

BELBaR



Meiringen, June 17-18, 2014

PROGRESS UPDATE OF CIEMAT'S LABORATORY RESULTS

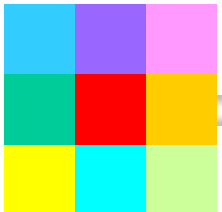
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Gutiérrez, Natalia Mayordomo, Ana Benedicto

(CIEMAT)

**Physico-chemistry of Actinides and
Fission Products Unit**



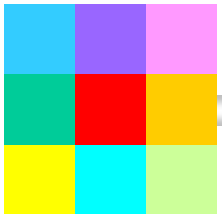
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2nd year - CIEMAT work has been focused on the following topics within WP2 and WP4:

1. Characterisation of different bentonites (and saponite) clays, to gather information on their chemical and structural properties for the analysis of their possible implications on erosion processes. Erosion experiments with these bentonites, comparison of their behaviour. CIEMAT's set-up, static tests, under very favourable conditions (DW).
2. Analysis of the **irreversibility of the colloid coagulation** processes.
3. Analysis of the **effects of the presence of different anions** on colloid stability.

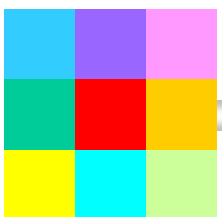
Information on these topics also available in Deliverable D2.4 and Deliverable D4.4.



The selected bentonites for comparison were:

- **FEBEX** from Spain
- IBECO from **Mylos** in Greece
- Wyoming **MX-80** from USA
- Czech **Rokle** Na-activated (B75)
- Russian bentonite from the **Khakassia** deposit.

and 1 Spanish saponite.



OBJECTIVE: to perform the characterisation (comparable) for all the clays and to start gathering information, for further analyses of erosion behaviour.

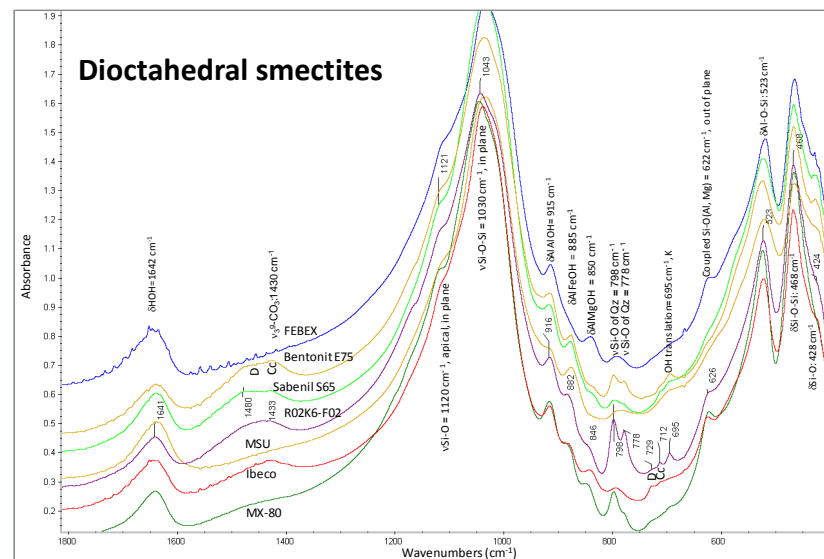
This characterisation includes:

- **Physical properties** (gravimetric water content, w.c.; specific gravity, γ_s ; density);
- **Mineralogical analysis:** XDR (random and oriented powders), SEM, FTIR and Thermal Analysis;
- **Chemical analysis** of the rock samples (major –trace elements in the total fraction and in the $< 2 \mu\text{m}$ fraction); total carbon and sulfur content; total reduction capacity (TRC); organic matter;
- **Physico-Chemical Characterization:** CEC (Cu-Trien), Cation Exchange Population, BET Surface area, Total Surface area;
- **Pore water chemistry** (squeezing and aqueous extracts);
- **Soluble salts** by aqueous leaching.

Fernández et al., CIEMAT Report, ongoing

Smectite		FEBEX	lbeco	MX-80
Tetrahedral layer	Si	7.90	7.80	8.00
	Al	0.10	0.20	0.00
	Total	8.00	8.00	8.00
Octahedral layer	Al	2.73	2.68	3.02
	Ti	0.01	0.09	0.01
	Fe ³⁺	0.41	0.52	0.44
	Mg	0.98	0.82	0.48
	Mn	0.00	0.00	0.00
	Total	4.14	4.11	3.96
Interlamellar layer:	Ca	0.17	0.20	0.13
	Sr	0.00	0.00	0.00
	K	0.13	0.09	0.02
	Na	0.20	0.11	0.30
	Mg	0.00	0.00	0.00
	Total	3.64	3.69	3.93
Tetrahedral charge:		-0.10	-0.20	0.00
Octahedral Charge:		-0.56	-0.40	-0.58
Total:		-0.66	-0.60	-0.58
Interlamellar Charge (+):		0.66	0.60	0.58
% tetrahedral charge		15	33	0
% octahedral Charge		85	67	100
F.W. (half-unit cell)		749.5	748.3	743.9
Charge per unit cell		0.74	0.67	0.72
a				
b				
c				
Cristallite size (Å)				
Number of lamellae/cristallite				
S (m ² /g)		750	750	750
Surface charge density (C/m ²)		0.126	0.116	0.108

Unit cell formula



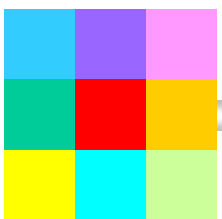
FTIR spectra of the total fraction in the bending region of the OH groups: 1000-600 cm⁻¹

Fernández et al., CIEMAT Report, ongoing

Data		MX-80	Febex	Ibeco	Czech B75	Khakassia
w.c. (% , 110°C)		8.6	13.1	18.1	6.2	6.5
w.c. (% , 220°C)		8.92	15.19	15.00	6.92	9.76
LOI (%)		14.30	24.16	20.79	16.89	18.16
Spec. weight (g/cm³)		2.760	2.700	2.705	2.727	2.672
Total C (%)		0.3	0.12	1.2	0.42	1.0
Organic C (%)		0.2	0.04	0.35	0.38	0.52
Total S (%)		0.2	<0.05	0.53	<0.05	0.07
CEC Cu-Trien(*)		84	98	90	60	68
Exchangeable Ca(*)		18.4 ± 3	35 ± 0.7	34.2 ± 2.2	3.6 ± 2.4	1.10 ± 0.9
Exchangeable Mg(*)		7.1 ± 0.2	35.1 ± 0.4	30.9 ± 0.7	22.4 ± 0.9	4.2 ± 3.1
Exchangeable Na(*)		57.5 ± 2	28.2 ± 1	27.2 ± 0.5	37 ± 0.74	77.7 ± 1.7
Exchangeable K(*)		2 ± 0.3	2.7 ± 0.2	2.4 ± 0.4	3.9 ± 0.6	2.2 ± 0.1
Clay minerals (wt.%)	Smectite	88.9	94	89	79	58
	Illite	0.1	--	1	1	2
	Kaolinite		--		1	12
	Chlorite		--			5
Quartz (wt.%)		5.1	2	0.4	8.7	13
K-Fd (wt.%)		2	1	0.1	0.6	--
Plagioclases (wt.%)		2	Trace	0.6	0.2	3
Calcite (wt.%)		Trace	2	5	4.2	3
Dolomite (wt.%)		--	--	3	1.3	0.6
Siderite (wt.%)		--	--	0.1	4.5	--
Pyrite (wt.%)		--	--	0.8	--	--
Cristobalite		1.9	--	--	--	--
Lepidocrocite		--	--	--	--	1.5

