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Evaluation of experimental results on bentonite erosion

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INTRODUCTION

The mechanisms of bentonite erosion from the compacted bentonite barrier of a high-level waste repository (HLWR) in crystalline rock, leading to the generation of (colloidal) particles detaching from the clay, are being deeply investigated in the EC-BELBAR Project. Two main reasons drive the interest of this study: the first concerns the integrity of the barrier at the long-term which will be compromised if a significant clay loss occurs; the second one is about the role that clay colloids may play on radionuclide transport.

Colloid generation from powdered bentonite, under different chemical conditions, was already studied before the BELBAR Project, but much fewer studies concerning compacted bentonite were available. Furthermore, even a general and qualitative picture of the processes that might affect bentonite erosion existed, for Safety Assessment (SA) analyses, it was demanded providing new data obtained under realistic (repository) conditions, to develop and validate models describing the bentonite barrier erosion.

In BELBAR, accounting for the repository scenario, different possible experimental approaches were envisaged. The bentonite will be hydrated by the groundwater coming from the rock and a gel, potentially transforming to a sol, will be formed at the clay surface. In a static (or *quasi* static system), the gel to sol transformation is expected to be mainly a chemically – driven process. Indeed, the worst scenario for a HLRW in crystalline rocks includes the presence of hydraulically active fractures near the buffer, therefore in a dynamic system, in which the water is flowing at the bentonite surface, other hydraulic aspects, as water velocity or fracture thickness must be considered, to establish the mechanisms of bentonite erosion.

In both cases, the extent of erosion is expected to depend mainly on the combination of the water chemistry and clay properties; but, in the dynamic system, the water flowing at the bentonite surface or gel-front may increase colloid detachment and this point must be analyzed.

Many different topics were considered of interest, in relation to the erosion of the bentonite barrier, which in BELBAR were studied by different groups with the objective of providing outcomes to Work Package 1 (WP1, Safety Assessment). The state of the art with respect to many of these topics and the safety case position were defined at the beginning of the Project and the main uncertainties highlighted. These main issues can be summarized as follow:

- *Mechanisms of erosion of clay particles from the bentonite surface*

If the clay barrier erosion is significant, this will cause a loss of the bentonite buffer performance: the risk associated to the actual performance of the bentonite barrier under different conditions must be realistically evaluated. Thus, in WP2, the mechanisms of clay colloid release have been investigated and new data are available for feeding improved quantitative models (WP5) on bentonite erosion.

- *Characteristics of the bentonite clays*

The erosion of the bentonite depends on the physico-chemical characteristics of the clay: its main composition and the presence of certain trace minerals, the quantity and type of smectite and by the principal ions in the exchange complex. All these issues have been

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studied in WP2; in particular, the role of divalent ions which are known to prevent clay particles dispersion has been studied systematically and in detail.

The analysis of the conditions that make stable or unstable a colloidal system is very important because those conditions that favour or hinder colloid stability are also expected to favour or hinder erosion processes too. For this reason, most of the studies carried out in Work Package 4 (WP4, Colloid Stability) were of extreme importance to understand the results within WP2. A comparative study of the stability and erosion behaviour of many different raw (and exchanged) bentonites, of interest in the frame of the HLWR concepts of the different participating organisations was also carried out.

- *Groundwater chemistry*

Groundwater chemistry is a key factor for the erosion of bentonite as it is for clay colloid stability. In particular, the ionic strength and the content in divalent cations are very relevant parameters; pH is less important in the safety case because the considered pH-range is limited. In WP2, the erosion of different bentonite has been analyzed under different chemical conditions considering simplified mono-ionic systems, mixed Na-Ca systems and also natural groundwaters.

- *Clay/groundwater interactions*

Groundwater evolution, mineral or salt dissolution and cation exchange processes may modify the chemistry of the clay/groundwater system and this is especially relevant for long-term evaluations. The evolution of the chemistry is expected to have an impact on the erosion behavior of the barrier and on the overall mass loss. Some important points related to clay/groundwater interactions have been identified in the tests performed in WP2.

- *Groundwater velocity*

The worst scenario for a repository in crystalline rocks is the presence of hydraulically active fractures and, for this reason, it is important to know if the water flowing at the bentonite surface or gel-front may increase colloid detachment and if a dependence between the groundwater velocity and erosion rates can be established. In WP2, different groups analyzed the effects of the groundwater velocity with different experimental sets-up.

