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WP2
MECHANISMS OF EROSION

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(CIEMAT)
## WP2 Overview

### Work Package 2: PARTICIPANTS and PMs

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**11 participants, 7 countries**

**Physico-chemistry of Actinides and Fission Products Unit**
To understand the main mechanisms of clay particle erosion from the bentonite surface and try to quantify the (maximum) extent of the possible erosion under different physico-chemical conditions.

1. Assessment of bentonite barrier functionality the at the long-term, which could be compromised if a significant clay loss occurs.

Conditions that favor colloid stability are also expected to favor colloid transport and erosion processes.

2. Interaction with RN and transport to the far-field of the repository.

Safety Assessment (SA) demanded new data obtained to develop and validate models describing the bentonite barrier erosion. Need to reduce uncertainties.
Starting from the analyses of the state-of-the-art at the beginning of the project, the treatment of several topics was suggested:

- Improved models with new data: output of WP 5.
- Characteristics of the bentonite clay: role of divalent cations; other clay characteristics.
- Groundwater chemistry: role of divalent cations; ionic strength, mixed electrolytes;
- Groundwater/clay interactions: modelling inclusion in Safety Case;
- Groundwater velocity: dependence of erosion on water velocity;
- Clay extrusion paths: dependence of fracture geometry.
Wrap-up

Where we were at the beginning

Initial Objectives & Issue (NDA Report)

Where we are now

Accomplished Objectives
Remaining Uncertainties

FINAL CONCLUSIONS FOR BELBAR

In this talk, a summary of the main results obtained by the organizations participating in WP 2. Source of information: deliverable and previous BELBAR Meetings.

Physico-chemistry of Actinides and Fission Products Unit
Extrusion/erosion behaviour of bentonite buffer material at a transmissive fracture interface allowing the free-swelling of the clay. With this system, the effects of solution chemistry, material composition, flow velocity, fracture geometry (aperture, slope angle) and other parameters could be analysed. Benchmark exercise.
Experiments maintaining the confinement of the clay and allowing its hydration through the filters, with a pore size of 100 µm. The mass loss is limited to the particles dispersed in the liquid phase (the *eluted mass*) plus some particles retained in the sintered filters.
EROSION OBSERVED IN DIFFERENT SYSTEMS: 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.

- Eluted clay mass: PCS, turbidity, ICP-MS.
- Extruded, remaining: gravimetry.

\[
\text{eroded mass} / \text{duration of test} = \text{average mass loss rate}
\]
Mechanisms of erosion of clay particles from the bentonite surface

• Clay must be hydrated enough, to allow the gel formation (which is the main colloids/particles source).

• Swelling pressure: driving force causing the gel intruding the fracture/pores of the rock; Particle detachment may occur when the driving force for water uptake (of osmotic nature) overcomes the attractive forces between the clay platelets.

• 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).

Repulsive electrostatic (double layer) forces separate particles, from the gel. Double layer depends on water (chemical forces); Conditions for particle “stability “ necessary.

Water flow can shear off particles: (physical forces);
Mechanisms of erosion of clay particles from the bentonite surface

Is erosion “linear”, continuous... (never-ending ?)

- In CIEMAT’s experiments in static system it has been observed that clay dispersion is not continuous.
- The eluted mass increased (linearly) 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, the type of bentonite, etc..
Mechanisms of erosion of clay particles from the bentonite surface

- In flow-trough artificial fractures the velocity of extruding phase into the fracture was not constant (as well as the eluted mass).
- With some exceptions (pure Na-smectite hydrated with DW, 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.

Eluted mass rates are not constant. Point to be discussed.
Eroding material is predominantly smectite;

Type of smectite is important. Distribution between tetrahedral/octahedral charge is relevant (CIEMAT): montmorillonites in general more erodible than beidellites;

Pure Ca-bentonite does not erode;

Na concentration above 20 % in the exchange complex is enough to make the clay erodible. In dispersed systems, a good correlation between colloids generated and Na has been found. However, the structure of bentonite even with exchanged Na-clay influences the erosion process.

In respect to pure Na-clays, average mass loss rates for the as-received bentonites are at least an order of magnitude lower.

Existence of minerals that may cause hetero-aggregation (kaolinite/oxides...) inhibits erosion (relation between erosion and stability).
Presence of accessory minerals (larger than the smectite particles) may slow down smectite and stop erosion because they remain behind and form bed layers.

However, no apparent attenuation of montmorillonite erosion observed with added accessory materials. The accessory mineral layer may (or not) be subject to erosion (not clear); in sloped fracture both smectite and minerals are removed.

Horizontal artificial fracture test with sodium montmorillonite / sand. Sand layer formation at the extrusion/erosion interface is clearly visible.
Groundwater chemistry plays a very important role on bentonite erosion. The conditions that favor clay colloid stability are expected to favor bentonite erosion; even though, they may not be enough for ensuring that the erosion process will take place.

The maximum erosion is always recorded when deionized water (DW) is used. The values of mass loss rate obtained with DW can be surely used as (overly) conservative upper limits for the erosion of each type of bentonite.