Physico-chemical and mineralogical properties of the bentonites;





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Clay colloid stability



Zetapotential measurements (surface potential)



PCS measurements (size, aggregation kinetics)



$$U_E = \frac{2 \varepsilon \zeta f(\kappa r)}{3\eta}$$

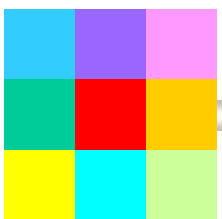
Colloids from Na-clay

pH and I

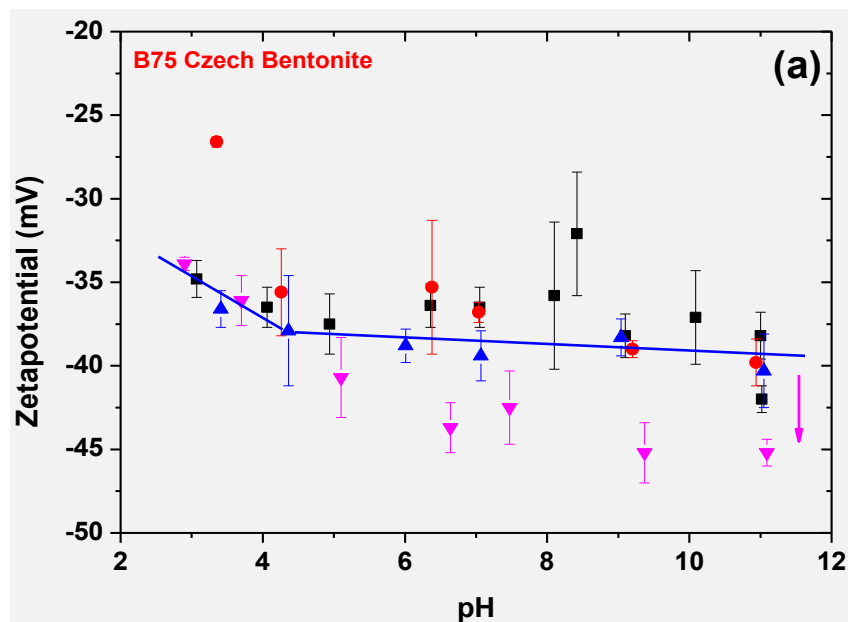
$$D = \frac{kT}{6n\pi \eta R_H}$$

Physico-chemistry of Actinides and
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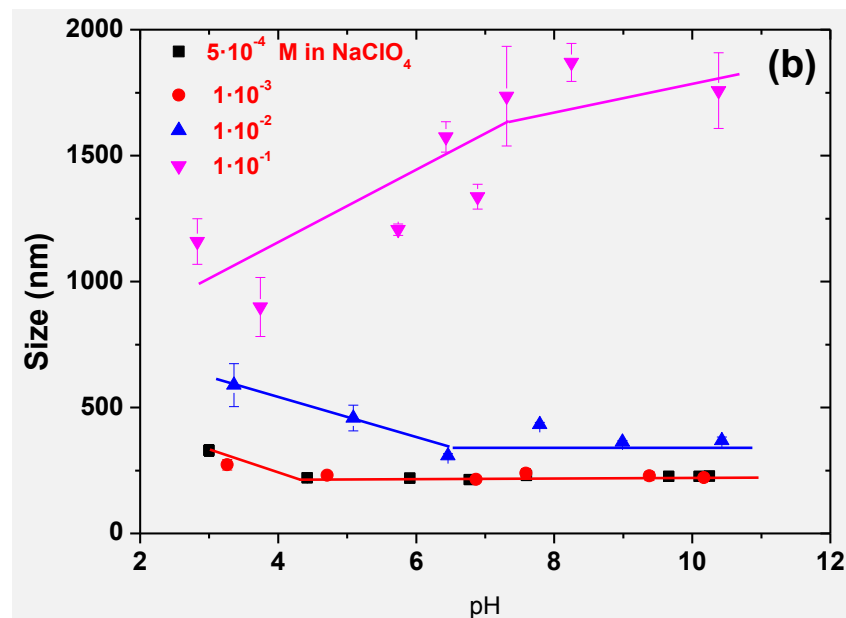




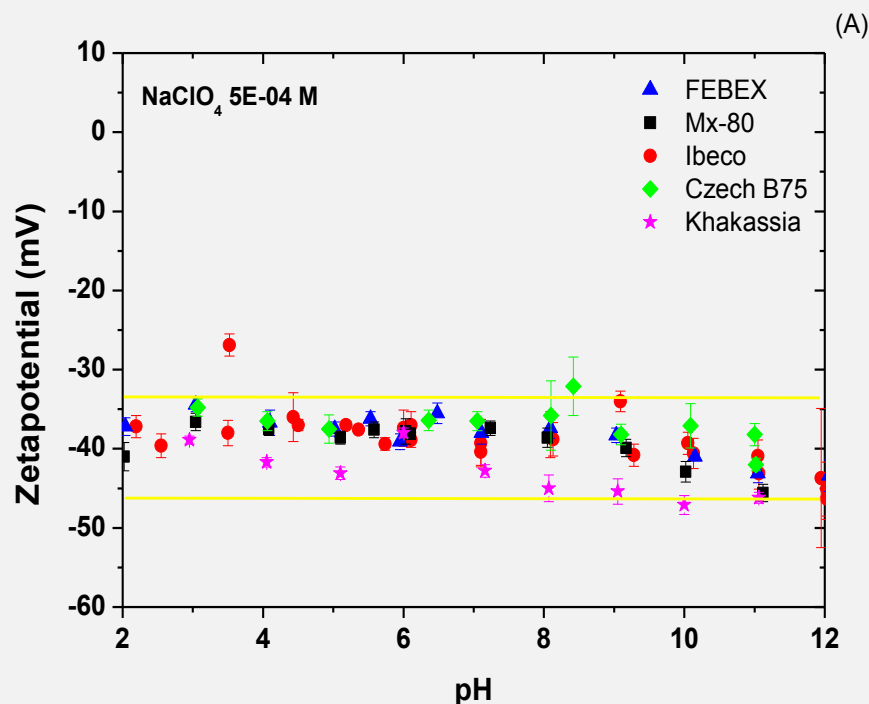
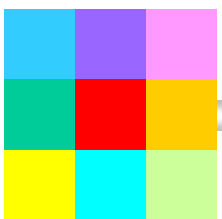
Zetapotential measurements (surface potential)



PCS measurements (size, aggregation kinetics)



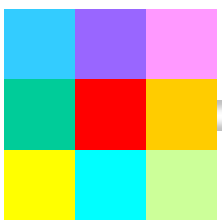
B75 Czech bentonite: a) zetapotential and b) size as a function of pH at different ionic strengths.



