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Final Report on the effects of the water chemistry and clay chemistry on erosion processes

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INTRODUCTION AND OBJECTIVES

The objective of Work Package 2 (WP2, Erosion) of the BELBaR Project is to study the mechanisms of bentonite erosion and colloid generation from the compacted bentonite in a high level radioactive waste (HLRW) repository under realistic conditions, identifying the most important mechanisms involved.

The reasons why it is important to study bentonite erosion are:

- 1) clay colloids may affect radionuclide transport in the repository and this represents one of the issues of concern in safety assessment (SA);
- 2) if erosion is significant, the functionality of the bentonite barrier at the long-term could be compromised.

Two possible scenarios are considered for the experiments: the static and the dynamic. In the static system, the transformation of the gel to a sol is mainly a chemically – driven process, as it depends only on the combination of the water chemistry and clay properties. However, the worst scenario in a repository in crystalline rocks would be the presence of hydraulically active fractures (the dynamic system). Thus, it is also important to study the water flow at the bentonite surface or gel-front may increase colloid detachment and the relative importance with respect to other chemical or physical aspects (fracture aperture or spatial orientation).

The objective of Deliverable 2.7 “Final report on the effects of water chemistry, clay chemistry and water/clay interactions on erosion processes” is to update the contributions of different BELBAR partners on the studies related to the role of water chemistry and clay chemistry on erosion processes and covers factors other than the effect of flow velocity and fracture aperture, that will be described in deliverable D2.11 “Erosion of bentonite in fractures under sol-forming conditions – effect of flow velocity and fracture aperture”.

EXPERIMENTAL CONTRIBUTIONS

1. B+Tech (Tim Schatz)

Background

This report summarizes work conducted at B+Tech during the period from 1.6.2014 to 15.5.2015 of the BELBaR Project. The work described below is related to BELBaR deliverable D2.7 “Final report on the effects of water chemistry, clay chemistry and water/clay interactions on erosion processes” and covers factors other than the effect of flow velocity and fracture aperture (which are described in BELBaR deliverable D2.11 “Erosion of bentonite in fractures under sol-forming conditions – effect of flow velocity and fracture aperture”) on erosion.

The work at B+Tech is conducted mainly using small-scale (24 cm × 24 cm fracture plane, 2 cm diameter × 2 cm height sample chamber), flow-through, artificial fracture systems in which swelling clay material can extrude/erode into a well-defined, intersecting fracture (see Figure 1). 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, slope angle) and the role of accessory minerals on erosion processes can be analyzed.

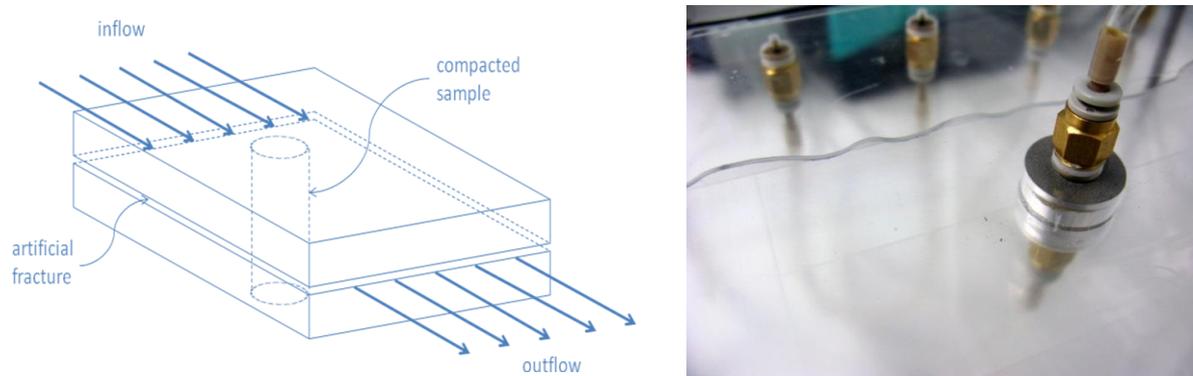


Figure 1. Schematic representation of the flow-through, artificial fracture test system design basis (left) and photographic image of a flow front approaching a compacted sample through a 1 mm aperture fracture (right).

Erosion of Bentonite Buffer Material in Sloped Fracture Environments

As discussed in BELBaR deliverable D2.5, a series of artificial fracture tests conducted in fractures positioned at steep slope angles (see Figure 2) for sodium montmorillonite or 50/50 calcium/sodium montmorillonite (all from MX-80 type bentonite) against deionized water or Grimsel groundwater simulant (relative to Na^+ and Ca^{2+} concentration only, i.e., 0.68 and 0.14 mM, respectively) were initiated. Tests were performed using downhill, uphill and stagnant (no) flow conditions. Work conducted at B+Tech since BELBaR deliverable D2.5 has largely

remained focussed on the erosion of bentonite buffer material in sloped fracture environments and the work has expanded to include tests with as-received bentonite samples (MX-80 and IBECO-RWC) and tests at larger scale.

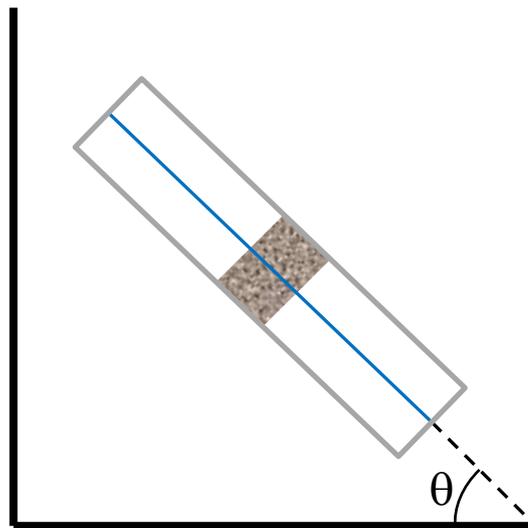


Figure 2. Schematic diagram showing artificial fracture test system positioned at steep slope angles ($\theta \geq 45^\circ$).

In artificial fracture tests conducted at steep slope angles ($\geq 45^\circ$) clay mass appears to be lost from the extruded source material via a predominantly sedimentary process (see Figure 3). This behaviour lies in sharp contrast to that observed in horizontal fractures where the mass release is interpreted as being dispersive in nature [Schatz et al. 2013]. Moreover, average mass loss rates in the sloped fractures were always larger than those of the corresponding horizontal cases with larger slope angles generally resulting in increased mass loss rates (see Figure 4). There is also limited evidence available showing increased mass loss rates over horizontal fractures even at much shallower slope angles (3-15°) [Jansson 2009, Vilks & Miller 2010].

