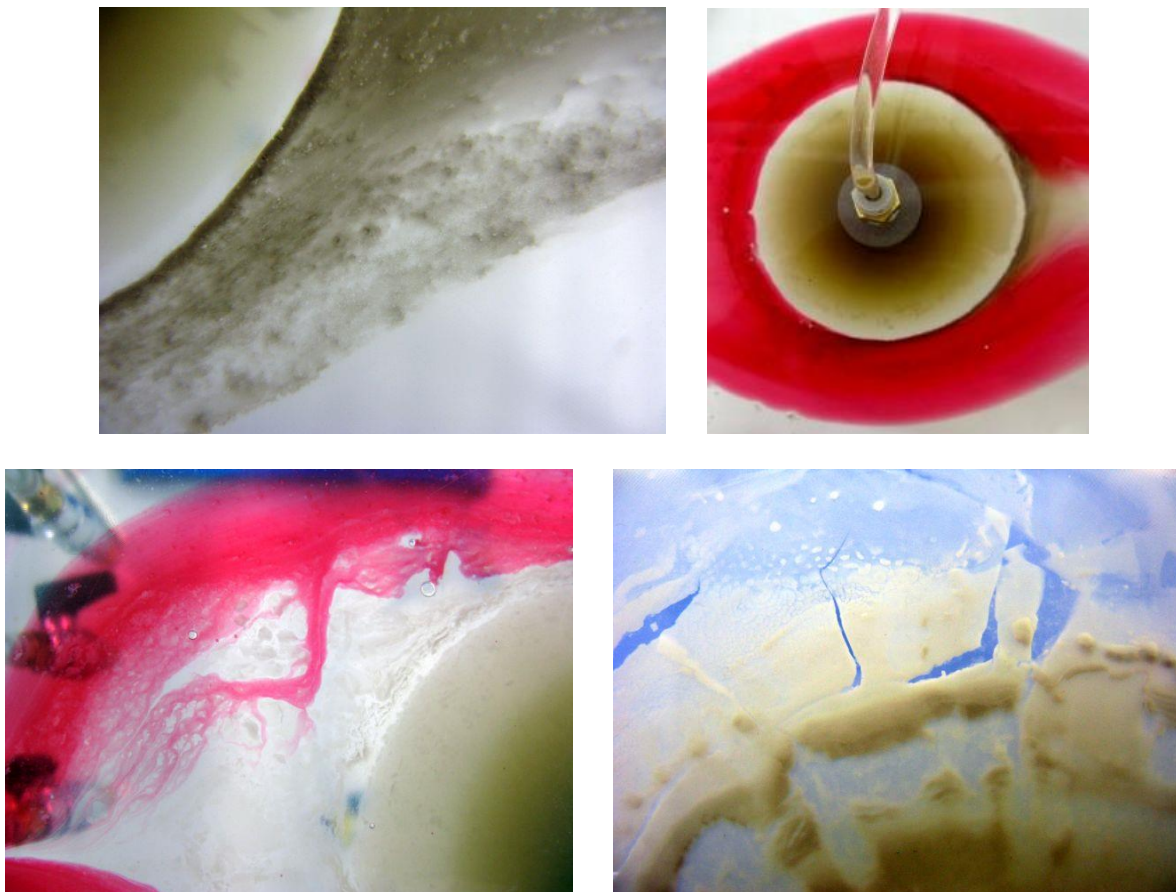


Figure 13. Photographic images showing a) the interface between the inner zone of extruded material and the outer zone of eroding material for a test with sodium montmorillonite against deionized water at 456 h, b) flow visualization of the same test highlighting the permeability of the eroding material zone and the relative impermeability of the extruded material zone, c) flow visualization of a test with 50/50 calcium/sodium montmorillonite against 4 mM NaCl indicating the semi-permeability of the eroding material zone and d) the extrusion/erosion interface from a test with 50/50 calcium/sodium montmorillonite against double strength Grimsel groundwater simulant demonstrating that the eroding material forms into extended sheets of rigid, coherent material.

Based on the set of results of the flow-through, artificial fracture tests described above, a stability to erosion was observed down to a dilute concentrations between 8.6 and 4.3 mM

for sodium montmorillonite and 8.6 and 4 mM NaCl for 50/50 calcium/sodium montmorillonite. The latter limit compares favorably with that postulated by Birgersson et al. [2009] for montmorillonite with calcium content greater than 20% based on observations using a completely different experimental technique, i.e., a modified swelling pressure test. Below this threshold value, erosion was sensitive to solution composition until an ionic strength of ~ 1 mM was reached. Evidence was found for structural formation and evolution of the eroding material which may account for the cases of attenuated erosion. Such structural formation was clearly evident only for the calcium containing systems.

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