Similar "colloidal" behaviour

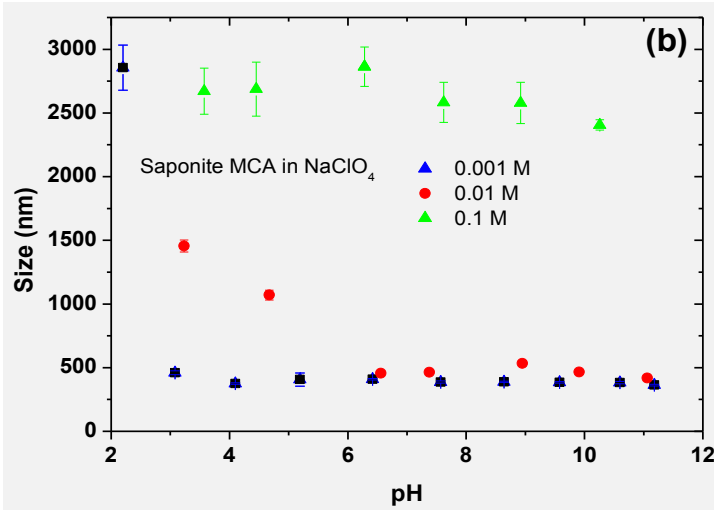
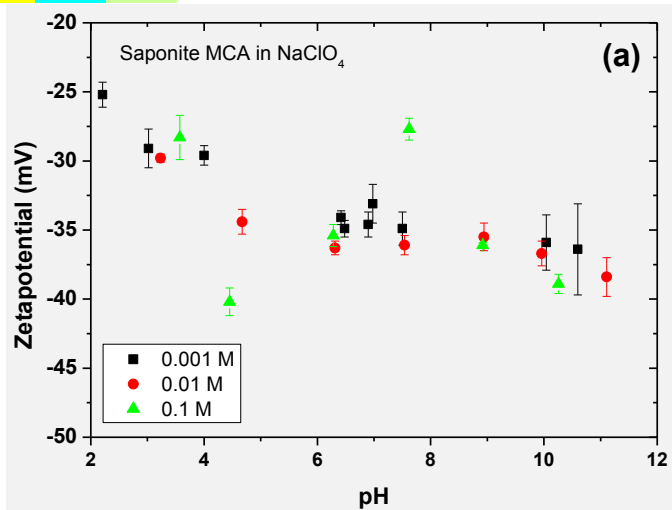
Zetapotential similar in all the cases, even at different ionic strengths. Not particularly relevant for the understanding of clay systems stability/erosion.

Coagulation behaviour: size unvaried up to $I=1 \cdot 10^{-3}$ M with slight increase for $\text{pH} < 4$ (edge-face interactions). Aggregation observed at 0.01 M in NaClO₄, accentuated at acid pH. At $I=0.1$ M, colloids are completely destabilized (size outside the colloidal range).

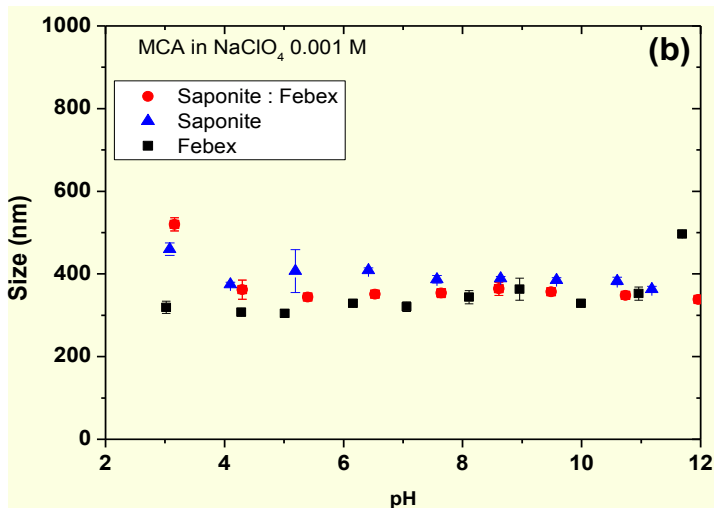
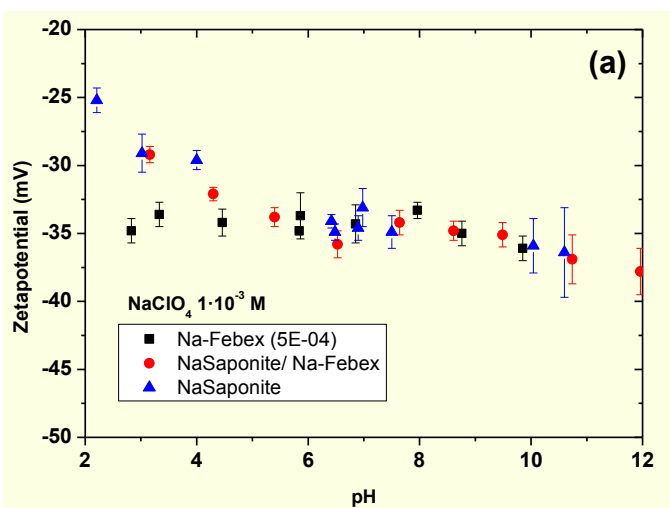


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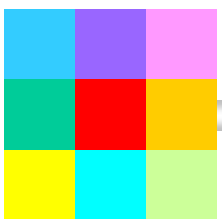
Saponite



Natural

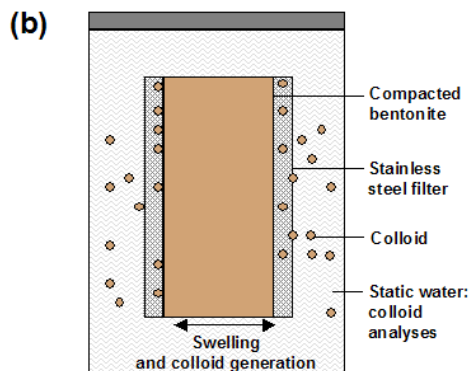
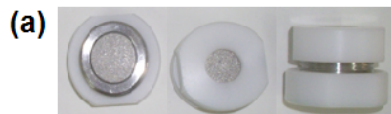