- *Clay extrusion paths*

In a fractured rock, apart from the hydraulic characteristics of the fracture also the geometrical (and physico-chemical) ones may have an impact on the bentonite mass loss. Different experiments have been designed in WP2 to elucidate some of the potentially critical parameters of the fracture: aperture, slope with respect to the bentonite, surface roughness (composition and fracture fillings).

In EC-BELBAR Work Package 2 (WP2, Erosion) several research groups collaborated to identifying the most important mechanisms involved in bentonite erosion and to quantify its possible extent (at least conservatively) under different environmental conditions.

Participated to WP2, eleven research organization from seven different countries: CIEMAT (Spain); MSU (Russia); KIT-INE (Germany); UJV-REZ (Czech Republic); SKB, ClayTech, KTH (Sweden); B+Tech, VTT, University of Jyväskylä (Finland); NDA (United Kingdom).

The objective of the Deliverable 2.*11 "Evaluation of experimental results on bentonite erosion"* is to summarize main conclusions of the work carried out in WP2, in the frame of the different topics, pointing out the main accomplished objectives and remaining uncertainties.

The main sources of the information for the summary provided in this report come from the Deliverable 2.11 *"WP2 Partners final report on bentonite erosion"* and the presented in its ANNEX, as well as from the presentations made during the different Project meetings and previous WP2 deliverables.

DESCRIPTION OF THE MAIN EXPERIMENTAL SETS-UP AND EROSION PARAMETERS DETERMINATION.

In order to address the goals of this WP, different experimental sets-up were used by the different organisations. Most of the tests were carried out simulating the potential extrusion/erosion behaviour of bentonite buffer material at a transmissive fracture interface (B+Tech, Clay Technology and CIEMAT) allowing the free-swelling of the clay. A schematic of this type of test can be seen in Figure 1 (from B+Tech). With this system, the effects of solution chemistry, material composition, flow velocity, fracture geometry (aperture, slope angle) and other parameters could be analysed. In this set-up, the swelling clay material can extrude/erode into an artificial fracture and it was selected for performing the tests of the benchmark exercise carried out in WP2 with a commercial purified Na-smectite (NANOCOR).
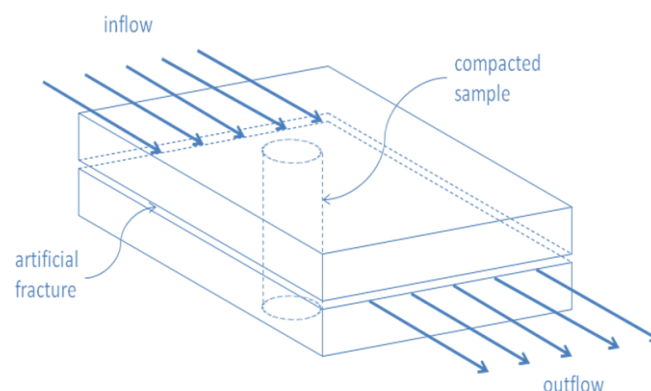
Figure 1. *Schematic representation of the flow-through, artificial fracture test (From B+Tech)*

Other types of experiments were designed, maintaining the confinement of the clay and allowing its hydration through the presence of sintered steel filters, with a pore size of approximately 100 μm, within cells similar to those presented in Figure 2 (CIEMAT).
These tests could represent *static conditions* (closed system with water in equilibrium with the clay, Figure 2a and 2b) or *dynamic conditions* (with water flowing at the surface of the bentonite, Figure 2c and 2d, through the sintered filters).
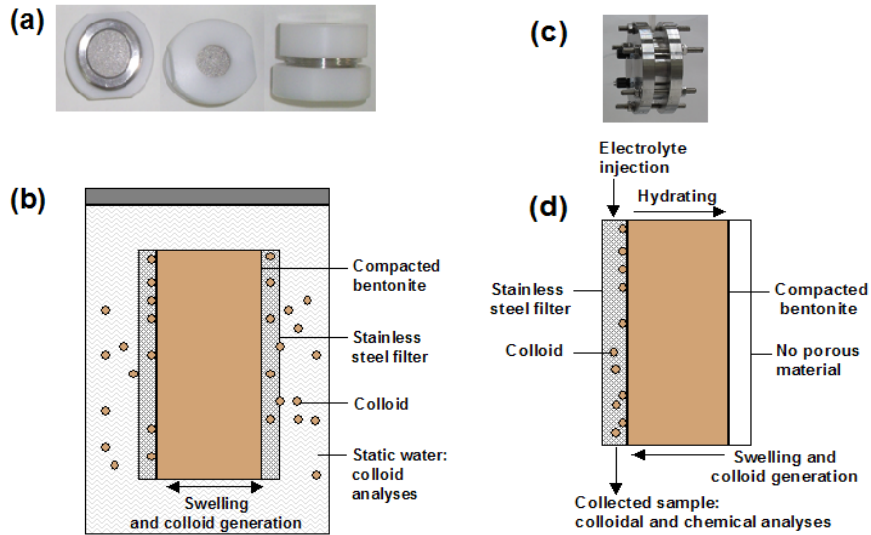
Figure 2. *Schematic representation of erosion tests with confined clay a and b) static; and c and d) dynamic tests (CIEMAT).*