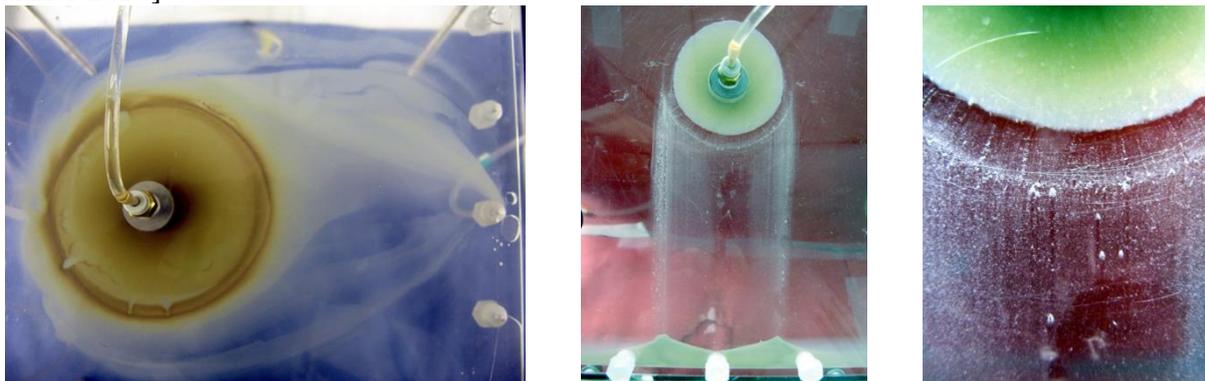


Figure 3. Images of artificial fracture tests on 50/50 calcium/sodium montmorillonite against Grimsel groundwater simulant flowing at $\sim 10^{-6}$ m/s in a horizontal (left) and 45° sloped fracture (middle and right) at 672 h.

Such sedimentary-type mass loss was observed in sloped fractures under stagnant (no flow) as well as flow-through conditions. An increase in flow velocity down the fracture from zero (stagnant) to $\sim 10^{-6}$ m/s produced a three-fold increase in mass loss whereas a further increase in flow velocity by roughly two orders of magnitude yielded only a 15% additional increase in mass loss (see Figure 5). Contrarily, a similar two order of magnitude flow velocity increase in horizontal fracture systems resulted in an 80% increase in mass loss further highlighting the distinct mass loss mechanisms at play due to slope angle imposition.

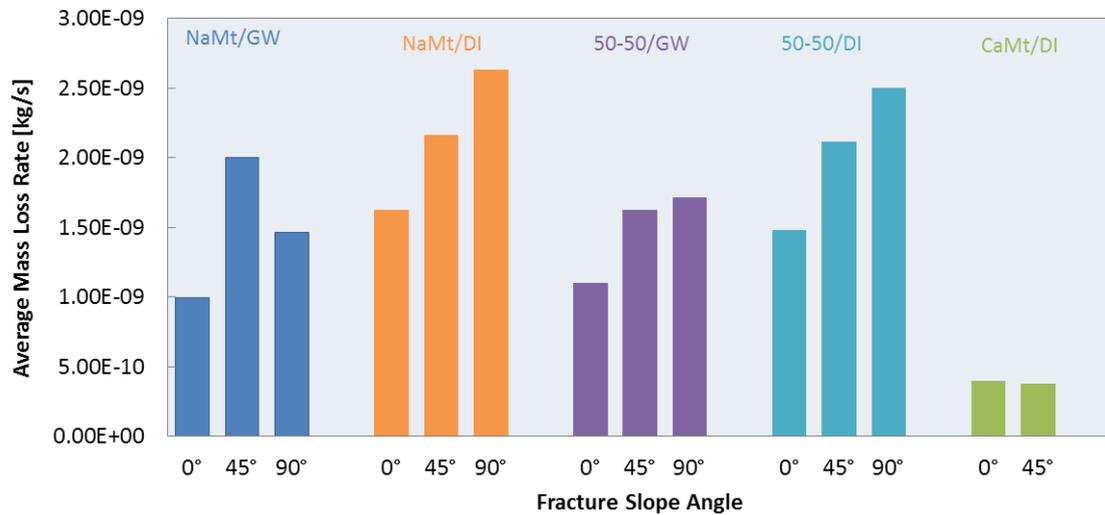


Figure 4. Average mass loss rates of montmorillonite (from MX-80 bentonite) in contact with Grimsel groundwater simulant (GW) and deionized water (DI), flowing at $\sim 10^{-6}$ m/s, in horizontal (0°), 45° and 90° sloped fractures. The observed mass loss from calcium montmorillonite is not attributed to sustained erosion, also note the lack of any effect due to slope angle on calcium montmorillonite mass loss.

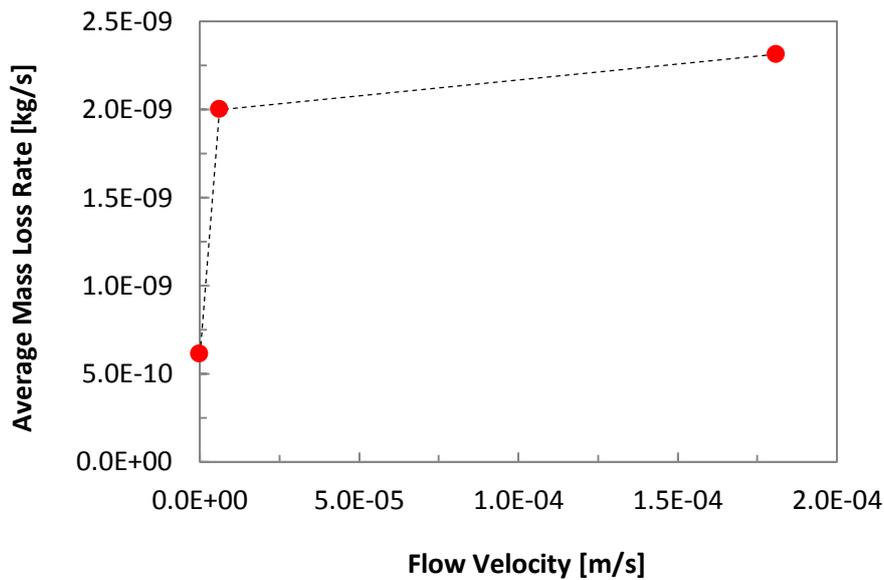


Figure 5. Average mass loss rates of sodium montmorillonite (from MX-80 bentonite) in contact with Grimsel groundwater simulant as a function of flow velocity in a 1 mm, 45° slope angle fracture.

As discussed earlier, artificial fracture tests at steep slope angles have been performed with as-received bentonites (see Figure 6). These tests show that average erosion rates for purified montmorillonites and as-received bentonites are comparable (see Figure 7). The results at steep slope angles differ completely from those observed in horizontal fracture tests (order of magnitude difference) and provide further evidence that gravity strongly influences mass loss in sloped fracture environments.