Na-exchanged
and mixture
with Na-smectite



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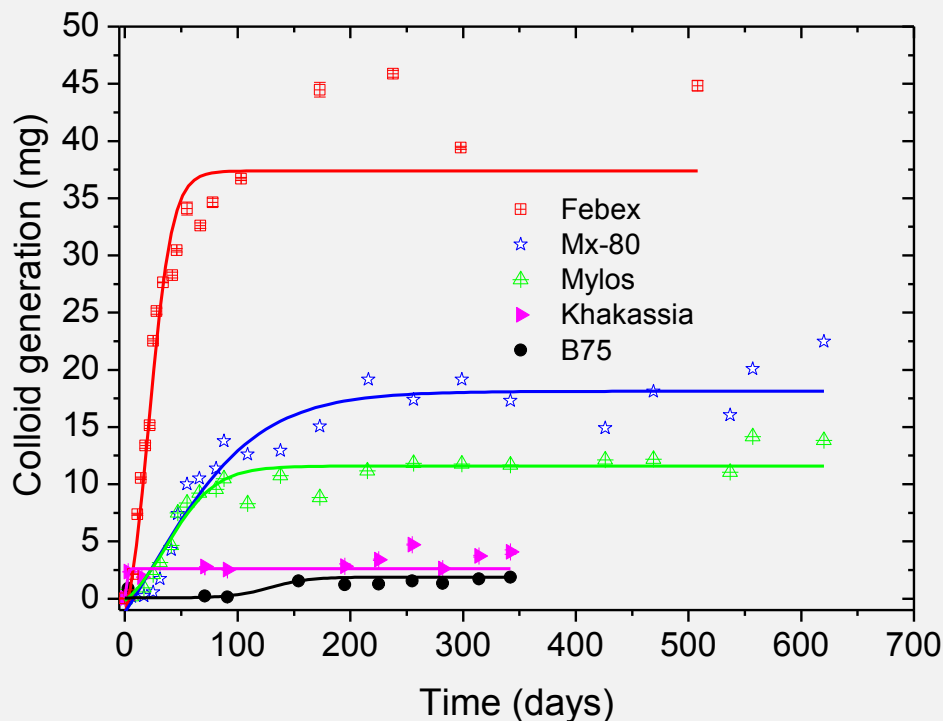
Erosion tests: static cnd.



4 g clay, 200 mL
Compacted & Confined
 $S = 3.5 \text{ cm}^2$

Saponite near DL at day 90

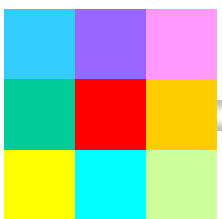
Colloidal masses eroded as a function of time from the five studied bentonite compacted at 1.65 g/cm^3 in DW



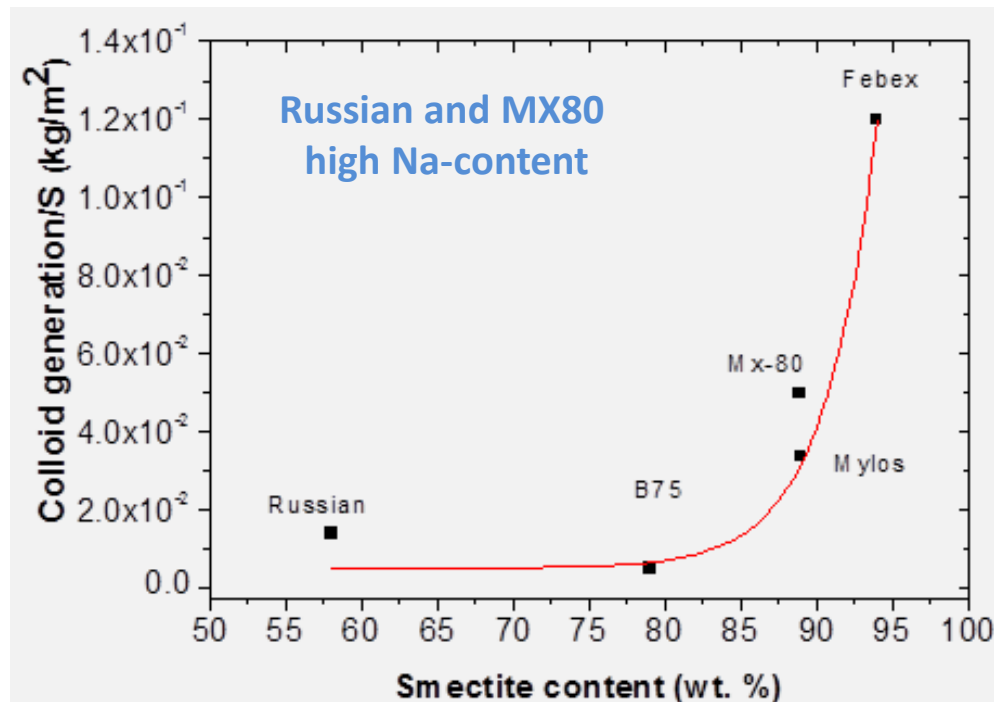
Different "erosion" behaviour

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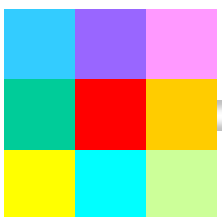




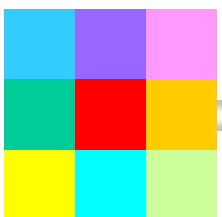
Bentonite	Colloid/S (Kg/m ²)	Mean size (nm)
FEBEX	$(1.2 \pm 0.5) \cdot 10^{-1}$	338 ± 24
Mx-80	$(5 \pm 0.5) \cdot 10^{-2}$	291 ± 31
Mylos	$(3.4 \pm 0.5) \cdot 10^{-2}$	367 ± 46
Russian Khakassia	$(1.4 \pm 0.5) \cdot 10^{-2}$	400 ± 150
Czech B75	$(5.3 \pm 0.5) \cdot 10^{-3}$	296 ± 75



Colloid generation seems to be mostly related to the smectite content (higher in the FEBEX case), rather than to the exchangeable Na (higher in Mx-80 or Khakassia).
Further studies based on complete characterization;

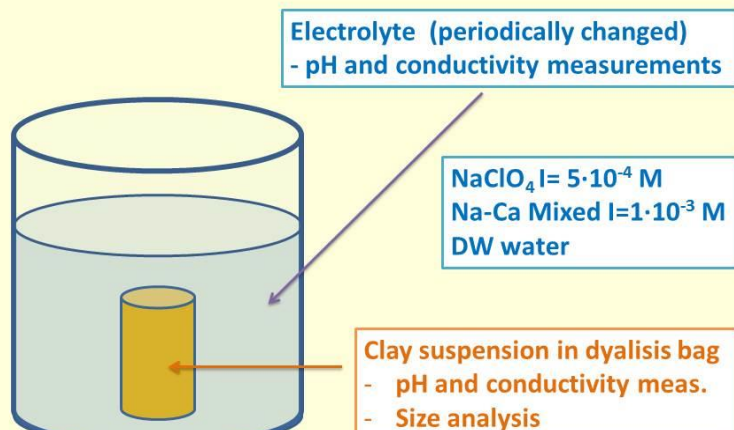


- Different bentonites are being analysed in parallel to gather information on their chemistry, mineralogy, accessory minerals, cations present in the interlayer; cation exchange capacity, pore water chemistry, charge distribution, cell formula etc...
- This characterization will be used for the interpretation better understanding of erosion tests.
- The colloidal properties (surface potential, zetapotential, and mean hydrodynamic size) and their coagulation processes as a function of pH and ionic strength were studied for all the bentonites (and a Spanish saponite). No clear differences observed.
- Erosion experiments with natural bentonites under the same conditions for comparison. The max quantity of mass detached (DW) was determined.
- Highest mass of detached colloids: Febex bentonite, slightly lower in MX-80 and Ibeco clay and lower for the other clays. In this comparison, smectite content (higher in the Febex case), rather than to the exchangeable Na (higher in MX-80 or Khakassia), seems to be important for erosion.