Given the differences in the type of experiments and the need of comparing the numerical results, obtained from the different organisations, it is important to make clear how the *"mass loss"* or the *"average mass loss rate"*, needed for quantitatively estimating erosion, is measured in each case.

When the clay is confined, no significant extrusion occurs and the mass loss is limited to the particles dispersed in the liquid phase (the *eluted mass*) plus some particles retained in the sintered filters, which can be determined by difference from the initial and final weight of the initially *emplaced* mass and filters. The eluted clay mass can be periodically measured by means of different techniques typically Photon Correlation Spectroscopy (PCS), turbidity or ICP-MS, during all the experiment duration.

In the artificial fracture tests, upon hydration, the bentonite clearly extrude within the fracture. In this case, the "eluted mass" is considered not representing the total eroding mass. The mass loss is then determined via post-mortem analysis considering the schematic of Figure 3, which includes the nomenclature and methodology to determine the eroded mass.
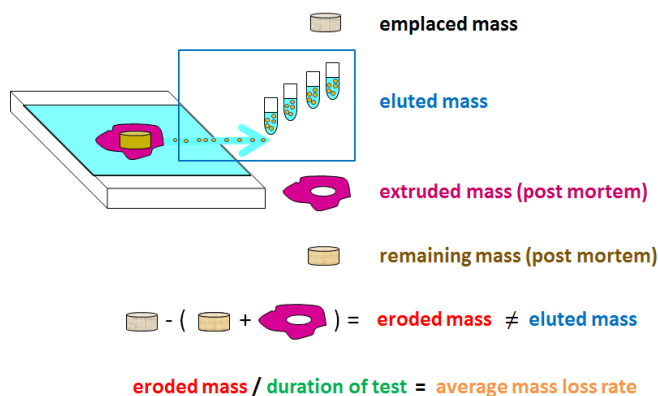
Figure 3. *Determination of the clay eroded mass in erosion tests.*

The methodology used for determining the eroded mass is the gravimetry.

In the experiments in which free-swelling is not possible, the mass loss is evidently lower (about two orders of magnitude) than that obtained in the artificial fracture configuration. Even though, the basic aspects related to the effects of chemistry, water flow, etc., on erosion are very similar.

Apart from the different experimental configuration, some other aspects must be taken into account when data obtained are evaluated as a whole, mostly related to their final representation.

For example, the (average) erosion rate is determined dividing the eroded (and/or) eluted mass by the duration of the experiment. Sometimes, the determination of an "erosion rate" is not straightforward, as the clay mass loss is not constant with time. Thus the selection of the *experimental time* results to be very critical for the adequate comparison of data and their interpretation. In general, there was not a previous agreement of the participant organisations on the duration of the tests (even under the same configuration): as can be appreciated in the Annex to the Deliverable 2.11, some tests lasted less than 24 hours and others more than 2500.

Another critical point for the comparison of is related to the normalisation of erosion data to the surface of the clay/water contact (or *eroding surface area*). In tests like those described in Figure 2, the surface of the filter in contact with water is the area to which erosion data are normalised, but not considering the porosity of the filters. In the case of the experiments described in Figure 3, this area depends on the fracture aperture and the diameter of the clay disk. Instead of using the initial diameter of the clay disk, most of the experimental groups decided to use the diameter measured at the end of the experiment i.e. average diameters of the extruding phase into the fracture volume. Without entering here in details on the possible implications of one choice or another, is important remarking that this can lead to a variation of about a factor 1.5 to 3 in the numerical value of the mass loss (Kg/m^2).

Finally, it has to be reminded here that many of the tests were carried out under very favorable conditions to clay dispersion and erosion (purified Na-smectite and deionized water). The erosion will be maximum under these *"unrealistic"* conditions, thus the values obtained will represent the upper and conservative limit for safety assessment consideration. In fact, the tests performed under more realistic conditions the mass loss is always lower (at least one of order of magnitude), even considering relatively diluted waters.