Ca in solution (I ~ 1 mM) inhibits erosion. The increase of ionic strength attenuates erosion;

Amongst crystalline waters, Grimsel groundwater is one the most favorable for colloid stability for its low salinity (1 mM). However, average mass loss is significantly lower than that of the limiting DW (30 %). The existence of more than ion influences erosion;
Groundwater chemistry

From B+Tech

MAXIMUM EROSION (DW)

A threshold electrolyte concentration exists, above which erosion does not occur, (this being related with also with the properties of solid).

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 further attenuates erosion, up to the threshold limit where mass loss is not observable anymore.
Threshold ≠ CCC. 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.
Clay-groundwater interactions chemically affects both clay and groundwater.

- Water/clay interactions may be very important for the evaluation of erosion and stability of colloids in a repository at a long-term.

- The soluble salts present in raw clays dissolved in contact with fresh water, causing an initial increase in salinity. Other dissolution/precipitation processes may occur.

- Ionic exchange: continuous income of Ca from fresh groundwater may increase the Ca content in the exchange complex, decreasing the erodibility of the clay.

- The use of geochemical modelling can be useful to establish the evolution of both groundwater and bentonite surface and indicate the possible evolution on the erosion process as complement to stability models.
Results

Clay-groundwater interactions

Reversibility?

- Hysteresis was observed in the erosion behavior passing form high ionic strengths to diluted ones. That means that smectite eroding at 10 mM NaCl, might be completely stable against erosion below the expected threshold value, if it has previously had a higher salinity present.

The “history” of the system should be accounted for in evaluating erosion rates (Case of scandinavian scenario)

Similar in stability experiments: after aggregation in high ionic strength, bentonite colloids did not completely recover their initial size (or aggregation state) coming back to more diluted conditions. At least, during the experimental time.
Are physical forces (produced by the water flow) relevant on bentonite erosion? Are they more/less important than chemical forces?

- In largely erosive systems (ion concentration well below the CCC, or erosion threshold), the average mass loss rates seem to be (slightly) correlated with the flow velocity, the highest the flow velocity the highest the mass loss.

- The observed variations are generally within the same order of magnitude.

In other cases, the water flow velocity did not seem a relevant parameter or, at least, no clear trend between water velocity and erosion could be observed.
Two different erosion cells under different flow conditions (changed periodically) showed practically the same erosion behavior.
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 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 over physical ones.
Does mass loss depend on the characteristics of the “extrusion paths”: dimensions, geometry, roughness (mineralogy?). Relations with filtration processes (WP3).

**FRACTURE APERTURE**

- The effect is not completely clear.

In static experiments, the erosion rate seemed to be roughly proportional to the area of the fracture (double areas double concentration of colloid in solution); consistent with a surface-area controlling effect on mass loss; difficult to determine under less erosive conditions.

One blind side: approximately half of eluted particles.
Does mass loss depends on the characteristics of the “extrusion paths”: dimensions, geometry, roughness (mineralogy ?). Relations with filtration processes (WP3).

From 1 to 0.1 mm nearly order of magnitude reduction in average erosion rates;

In other experiments this was not clearly seen.
GEOMETRY: SLOPE ANGLE (& Gravity)

- Artificial fracture tests 45° / 90°: they showed a purely sedimentary mass loss mechanism compared to horizontal fractures, where the mass is released by dispersion.
- Average mass loss rates in sloped fractures, always larger than in horizontal case. (Larger slopes, increased mass loss rates). Such sedimentary-type mass loss was observed in sloped fractures under stagnant (no flow) as well as flow-through conditions.
• 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.
Experiments were carried out by B+TECH 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.

This is in agreement with previous studies of bentonite colloid migration in fracture;

Nevertheless, “filtration” existed below a threshold value for water velocity. CIEMAT analyzed in horizontal flow through test with/without granite (at high flow rates). No large differences were observed.
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.
Data obtained from different experimental sets-up leads to similar conclusions in regard to the different treated topics even if numerical values are sometimes not directly comparable. Some additional work should be done on data representation as a whole, and on normalising procedures to fix the degree of uncertainty.

NORMALISATION of Eroded Mass

If the eroded mass varies with time is not constant, the experimental time becomes a critical parameter! Average mass loss rates with large errors.

Experimental times from less than 24 to more than 1000 hours
NORMALISATION of Eroded Mass

Data are recalculated considering the “final” radium of the clay (after extrusion)

Time dependent parameter; sometimes not very precise measurement, above all for raw materials.

Why not initial r?

Numerically factor 2-3. Larger differences for highly erodible systems.
• All the topics proposed at the beginning of the project related to erosion mechanisms have been analysed.

• The chemistry of both clay and groundwater are critical 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 depend on ionic strength; they 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.

• 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.

• Some additional effort needed on data representation and normalising procedures to fix the degree of uncertainty.
The research leading to these results has received funding from the European Atomic Energy Community’s Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.
Thanks for your attention
Physico-chemistry of Actinides and Fission Products Unit
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