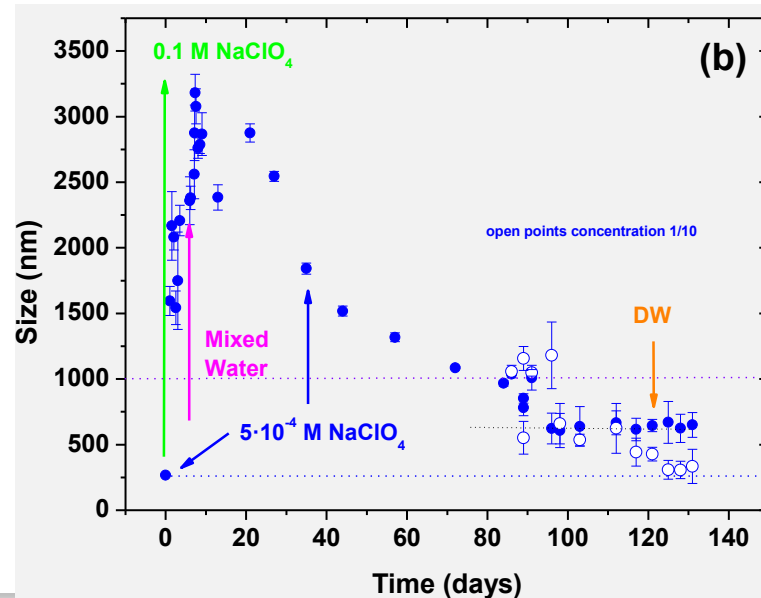
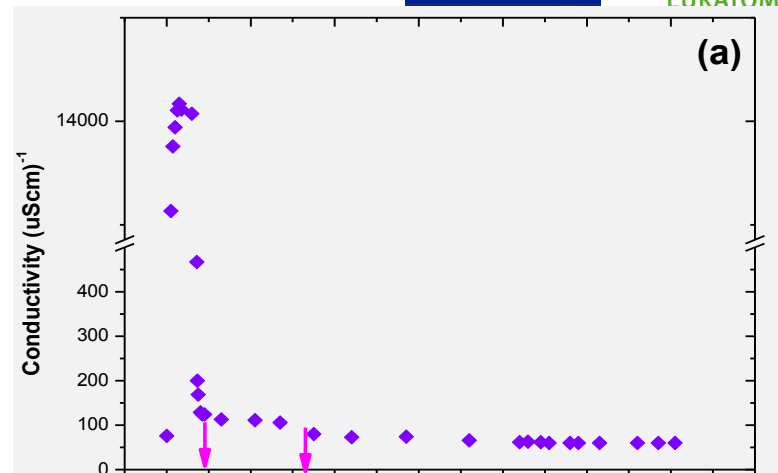
- Bentonite erosion favored if chemical conditions favor colloid stability: in an “aggregated” system formation and erosion of particles of colloidal size are not expected.
- To evaluate the (ir)-reversibility of the coagulation process and its kinetic, when the conditions of the aqueous solution are modified to conditions favorable to stability, is important.
- In the highly saline conditions of Äspö waters, colloid generation is almost negligible, but intrusions of diluted water (glacial melt water) may induce disaggregation.
- Aggregation/disaggregation processes produced by the changes in ionic strength in smectite and illite were be studied by PCS and single particle counting (SPC).

Disaggregation experiment (1)

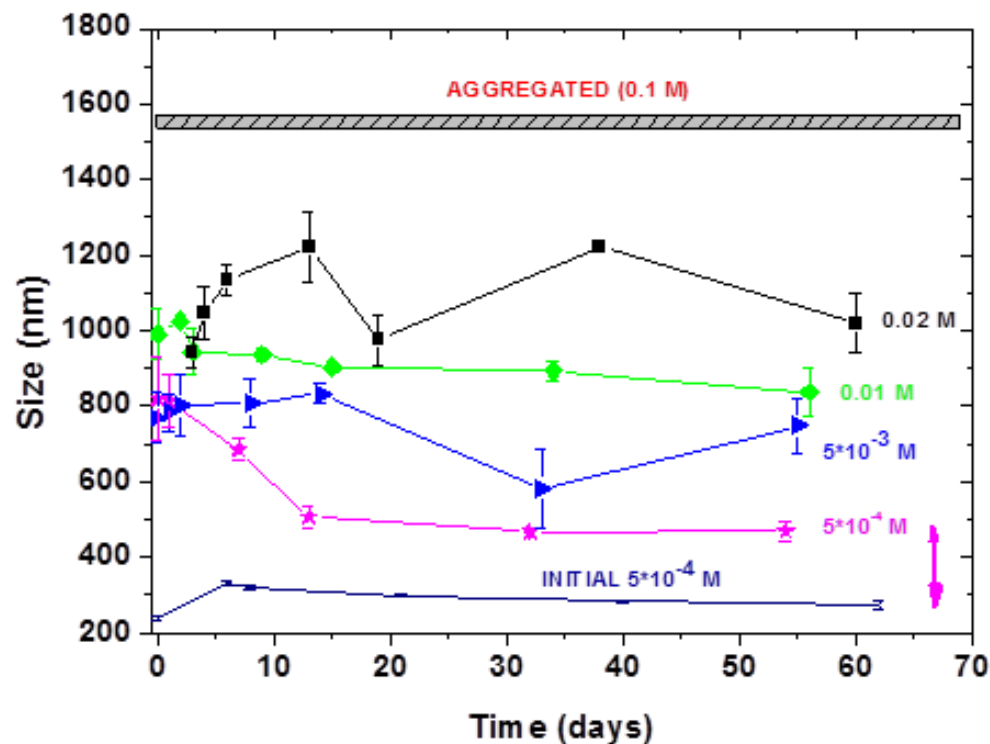
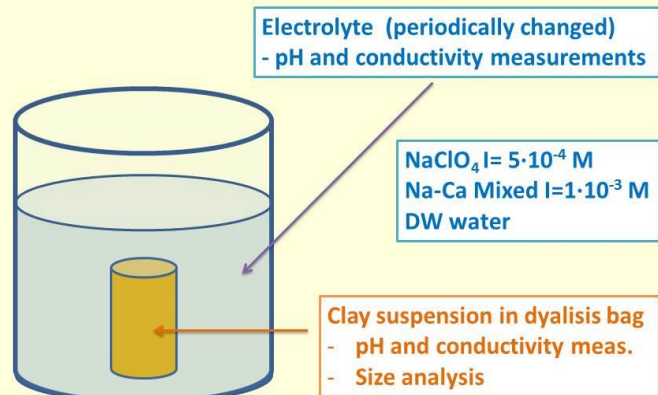