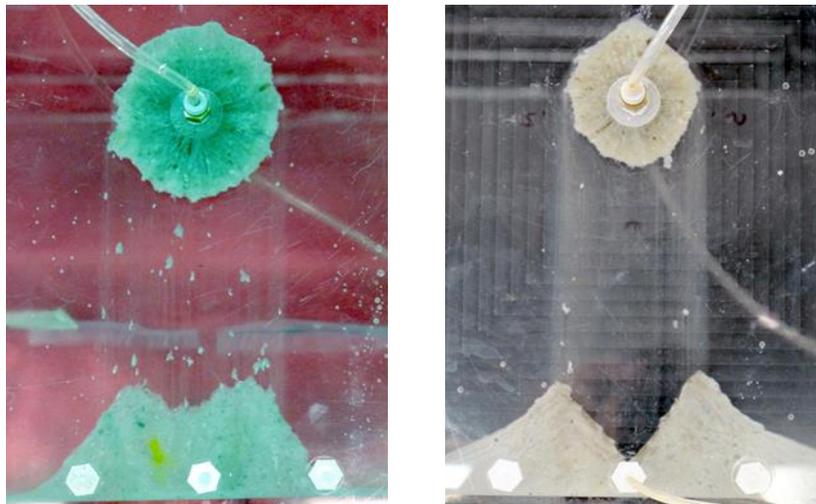


Figure 6. Images of artificial fracture tests on as-received MX-80 against Grimsel groundwater simulant under stagnant conditions (left image) and flowing at $\sim 10^{-6}$ m/s (right image) in a 45° sloped fracture at 672 h.

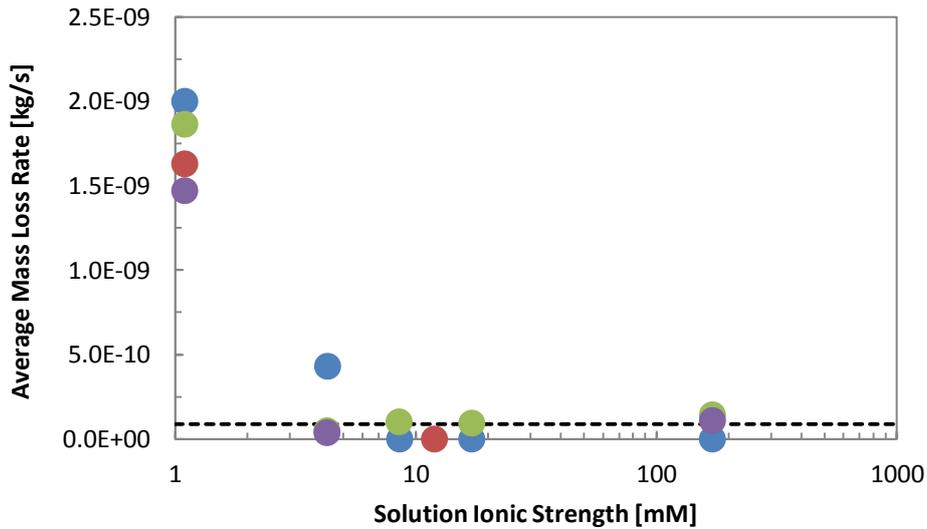


Figure 7. Average mass loss rates of sodium montmorillonite (blue), 50/50 calcium/sodium montmorillonite (red), as-received MX-80 bentonite (green) and as-received IBECO-RWC bentonite (purple) in 1 mm aperture, 45° slope angle fractures as a function of contact solution ionic strength. Flow velocities were $\sim 10^{-6}$ m/s in all cases. Mass loss rates at or below the level corresponding to the dashed line are not attributed to sustained erosion.

Also indicated by Figure 7 is that, similar to earlier observations in horizontal fractures (Schatz et al., 2013), a clear erosion stability limit down to an ionic strength of at least 8 mM (corresponding to NaCl solution) could be identified in the sloped fracture environments for isolated montmorillonites and both as-received MX-80 and IBECO-RWC bentonites. The initial, exchangeable sodium and calcium contents for these bentonite materials is 68% : 22% and 24% : 43%, respectively.

The use of a larger artificial fracture cell was also started at B+Tech. This system is comprised of a roughly 1 m \times 1 m fracture plane and a 5 cm diameter \times 5 cm height sample chamber and allows for variable fracture aperture configuration. A test was run in this system using as-received MX-80 (see Figure 8).

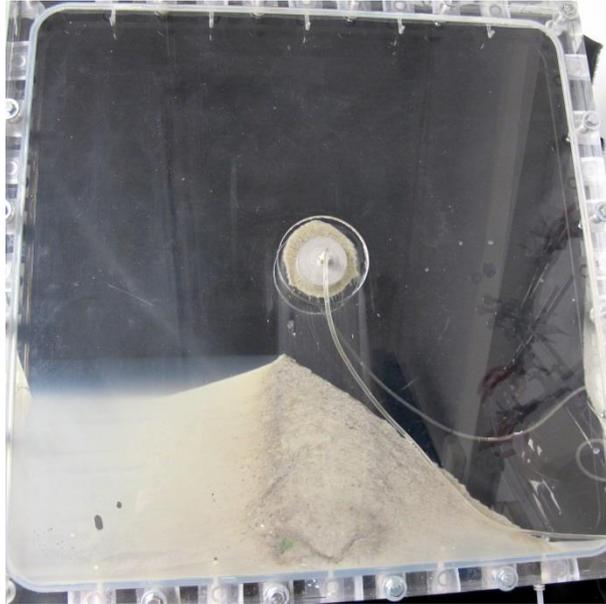


Figure 8. *As-received, MX-80 bentonite in contact with a Grimsel groundwater simulant at an average flow rate of 0.09 ml/min through the large, 1 mm aperture artificial fracture system positioned at a 45° slope angle.*

In principle mass loss results observed in the larger artificial fracture system can be compared to those from the smaller artificial fracture cell with the aim of deriving scaling arguments with respect to observed mass loss. Aside from scale, tests conducted in the large and small artificial fracture systems can be held constant with respect to all other experimental variables: sample, solution, fracture aperture, slope angle, and flow velocity. However, it should be kept in mind that the larger artificial fracture system also has a larger initial sample volume which correspondingly requires a larger amount of sample mass than the smaller system at a given density. As such, any mass limiting effects encountered in the smaller cell may not be similarly reproduced in the larger system.

Tests have been conducted in both the large and small artificial fracture test systems configured to 1 mm fracture apertures and positioned at 45° slope angles for as-received MX-80 in contact with Grimsel groundwater simulant flowing at $\sim 10^{-6}$ m/s for a period of 30 days. In order to assess the effect of scale through the experimental data, the observed mass loss results can be normalized to eroding surface area. As discussed earlier in BELBaR deliverable D2.5, steady-state extrusion distances are not observed in artificial fracture tests conducted at steep slope angles. Therefore using extrusion distances in determining eroding surface areas is somewhat uncertain. In order to compare the test results from the large and small artificial fracture test systems, the data can be normalized to eroding surface areas based on the initial sample diameters. An eroding surface area of 6.28×10^{-5} m² can be calculated for the smaller system and for the larger system this value is 1.57×10^{-4} m². Normalizing the average mass loss rates (kg/s) observed for the small and large artificial fracture tests, one arrives at values of 2.97×10^{-5} and 6.92×10^{-5} kg/m²·yr, respectively. The normalized rate for the large fracture system is faster than that of the small fracture system by a factor of 2.3. On one hand it seems that the normalized rates are in reasonable enough accord to suggest that a

similar linear scaling approach could be used to predict mass loss rates in steeply sloped fractures at repository scale and further that implementing actual extrusion distances should be examined. On the other hand the rate in the larger system is faster and this system incorporates a factor of 10 more sample mass than the small system so mass limiting effects cannot be ruled out.