In the following sections, the main conclusion obtained with respect to the demanded outcomes from WP2 to WP1 will be summarised. In general it can be concluded that main concepts related to erosion mechanisms, and the processes that mostly affect them, have been clarified, but some additional efforts should be done on data representation as a whole, and on normalising procedures as to fix the degree of uncertainty on numerical data.

OUTCOMES OF THE STUDIES PERFORMED IN WP2

Mechanisms of erosion of clay particles from the bentonite surface

Erosion of clay particles from compacted bentonite has been analyzed by different experimental techniques as explained in the previous section. The first condition needed for particle formation is that clay must be hydrated enough, to allow the gel formation (which is the main colloids/particles source).

The swelling pressure is the driving force causing the gel intruding the fracture and/or pores of the rock and thus determining the thickness of the extruded gel layer, potentially subject to erosion. Particle detachment may occur when the driving force for water uptake (of osmotic nature) overcomes the attractive forces between the clay platelets.

In order to produce an erodible gel layer, the bentonite must have a place to expand (for this reason the geometry of the fracture or the characteristic of the porous space in the rock are critical, as will be discussed later). Water can reach and hydrate the bentonite but clay particles cannot move within pores with a size similar or lower than the size of clay particles thus, even in very favorable chemical conditions, clay mass loss would be impossible without the presence of adequate transport paths. This will imply the need of normalizing the erosion data to the dimensions of the pores/fractures.

One of the possible mechanisms for particle detachment from the clay surface is related to the water flow. This can shear off particles by physical forces. However, the existence of repulsive electrostatic forces caused by the presence of a double layer which separates the particles seems to be much more relevant for particles detachment from the compacted clay.

The existence and characteristic of the double layer and consequent particle interactions mainly depends on the chemistry of the groundwater, thus chemical forces are especially relevant on erosion processes.

Electrostatic repulsion is stronger when the double layer is highly developed (low ionic strength) whether particle interaction and aggregation are favored when the double layer is weak (high ionic strength). When a repulsive force between particles exists they are pulled away until the attraction between is so weak that they can diffuse away or be transported by the water flow (if present).

For this reason, in general, it is very important to establish under which conditions clay colloids are stable, because the conditions favoring colloid stability, also will favor erosion through clay dispersion.

In most of the tests performed within WP2 related to closed or static systems (without water flowing on the gel surface), it has been observed that clay dispersion is not continuous. In CIEMAT's static tests (Figure 2a and 2b) a mass of clay particles (eluted) increased with time after reaching a maximum value after a certain time. This (equilibrium) mass depended on different factors, for example the ionic strength of the water or the Ca content in the system.

Also in the tests where free swelling of clay in the fracture was studied, the velocity of the extruding phase into the fracture volumes was not constant. With some exceptions related to pure Na-smectite hydrated with deionized water (*i.e.* the most favorable case for erosion) the velocity of the bentonite within the fracture always decreased until reaching zero values in many cases.

These results suggest the possibility that the experimental and physico-chemical conditions determine somehow a maximum quantity of clay that can be dispersed and afterward eroded, as will be detailed in the next paragraphs.

Characteristics of the bentonite clay

For what concerns the role of divalent ions in the erosion process, it was clearly shown (independently on the type of experiment) that pure Ca-clays do not suffer any erosion. However, a quantity of Na in the clay exchange complex around 20-30 % (even in the presence of other divalent cation) is enough to make the clay erodible, to a similar extent than Na-clays. Nevertheless, a certain dependence on clay erodibility and Na content in the exchange complex can be suggested as Na increases the dispersivity of the clay.

It is important noticing that, in respect to pure Na-clays, below the erosion threshold solution composition, average mass loss rates for the as-received bentonites are at least an order of magnitude lower.

Comparative studies, under similar experimental conditions, showed that the extrusion and erosion behavior was not exactly the same for all the analyzed bentonites (even when Na-exchanged) indicating that the erosion behavior also stems from intrinsic physico-chemical properties of the clays.

The capability of the different bentonite to disperse (clay) colloids is quite important on the potential of erosion process. This means that the smectite content plays a role, but also the type of smectite might be crucial. For example, ongoing tests carried out at CIEMAT, seem indicating that the smectites with the charge mostly located in the tetrahedral layer form, in average, less colloids than those with the charge mostly located in the octahedral layer. However, the comparison made directly with raw clays is not straightforward, because other factors have been evidenced as important, including the overall mineral composition of the bentonite.