PCS measurements

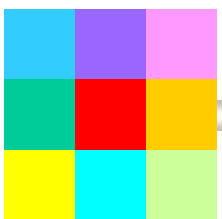
Results of the disaggregation experiment with dialysis bags with Na-Febex smectite. (a) conductivity and (b) colloid mean size measurements. pH between 5.5 and 6.5



Disaggregation experiment (1)

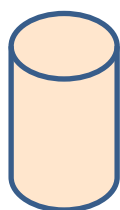


Average size measured by PCS on FEBEX Na-smectite in: initial, aggregated and disaggregated samples (0.02, 0.01, $5 \cdot 10^{-3}$ and $5 \cdot 10^{-4}$ M) as a function of time.

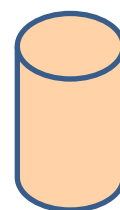


Disaggregation experiments (2)

“Disaggregated”
 $1 \cdot 10^{-4}$ M
in NaClO_4
Reference



“Aggregated”
 $1 \cdot 10^{-1}$ M
in NaClO_4



“Dilutions”

$1 \cdot 10^{-1}$ M - Reference

$1 \cdot 10^{-2}$ M

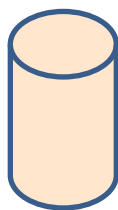
$1 \cdot 10^{-3}$ M

$1 \cdot 10^{-4}$ M

in NaClO_4

SPC measurements

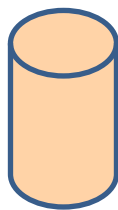
$1 \cdot 10^{-4}$ M



$1 \cdot 10^{-2}$ M



$1 \cdot 10^{-1}$ M

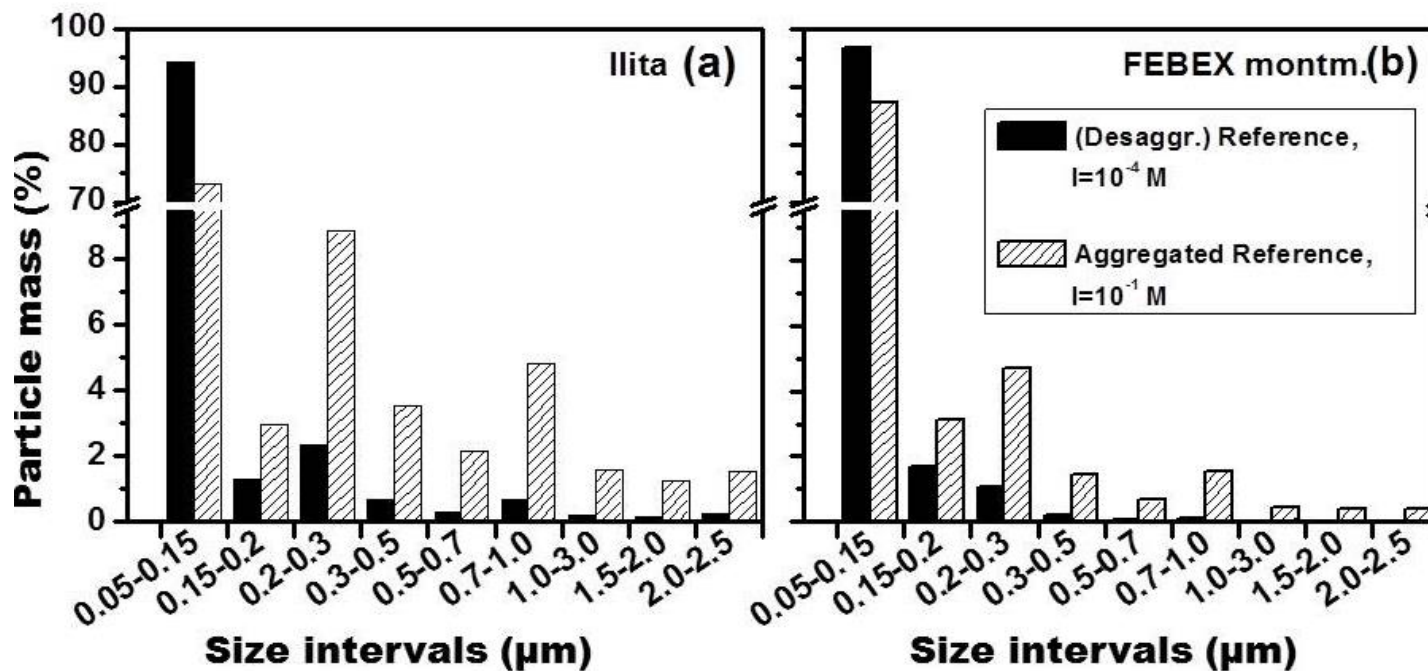
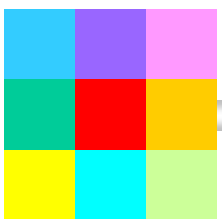