References

Jansson 2009, SKB TR-09-33

Schatz et al, 2013 Posiva Report 2012-44

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2. ÚJV Řež, a. s. (R. Červinka, J. Gondolli)

Overview of results from coagulation experiments and some implications for bentonite erosion,

Introduction

The coagulation experiments with dilute clay suspensions are performed mainly for prediction of colloids stability during the transport in the far field. The obtained critical coagulation concentration (CCC) is essentially the minimum concentration of coagulant that causes rapid coagulation. Knowing CCC enable to decide about stability of clay dispersion in a given conditions (e.g. groundwater composition). For much more dense systems, which are expected at the boundary of swelling compacted bentonite and the groundwater (gel like structure), the transfer of CCC principle is not straightforward (some restrictions due to clay structure, cation exchange, etc.). Generation of clay colloids and their stability is tightly connected with groundwater chemistry, bentonite composition and parameters of fracture zone (see the general scheme in Figure 9). This overview is a summary of our previous results which some implications for erosion of bentonite barrier.

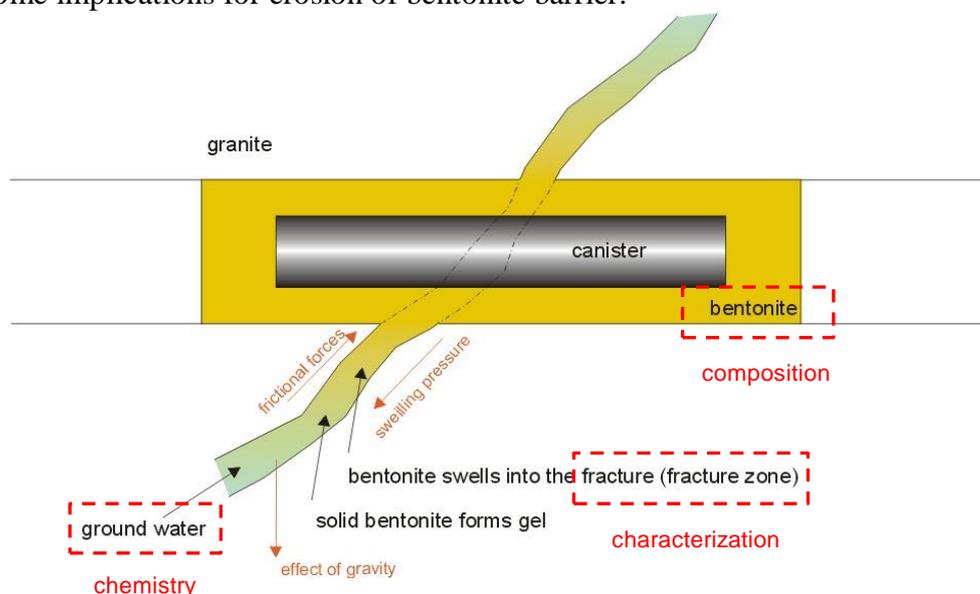


Figure 9: Conceptual scheme of bentonite erosion process in horizontal deposition hole. The main components influencing the erosion are, among others, groundwater chemistry, bentonite composition and parameters of fracture zone.

Coagulation experiments

The basic coagulation of diluted clay dispersions by univalent cations (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), divalent cations (Ca^{2+} , Mg^{2+}), anions (Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , OH^-) and organic substances (humic acid) was studied (see deliverables D4.6, D4.7 and D4.8) in a series of test-tube coagulation tests. Four clay dispersions (0.0005, 0.005, 0.05, 0.5 % w/w, i.e. 0.005, 0.05, 0.5 and 5 g/l) of purified bentonite “Bentonite 75” denoted as B75 in Na^+ form were used.

For comparison raw bentonite “Bentonite and Montmorillonite” denoted as BaM of similar origin as purified bentonite was selected. The obtained CCC are summarised in Table 1. The minor effect of increasing CCC with solid content is illustrated in Figure 10.

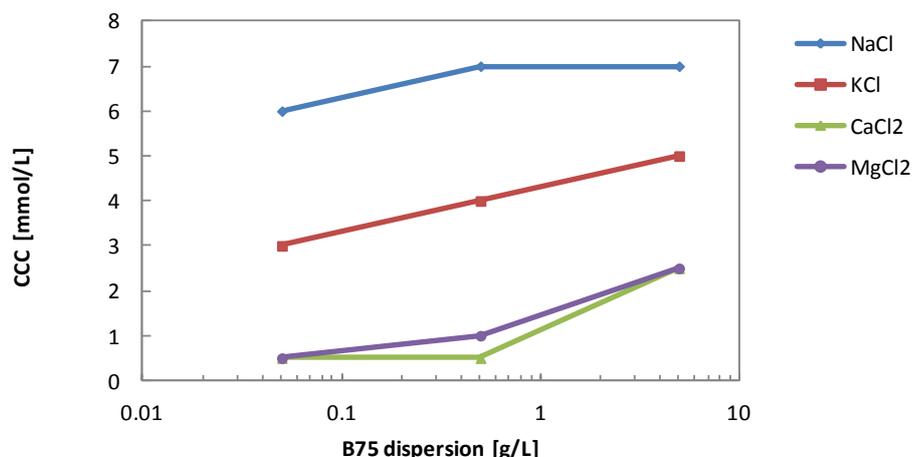


Figure 10: Changing of CCC with the solid content of clay in the dispersion.

For this type of experiments the exchange of cations plays a dominant role. Initially sodium dominant montmorillonite is exchanged by cation in solution during the coagulation test. For instance Na-montmorillonite is coagulated by KCl, where complete exchange of Na for K is occurred. Correctly, the CCC is determined for K-montmorillonite instead of Na-montmorillonite. The following Table 1 shows the pool of exchangeable cations for different concentrations of clay dispersions. These cations can be exchanged by coagulant and contribute to coagulation process. Only in the case of dispersion with clay concentration 5000 mg/l the amount of exchangeable cations is not negligible and can influence determined CCC. Nevertheless we did not observe the effect of cation exchange on CCC for these concentrations of clay dispersions in the coagulation tests.

Table 1: Pool of exchangeable cations for different clay dispersions.

B75 Na+	Cation occupancy meq/100g	Clay dispersions - pool of exchangeable cations		
		0.005 50	0.05 500	0.5 % w/w 5000 mg/l
Na+	33.97	0.0	0.2	1.7 mmol/l
K+	1.39	0.0	0.0	0.1 mmol/l
Mg2+	6.21	0.0	0.0	0.2 mmol/l
Ca2+	19.24	0.0	0.0	0.5 mmol/l

Granitic groundwater interaction

The chemistry of groundwater has dominant impact on erosion process and its extent. The Czech concept of deep geological repository (DGR) considers the granite as a host rock and the hydrochemistry of groundwater from this granitic environment was summarised elsewhere (Rukavičková et al., 2009). Three different types of groundwaters were identified in granitic

Bohemian Massif: groundwater – meteoric water in contact with granite (depths 30-100 m), mineral groundwater – meteoric water in contact with granite and deep CO₂ and fossil groundwater – old saline waters (see Table 2). The expected chemistry of groundwater in DGR is a combination of these three types. Synthetic granitic groundwater (SGW) for experiments was prepared in laboratory, representing shallow granitic groundwater.