The eroding material is expected to be predominantly smectite, but the existence of materials that can induce bentonite particles destabilization through hetero-aggregation (for example kaolinite or oxides like alumina) may affect significantly and limit the erosion of the clay. In stability tests, a small percentage of kaolinite (less than about 15 %), was shown to produce an evident destabilization of bentonite clay colloids, promoting fast aggregation. In erosion experiments, the compacted bentonite mixed with kaolinite, under the same experimental conditions, eroded significantly less than the bentonite alone. A different process was observed for the illite/smectite mixture where the eroded mass was roughly proportional to the smectite content.

Finally, the presence of accessory minerals (or *detritus*), usually larger than the smectite particles, has been identified as potentially relevant on the overall erosion behavior of the raw clays. During the clay extrusion in fractures, accessory phases remain behind and form bed layers. Such process may provide the bentonite buffer system with self-filtration mechanism which may limit the effects of colloidal erosion, limiting the rate of mass transfer and even stopping it, but is not totally clear if this accessory mineral layer may (or not) be subject to erosion. No apparent attenuation of Na-smectite erosion was observed by B+TECH adding accessory materials (sand) and, in sloped fractures, both the smectite and minerals could be removed

Groundwater chemistry

Groundwater chemistry definitely plays a very important role on bentonite erosion. As mentioned before, the conditions that favor clay colloid stability are expected to favor bentonite erosion; even if they may be not enough for ensuring that the erosion process will take place. The maximum erosion, as expected, is always recorded when deionized water is used. The values of mass loss rate obtained with deionized water can be surely used as (overly) conservative upper limits for the erosion of each bentonite.

The critical coagulation concentration (CCC) determined in batch stability experiments, often overestimates the limits observed for erosion. Probably the CCC concept is not directly applicable to erosion experiments with natural bentonites and, in general, in those systems where more than one type of ion is present. Particularly, it is ill-defined when ion exchange processes occur. However, in erosion experiments it has been shown that, for all the analyzed bentonites, a threshold electrolyte concentration exists, above which erosion does not occur, (this being related with also with the properties of solid).

In the simple and favorable case to erosion, of pure Na-smectite in Na electrolyte, mass loss in fracture was observed only below a threshold of approximately 10 mM. This is a very important finding in the sense that chemical erosion can take place only under highly dilute solution conditions. The increase of ionic strength clearly attenuates erosion, up to the threshold limit where mass loss is not observable anymore.

Despite the mass loss mechanisms are different in the horizontal (dispersion and transport) and sloped angle fractures (structural collapse and sedimentation) they are both operational only under similar chemical environment, i.e with similar threshold for the ionic strength of the solution. Observations of mass loss at or above this threshold cannot be attributed to erosion, but rather to disintegration or breakdown of aggregates.

In erosion experiments with mixed (Na-Ca) electrolytes, it has been observed that 1 mM of Ca is enough to inhibit erosion.

Amongst crystalline natural waters, Grimsel groundwater is one the most favorable for clay colloid stability for its low salinity (1 mM). However, the average mass loss in this diluted water is significantly lower (30-40 %) than that measured in deionized water in all the different experimental set-up used.

Clay-groundwater interactions

Apart from the direct consequence of the solution chemistry (and its variability) on clay erosion, other processes should be taken into account, related to the water/clay interactions. In long term dynamic erosion experiments (CIEMAT and KIT-INE) it was observed a variation of the initial water composition due to the contact with the clay. The soluble salts present in raw clays dissolved in contact with fresh water, causing an initial increase in salinity. Apart of salts/minerals dissolution in the natural clays, cation exchange will be also present. A depletion of Ca from the solution coming out from the erosion cell, indicating that it is absorbed in the clay. At the long term-this progressive enrichment of Ca, might change (inhibiting) the erosion of the gel. The use of geochemical modelling can be therefore useful to establish the evolution of both groundwater and bentonite surface and indicate the possible evolution on the erosion process.

CLAY TECHNOLOGY clearly observed hysteresis in the erosion behavior, passing from high ionic strengths to low ones. They suggested that if a bentonite previously had a higher salinity present, it might be completely stable against erosion below the expected threshold value. Similar results could be deduced from stability experiments, where it was observed that after aggregation in high ionic strength, bentonite colloids do not completely recover their initial size (or aggregation state) coming back to very diluted conditions. This indicated that the awareness of the system's history seems also crucial importance for evaluating erosion rates.