$1 \cdot 10^{-2}$ M



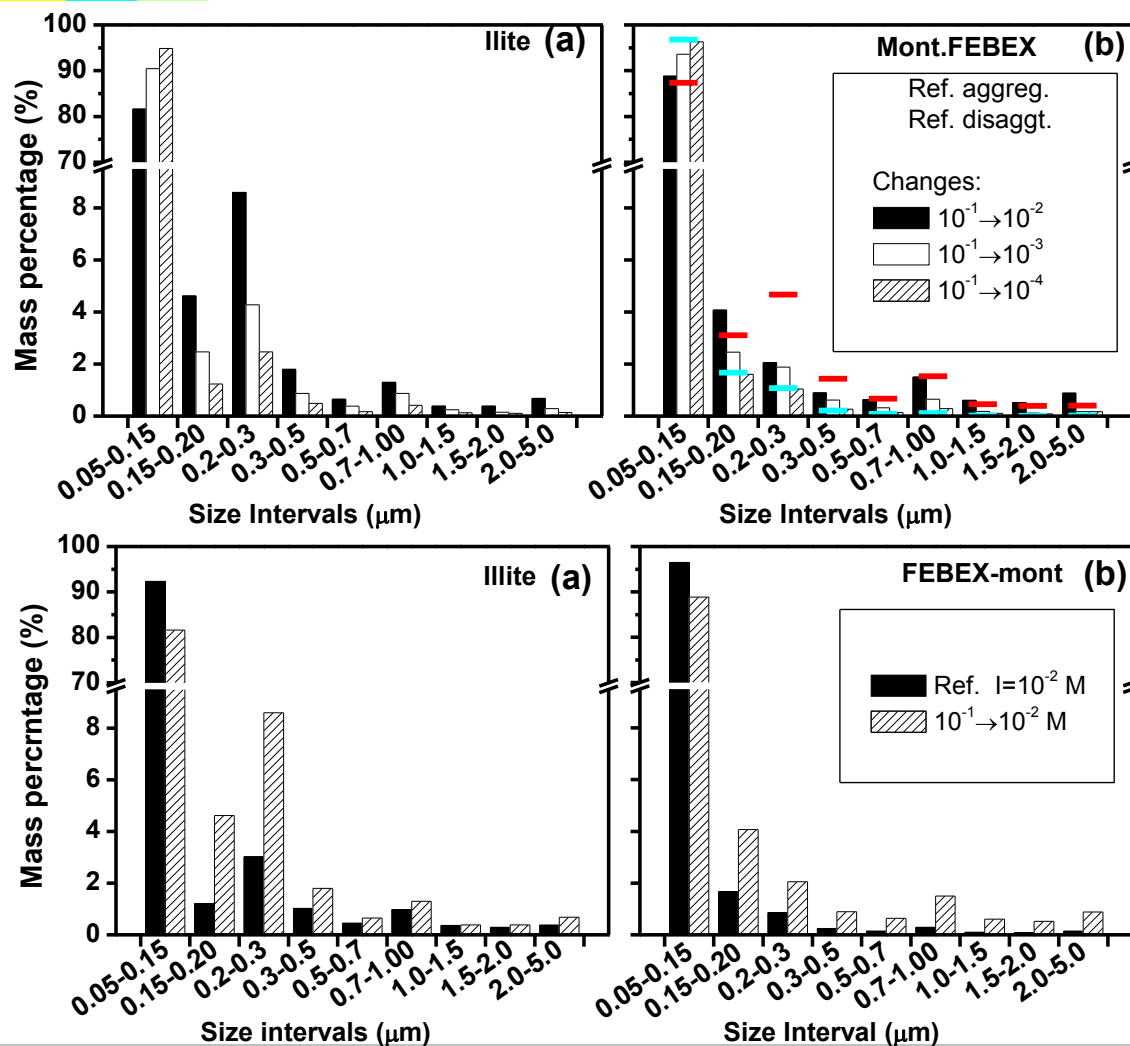
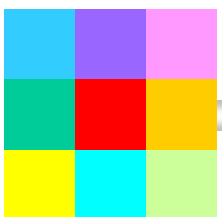
Are they equivalent ?

SPC measurements



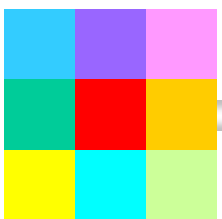
Large number of particles of smallest size exist even in “aggregated” conditions, especially in smectite. SPC ?

Size distribution of (a) Na-illite and (b) Na-FEBEX smectite at $I=10^{-1}$ M (aggregated reference) compared to that of $I=10^{-4}$ M (disaggregated). pH between 6 and 7.

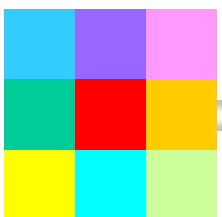


From $I = 0.1$ M to different ionic strengths (pH 6-7). Red line represent the values previously obtained of the “aggregated” reference sample (0.1 M) and the cyan line those for the “disaggregated” one ($1 \cdot 10^{-4}$ M).

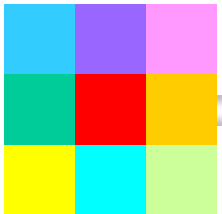
Comparison sample prepared from $I = 1 \cdot 10^{-4}$ M to $I = 10^{-2}$ M and the other from $I = 0.1$ M to $I = 1 \cdot 10^{-2}$ M (previously aggregated).



- The disaggregation process of illite and smectite clays has been shown to be not completely reversible: the aggregation process is very rapid (minutes) but the kinetic of disaggregation, until reaching a complete disaggregated state, largely depends on the initial conditions of the experiments.
- Recovery at the long-term.
- Very favorable electrolytes like deionized water accelerate the process. In mildly saline electrolyte hysteresis is observed. The concentration of colloids is also another point to be taken into account. The disaggregation process faster in more diluted suspensions (PCS –SPC).
- The reversibility of the aggregation for changes in pH has to be investigated as well as the role of divalent ions on disaggregation kinetics.

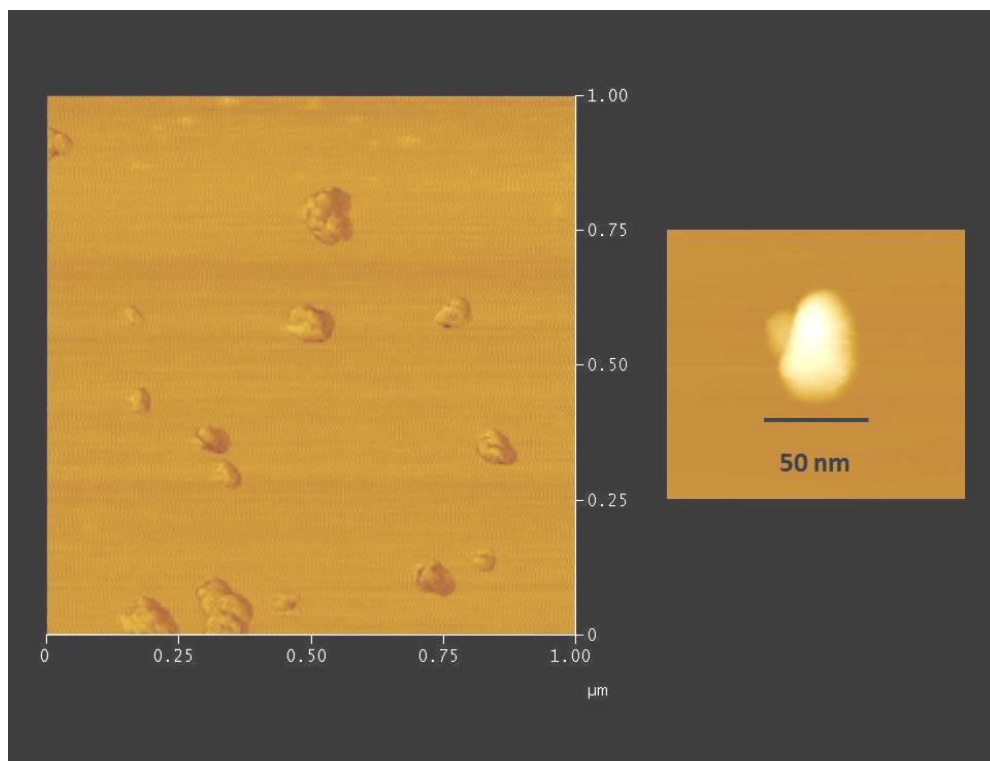


- “Stable” system: (1) low ionic strength ($\leq 1 \cdot 10^{-3}$ M) and (2) pH far from the point of zero charge (pH_{PZC}).
- Critical coagulation concentration, CCC, pH_{PCZ} or pH_{IEP} are adopted to define the stability of colloidal systems.
- Presence of sorbable usually not taken into account. In particular, the effect of inorganic anion adsorption on colloid stability is scarcely investigated.
- We evaluated the effects of the adsorption of inorganic anions on Al_2O_3 oxide (similar behaviour of edge sites in clays) and bentonite stability.