With respect to the experimental uncertainties regarding the CCC determination (especially significant coagulation kinetics) it can be said that the CCC of univalent alkaline metal cations lies in range 2 to 5 mmol/l and their effect on coagulation is similar for 50 mg/l clay dispersion. For more dense dispersion the obtained CCC is slightly increasing with clay content. As expected, divalent cations are more effective coagulants and their CCC is lower than for univalent cations (see Table 2). No significant effect of varying anions at given conditions was found, although such an effect is reported in the literature (Lagaly and Ziesmer, 2003).

Table 2: Summary of results from coagulation experiments (bentonite B75-Na⁺ dispersions in contact with electrolytes) and comparison with chemical composition of different groundwaters. SGW – synthetic granitic groundwater used as a liquid phase for various experiments. Groundwater, Mineral groundwater and Fossil groundwater are three types of groundwaters, which are expected in granitic Bohemian Massif (CZ), (after Rukavičková et al., 2009).

Component		Na	K	Ca	Mg	F	Cl	SO ₄	HCO ₃	NO ₃
SGW	mg/l	10.6	1.8	27.0	6.4	0.2	42.4	27.7	30.4	6.3
	mmol/l	0.5	0.0	0.7	0.3	0.0	1.2	0.3	0.5	0.1
Groundwater (median, n > 351)	mg/l	11.4	2.3	30.1	8.0	-	11.7	34.1	85.4	-
	mmol/l	0.5	0.1	0.8	0.3	-	0.3	0.4	1.4	-
Mineral groundwater (median, n = 16)	mg/l	501.5	25.5	60.9	28.7	-	92.6	162.5	1220.5	-
	mmol/l	21.8	0.7	1.5	1.2	-	2.6	1.7	20.0	-
Fossil groundwater (median, n = 15)	mg/l	1050.0	52.5	55.9	22.0	-	644.0	26.3	863.0	-
	mmol/l	45.7	1.3	1.4	0.9	-	18.2	0.3	14.1	-
CCC for selected cations		Na	K	Ca	Mg	Li	Rb	Cs		
0.5 % w/w	mg/l	138-161	157-196	40-100	24-61	-	-	-		
	mmol/l	6-7	4-5	1-2.5	1-2.5	-	-	-		
0.05 % w/w	mg/l	138-161	117-157	4-20	12-24	-	-	-		
	mmol/l	6-7	3-4	0.1-0.5	0.5-1	-	-	-		
0.005 % w/w	mg/l	115-138	78-117	4-20	2-12	28-35	171-256	266-399		
	mmol/l	5-6	2-3	0.1-0.5	0.1-0.5	4-5	2-3	2-3		
CCC for selected anions		NaCl	NaNO₃	Na₂SO₄	MgCl₂	Mg(NO₃)₂	MgSO₄			
0.005 % w/w	mmol/l	5.0	6.0	3.0	0.5	0.5	0.5			

Note: n = number of real groundwater analyses, for NaCl, NaNO₃ and Na₂SO₄ the CCC in meq/l are almost the same 5, 6 and 6 respectively.

It can be concluded that in complex system (e.g. groundwater), the coagulation effect of selected ions can be added up separately for the univalent ions, and divalent ions that are more effective coagulants. This conclusion was confirmed in coagulation test of bentonite suspensions in SGW in which the total concentrations of univalent cations was lower than their CCC (also in the sum of individual CCC) but the concentrations of divalent cations was above their CCC (in one case and also in the sum of individual CCC). It was confirmed that at given condition (SGW simulating real groundwater) bentonite colloids (both B75 and BaM) are not stable and coagulate (see Table 3).

Table 3: Coagulation of bentonite colloids in SGW. Data from the PCCS measurement, $>1\mu\text{m}$ means sporadic presence of clumps; N.A. means not available (for the measurements near detection limit the mean hydrodynamic diameter cannot be calculated).

SGW	Mean hydrodynamic diameter (nm) PCCS	
	B75	BaM
Concentration of suspension	Coagulation time 192 hours	Coagulation time 144 hours
pH	7.6 ± 0.1	8.0 ± 0.1
500 mg/l	N.A.	$>1\mu\text{m}$
50 mg/l	N.A.	N.A.
5 mg/l	N.A.	N.A.

Presence of organic substances

Although the expected concentrations of natural organic substances in granitic host rock are generally low and presence of organic substances will be more associated with microbial and anthropogenic activities and materials used for the constructions, the interaction between clay colloids and organic molecules influences the CCC.

We aimed on the coagulation of clay dispersion in presence of NaCl and CaCl₂ electrolyte and humic acids (HA). Because HA are natural organic substances often occurring in surface waters and near-surface groundwaters we used them as an analogue for potential organic substances in DGR. In our experiments the HA was previously extracted by alkaline method from organic rich sample, which comes from near-surface sediments (natural analogue Ruprechtov, for details see Červinka et al., 2011).

Results showed, that presence of HA significantly increases the colloidal stability of bentonite particles in case of NaCl electrolyte. The CCC for Na⁺ is four times higher for system (0.005% w/w dispersion of B75 in Na⁺ form) with 0.5 mg/L TOC than for system without HA. In case of CaCl₂ electrolyte only minor effect on colloidal stability was occurred. It seems that the stabilizing effect of humic acid is different for univalent and divalent cations (see Fig) within the range of measured concentrations.

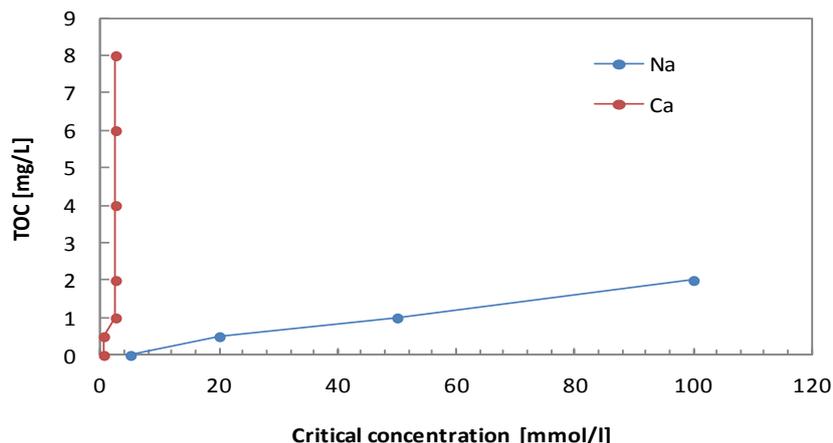


Figure 11: The evolution of CCC for clay suspension (0.005 % w/w) in presence of cation Na^+ and Ca^{2+} (as electrolyte NaCl and CaCl_2 respectively) and HA (expressed as total organic carbon – TOC).

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3. CIEMAT (T. Missana, U. Alonso, A.M. Fernández)

Introduction

During the BELBAR Project, CIEMAT carried out different experiments to understand the effect of different parameters (density of the clay, the exchange complex of the clay and chemistry of the contacting water) using both static and dynamic experiments. The first results obtained were already described in the Deliverable 2.1.