Groundwater velocity

The effects of groundwater velocity on the mass loss seem to be less relevant than those of groundwater chemistry and somewhat also related with the chemistry of the system. In general, in very diluted systems (deionized water or salinity well below the CCC in Na electrolytes) the mass loss appear to be correlated to flow velocity (the higher the flow rate the higher the mass loss) even if the variations are generally within the same order of magnitude. However, in less dispersive systems the water flow velocity do not seem to be a relevant parameter and no clear trend between water velocity and erosion has been observed in the different experimental tests.

In some cases, it was reported that increased flow velocities lead to decreased effluent solids concentrations. This fact would suggest that a rate-limited erosion mechanism exist, at least within the range of tested flow velocities, and that hydrodynamic shear forces maybe not significant in the erosion process.

Thus this can be interpreted considering that the loss of smectite is governed by chemical dispersion/diffusion and that flow just mobilizes the particles present. This would mean that chemical effects prevail in any case.

Clay extrusion paths

Different characteristics of the clay extrusion paths were considered in the experimental tests: the fracture aperture; its geometry and slope angles and its roughness. Some test to verify if the overall dimensions of the test might be relevant (scaling effects) were also carried out.

Fracture aperture

In CIEMAT's static tests, the eluted mass was fairly proportional to the extrusion area (doubling this areas double concentration of eluted colloid was found). On the other hand, B+TECH reported that in artificial fracture experiments conducted at 0.1 mm nearly one order of magnitude reduction in average erosion rates, were observed with respect to results from 1 mm artificial fractures. These results seem to be consistent with a surface-area controlling effect on mass loss.

Geometry: slope angle and gravity

In artificial fracture test with a slope angle of 45° or even 90º, the mass loss rate increased significantly. 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

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mass loss rates. Obviously the mechanisms affecting the mass loss are different in the sloped fracture with respect to horizontal fractures. In horizontal fracture the mass is released by dispersion whether in sloped fracture the gravity induces a purely sedimentary mass loss mechanism. Such sedimentary-type mass loss was observed in sloped fractures under stagnant (no flow) as well as flow-through conditions.

Surface roughness

Few experiments were carried out to understand the effects of fracture roughness on mass loss. In the rough system, the average mass loss rate was found to be lower. Natural fractures are characterized by rough surfaces and probably buffer mass loss in rough-walled fractures may be significantly attenuated relative to that in smooth-walled systems.

Scaling effects

In order to try to assess the effect of scale through the experimental data, erosion tests with cells of different dimensions were carried out by B+TECH. The observed normalized average mass loss rates are in reasonable agreement.

CONCLUSIONS

This report summarizes the main outcomes of the experimental work carried out in WP2 on bentonite erosion. Several topics have been treated and many concepts related to erosion mechanisms have been analysed.

The chemistry of both clay and groundwater are crucial on the erosion behavior. Erosion will occur only below a threshold value for the ionic strength, depending on the clay and the solution, and basically under diluted solution conditions. The maximum mass loss is measured under both dynamic and static conditions with pure Na-smectite and deionized water. These maximum values will represent the upper and (overly) conservative limit for safety assessment consideration. The mass loss rates are dependent on the ionic strength and are about one order of magnitude lower for the as-received than for the purified Na-smectite. Ca-clays do not suffer any erosion but a quantity of Na in the clay exchange complex around 20-30 allows the clay to disperse. In solution 1 mM of Ca is enough to hinder erosion.

In horizontal fractures the mass is lost from the extruded source material through dispersive release and transport. In sloped fractures structural collapse and sedimentation are the main processes causing the mass loss. However in both cases they are operational under a similar chemical threshold. Comparative studies showed that the extrusion and erosion behavior of different bentonite (even when Na-exchanged) was not exactly the same, suggesting the importance of intrinsic physico-chemical properties of the clays (mineralogy, smectite content, charge density and location).

The effects of groundwater velocity on the mass loss seem to be less relevant than those of groundwater chemistry and somewhat also related with the chemistry of the system. In highly diluted systems the mass loss appears to be correlated to flow velocity even if these variations are generally within the same order of magnitude. However, in less dispersive systems the water flow velocity do not seem to be a relevant parameter and no clear trend between water velocity and erosion has been observed in the different experimental tests.

In general the mass loss values seem to be consistent with a surface-area controlling effect on mass loss.

Data obtained from different experimental sets-up leads to the same conclusion in regard to the different treated topics even if numerical values are sometimes not direcly comparable. Some additional work should be done on data representation as a whole, and on normalising procedures to fix the degree of uncertainty.

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