As main conclusions of the previous work, we reported that:

- 1) the swelling pressure seems to be the first driving force causing the gel intrusion in rock fissures and pores, thus the density of the clay determines the thickness of the extruded gel layer, potentially subject to erosion;
- 2) the presence of colloids in solution will be limited to the surface available for colloid transport from the clay surface to the liquid phase (extrusion paths);
- 3) in a closed system, a concentration of colloids in equilibrium with the clay surface is reached and dispersion is not continuous;
- 4) 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;
- 5) Ca-bentonite forms colloids in quantities very near or lower than to the detection limit of our techniques, even in chemical conditions which are favourable 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;
- 6) water/clay interactions are very important for the evaluation of erosion and stability of colloids in a repository at a long-term.

The first tests were performed with raw FEBEX bentonite at different compaction densities, and with exchanged (Na/Ca) FEBEX clay using different contact aqueous solutions. Then, a comparative study of the erosion process of different raw bentonites (FEBEX, IBECO-Mylos, Wyoming MX-80, B75 and S65 Czech bentonites and Khakassia Russian bentonite), was also done.

The work was initiated in the previous reporting period and partial results were already presented in the deliverable D.2.4. The main conclusion from this preliminary work was that, under the same experimental conditions, the highest quantity of colloidal mass was measured for the FEBEX clay and the lowest for the B75 clay. These differences must be related to differences in the clay composition and geochemistry or other characteristics, which are currently still under study.

From the previous tests two points were also remarked:

- 1) as far as the Na content in the exchange complex is higher than 20 %, the generation is not largely affected by the exchange complex;
- 2) the smectite content may play an important role on natural clay erosion behavior.

Thus new studies were carried out focusing in clay mixed systems with different smectite content, trying to evaluate if only the presence of smectite affects the erosion degree, or if the interaction between particles of different minerals may play a role.

In the present deliverable, a summary on the physico-chemical characterisation of different bentonites, work that is still ongoing, will be presented. The completion of this work will allow interpreting the main results obtained from erosion tests in different bentonites or mixed systems. The comparative study on erosion behaviour of different clayey systems has been carried out with static tests, using deionised water to favour the maximum generation of colloidal particles.

The difference in the physico-chemical properties on the erosion mechanisms, in particular the content in swelling / non-swelling clay minerals (smectite/ illite kaolinite) or trace impurities like oxides are discussed.

Clay characterization

A complete geochemical and mineralogical characterization is being carried out by different techniques (XRD, FRX, FTIR, TG-DSC, etc.,) to evaluate major and minor minerals, clays content, cation exchange capacity, major cations, water content, pore water chemistry, charge distribution and cell formula of the five bentonites. Full details on the characterization can be found in (Fernandez, 2013).

The selected bentonites were: FEBEX bentonite from Spain (Huertas et al., 2000); IBECO bentonite from Mylos island in Greece (Koch, 2002; Koch, 2008); Wyoming MX-80 bentonite (USA) (Müller-Vonmoss and Kahr, 1983); Czech bentonites from the Rockle deposits; Na-activated (B75), RO2K8-F02 and S65 (Konta, 1986) and a Russian bentonite (MSU) from the Khakassia deposit (Sabodina et al., 2006).

Kaolinite and illite minerals were also analysed, because erosion experiments on smectite/kaolinite and smectite/illite mixtures (50%-50% and 75%-25%) were planned. The kaolinite used was the natural KGa-1-b, obtained from the Clay Mineral Society (CMS, EEUU). The purity of this material is higher than 93%. The illite used in this study was the natural illite du Puy, France (Gabis,1958).

One of the most important factors affecting the erosion of the bentonite may be its mineralogical composition. In the preliminary tests, in fact a certain dependence between smectite content and erodibility was observed. Figure 12, mineralogical composition of the different bentonites obtained by XRD (additional information on mineralogical composition was also obtained by FTIR and TG-DSC; see report of Fernandez, 2014).

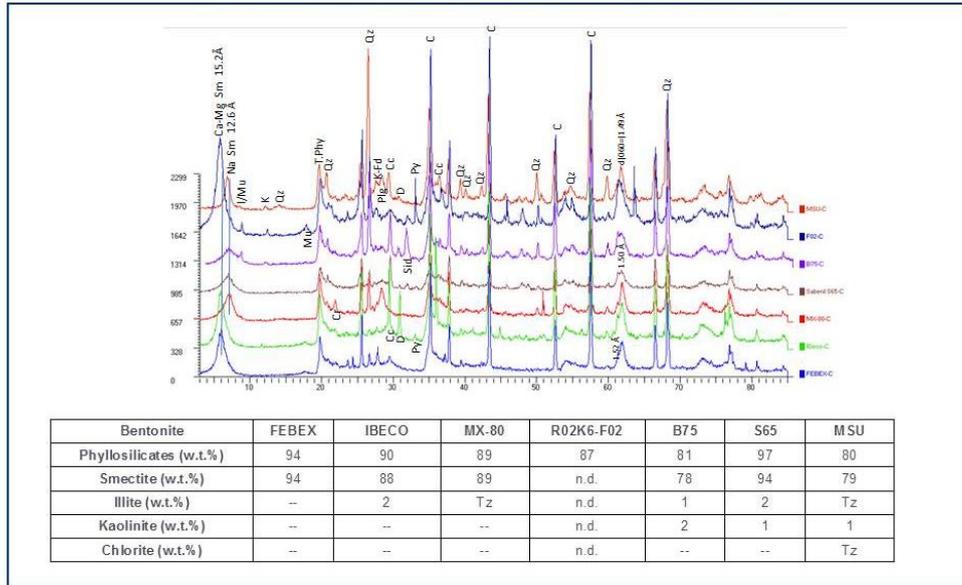


Figure 12: Mineralogical composition by XRD of random powders from the different bentonites and semi-quantitative mineral composition

The highest quantity of smectite is present in FEBEX (the bentonite which generate the maximum quantity of colloids) and S65 bentonites (94 %) followed by MX-80 and IBECO (88-89 %); finally B75 and MSU present the lowest smectite content. Small percentages of minerals like illite and kaolinite (not swelling clays) are also present in several bentonites, which could also affect their erosion behaviour.

Another important point that can affect bentonite erosion is the presence of certain cations in the exchange complex. Ca has been observed to inhibit erosion while Na facilitates it; however it was shown, for example in the raw and exchanged FEBEX clay, that if Na is present in enough percentage (above approximately 20 %) the erosion behaviour of the clay is not very different from a Na-clay. Figure 13 shows a summary of the CEC measured in the selected bentonites, and their exchange complex.

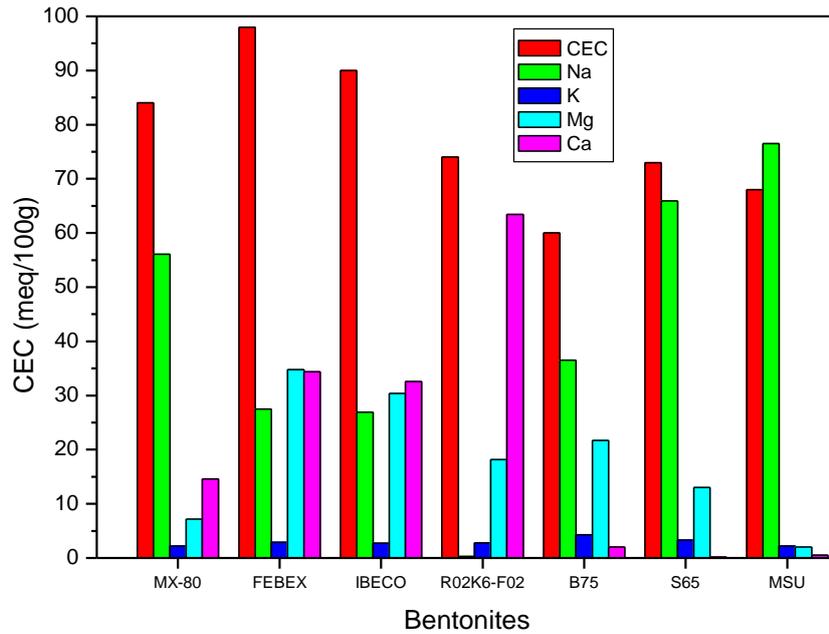


Figure 13: CEC and main exchangeable cations

Mx-80 and MSU and S65 are mainly Na bentonite; 02K6-F02 is a Ca bentonite; the FEBEX a Ca-Mg-Na bentonites, B75 a Na-Mg bentonite. This Figure confirms the previous findings as there is not a very clear relation on the exchange complex and the erosion observed (under the same experimental conditions, the highest quantity of colloidal mass was measured for the FEBEX clay and the lowest for the B75 clay).

Another potentially important characteristic of the bentonite which is being investigated, affecting its erosion, is related to the crystallographic characteristics of the clay, summarized for five of the seven selected bentonites in Table 3.

Table 3: Crystallographic properties and structural formula of five bentonites

Smectite		FEBEX	Ibeco	MX-80	B-75	S-65
Tetrahedral layer	Si	7.90	7.80	8.00	7.48	7.00
	Al	0.10	0.20	0.00	0.52	1.00
	Total	8.00	8.00	8.00	8.00	8.00
Octahedral layer	Al	2.73	2.68	3.02	2.30	1.56
	Ti	0.01	0.09	0.01	0.37	0.74
	Fe ³⁺	0.41	0.52	0.44	0.84	1.26
	Mg	0.98	0.82	0.48	0.45	0.47
	Total	4.14	4.11	3.96	3.96	4.02
Interlamellar layer:	Ca	0.17	0.20	0.13	0.08	0.13
	K	0.13	0.09	0.02	0.23	0.13
	Na	0.20	0.11	0.30	0.34	0.28
	Total	0.49	0.40	0.45	0.64	0.54
Tetrahedral charge:		-0.10	-0.20	0.00	-0.52	-1.00
Octahedral Charge:		-0.56	-0.40	-0.58	-0.20	0.00
Total:		-0.66	-0.60	-0.58	-0.72	-1.00
Interlamellar Charge (+):		0.66	0.60	0.58	0.72	0.67
% tetrahedral charge		15	33	0	73	100
% octahedral Charge		85	67	100	27	0
F.W. (half-unit cell)		749.76	752.10	744.26	769.35	787.28
a (Å)		1.2889	1.2896	1.2902	1.2898	1.2871
b (Å)		1.5002	1.4994	1.5001	1.5010	1.5045
c (Å)		14.74	14.86	12.33	12.76	12.60
Surface charge density (C/m ²)		0.126	0.116	0.108	0.077	0.126
Charge per unit cell		0.73	0.67	0.63	0.45	0.55
S (m ² /g)		747	744	752	730	713

The highest (in absolute value) total charge belongs to the S65 clay, than in decreasing order B75, FEBEX, IBECO and MX80. For what concerns the charge distribution between the octahedral and tetrahedral charge, it is interesting noticing that all the charge is located in octahedral positions in the case of MX-80 whether in the S65 all the charge is tetrahedral. For the other clays the % of tetrahedral and octahedral charge is the following: FEBEX (15/85); IBECO (33/67) and B75 (73/27). All these parameters are being analyzed and their importance on erosion investigated. The work is still ongoing.

Erosion tests

As mentioned in the introduction, in the deliverable D2.4 erosion tests carried out with five different bentonites, were already described.

Figure 14 shows the standard experimental cell to determine bentonite colloids generation under static (no flow) conditions. In this experimental set-up a tablet of approximately 4 grams of compacted bentonite, is introduced in a stainless steel cylinder (Figure 14a) and located between two sintered stainless steel porous filters. The cell is closed by two open Delrin grids and immersed in the desired aqueous solution within a closed vessel (Figure 14b). The porous filters (Figure 14c) have a thickness of 3.1 mm, a mean pore size of 100 μm and a porosity of approximately 40 %.

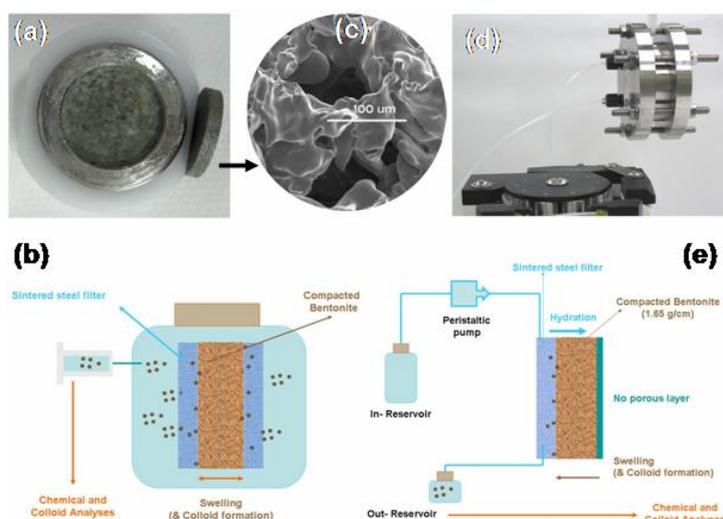


Figure 14: Experimental cells and schematic of the generation tests for static (a and b) or dynamic (d and e) experiments. In (c) a SEM image of the sintered steel porous filter shows large pores.

A periodical sampling of the aqueous solution is carried out to analyse 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 analysed.

Another experimental cell was used to determine colloid generation under dynamic (flow) conditions, where 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 (Figure 12d). A large reservoir (in-reservoir) contains the initial aqueous solution that entered into the cell through Teflon tubing. The solution is 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 12e). The water eluted was collected in polyethylene tubes of 20-60 mL for colloid analysis. Results of dynamic experiments were already described in Deliverable 2.4.

In all the cases, 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° or a Malvern NanoS system equipped with a HeNe 1 mW laser ($\lambda = 633$ nm) with the photomultiplier located at 173° . PCS was used to determine the size and concentration of colloids in the aqueous solutions as a function of time under the different experimental conditions.

Figure 15 presents the masses of colloids eroded, as function of time, from the different raw bentonites compacted at 1.65 g/cm^3 in deionized water. Under the same experimental conditions, the behavior is equivalent, generated mass initially increased linearly with time, but after about 100 days equilibrium is reached. Higher values are measured in the FEBEX case, and lower form B75 bentonite.

The obtained maximum colloidal masses, normalized to area available for colloid transport (bentonite surface, 3.5 cm²) are summarized in Table 4. The mean size of eroded particles is also indicated and all values are in the colloid range.

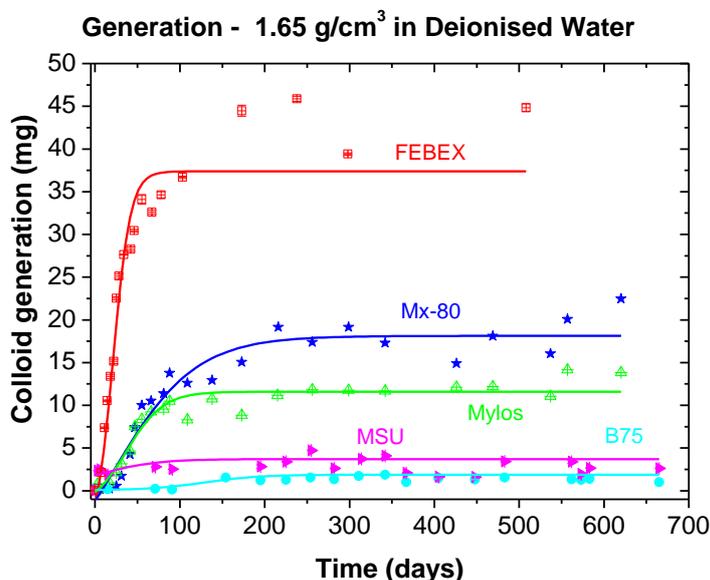


Figure 15. Colloidal masses generated as a function of time from the five studied bentonite compacted at 1.65 g/cm³ in deionized water, under static conditions.

Table 4: Maximum bentonite colloid masses eroded from bentonites at 1.65 g/cm³ in deionised water, and average particle diameter measured by PCS.

Bentonite	Colloid/S (Kg/m ²)	Mean size (nm)
FEBEX	$(1.2 \pm 0.5) \cdot 10^{-1}$	338 ± 24
Mx-80	$(5 \pm 0.5) \cdot 10^{-2}$	291 ± 31
Mylos	$(3.4 \pm 0.5) \cdot 10^{-2}$	367 ± 46
MSU Russian Khakassia	$(1.4 \pm 0.5) \cdot 10^{-2}$	400 ± 150
Czech B75	$(5.3 \pm 0.5) \cdot 10^{-3}$	296 ± 75

As already mentioned, as far as the Na content in the exchange complex is higher than 20 %, the generation is not affected by the exchange complex furthermore the smectite content may play an important role on natural clay erosion behavior. Nonetheless, the presence of other minerals, like kaolinite or illite, naturally present in bentonites (Figure 13) might also play a

role on erosion. In fact, erosion tests on pure kaolinite and illite, carried out at CIEMAT, showed that these clay minerals do not generate colloids, therefore their presence in enough concentration could affect the generation behavior of the smectite.

To analyze their effect, FEBEX bentonite was mixed with known proportions of illite or kaolinite (50% or 75% weight percent). The experimental set-up and experimental conditions used to evaluate their erosion behavior were totally equivalent to that described for the raw bentonites (compaction density at 1.65 g/cm^3 and deionised water).

Figure 16 presents the masses of colloids eroded, as function of time, from selected clay mixtures. Erosion values from pure (100 %) illite or kaolinite are not included in the figure, because measured masses were always under detection limit.

The bentonite mixtures with illite or kaolinite exhibited a different erosion behavior. The presence of illite decreases bentonite erosion masses, proportionally to the illite content. However, kaolinite totally inhibits bentonite erosion. This is a quite interesting finding, which probably indicates that the interactions between smectite and illite particles are different from those between smectite and kaolinite. To investigate this effect, stability studies of the mixtures (smectite/illite and smectite/kaolinite) were carried out and the results are presented in Deliverable D4.8

In summary, it was observed that addition of illite colloids to smectite did not produce clear changes in the mean size of colloids in the mixture, indicating that their interaction does not promote aggregation. However, in the case of smectite/kaolinite mixtures it was observed that a small percentage of kaolinite (less than about 15 %), produced an evident destabilization of the colloidal system, promoting fast aggregation. This aggregation is probably the reason why the system with kaolinite is less favorable to erosion.

Results obtained on clay mixtures suggests that the presence of other clay minerals or even oxides or other elements affecting bentonite colloid stability may play a major role on decreasing, or even inhibiting, bentonite erosion.

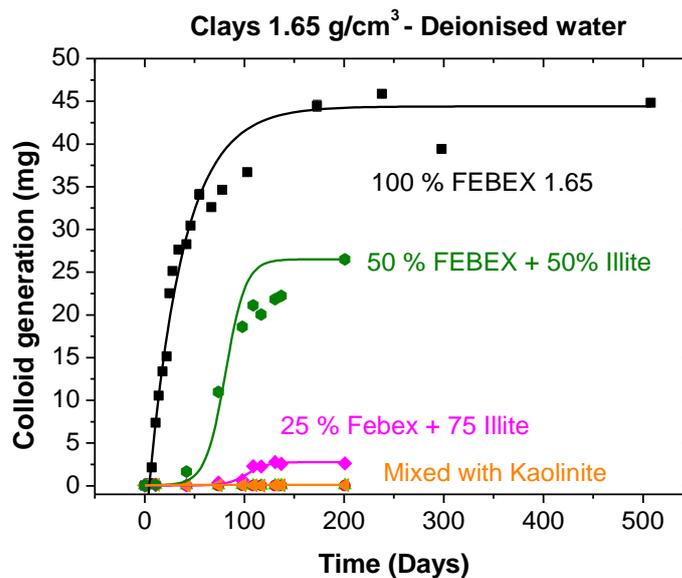


Figure 15. Colloidal masses generated as a function of time from FEBEX bentonite, and mixtures of smectite/illite and smectite /kaolinite (50%-50% and 25%-75%), compacted at 1.65 g/cm^3 in deionized water, under static conditions. The results of pure illite and kaolinite (100 %) are not shown because measured values were under detection limit.

Conclusions

CIEMAT analyzed the erosion behavior of different raw bentonites, under compacted and confined static conditions, in deionized water. A complete characterization of selected bentonites is being carried out which will allow to relate erosion behavior to clay chemistry and structural characteristics. The maximum eroded masses were determined for the FEBEX bentonite (0.15 kg/m^2). Results indicated that smectite content of the bentonite plays more relevant role on erosion rather than the sodium concentration at the exchangeable interlayer sites. However, the analysis of preliminary data on clay physic-chemical characterization, demonstrates that the nature of the clays, specially their composition, structural and charge characteristics might be also very relevant. In particular it was shown that the addition of non-swelling clays like illite or kaolinite, affects the erosion behavior, even if in different ways.

If smectite is mixed with illite, the erosion of the system is more or less proportional to the smectite content; on the other hand, the addition of 25 % of kaolinite completely inhibits the erosion of the smectite. This behavior has been related to the stability behavior of the illite/smectite and illite/kaolinite systems. Other stability tests with smectite/oxides systems are ongoing and the preliminary results will be discussed in Deliverable 4.8.

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