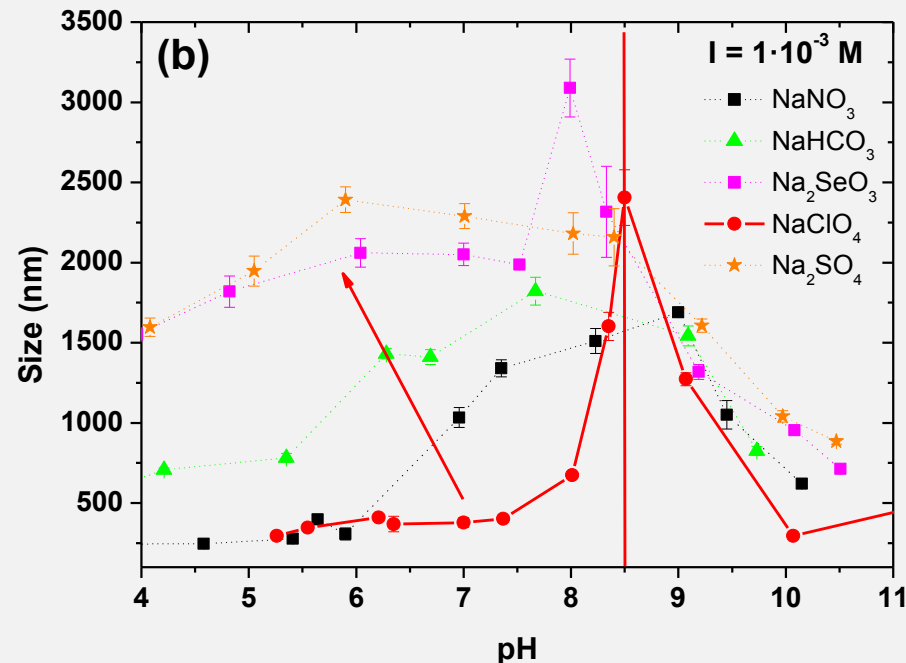
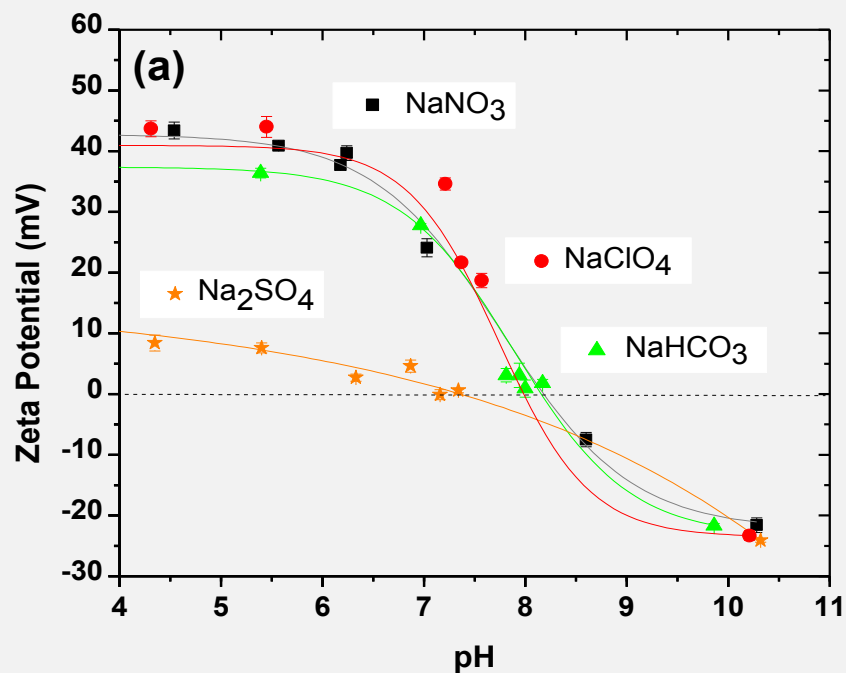
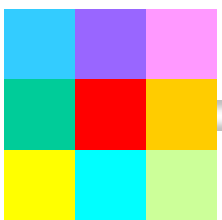
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Effects of inorganic anions on colloid stability

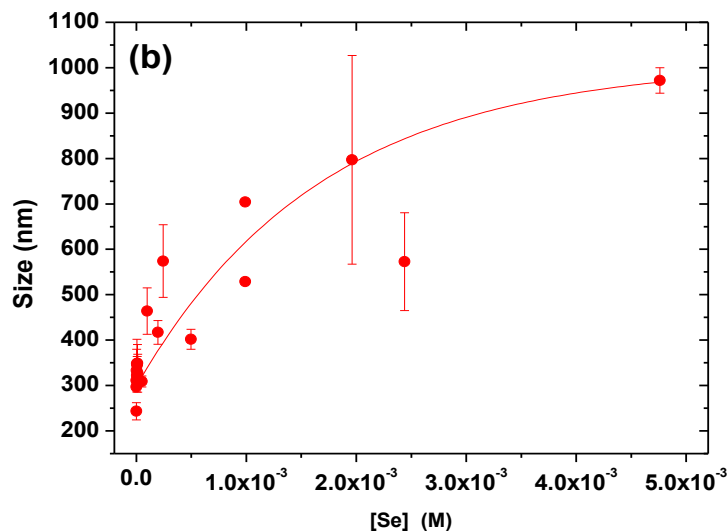
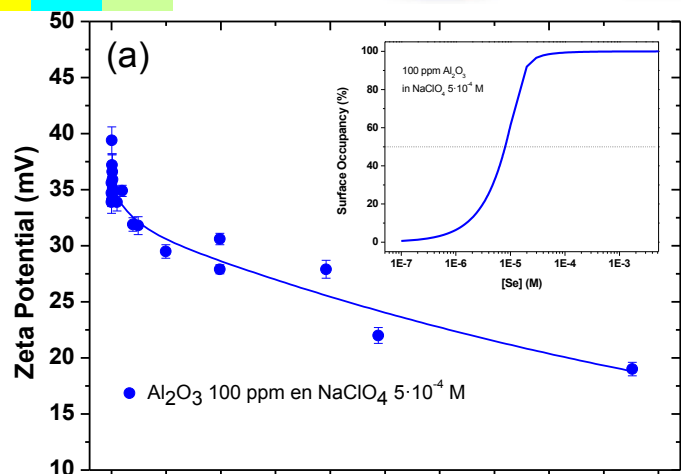


AFM : 50 nm particles
PCS : 250 nm mean size

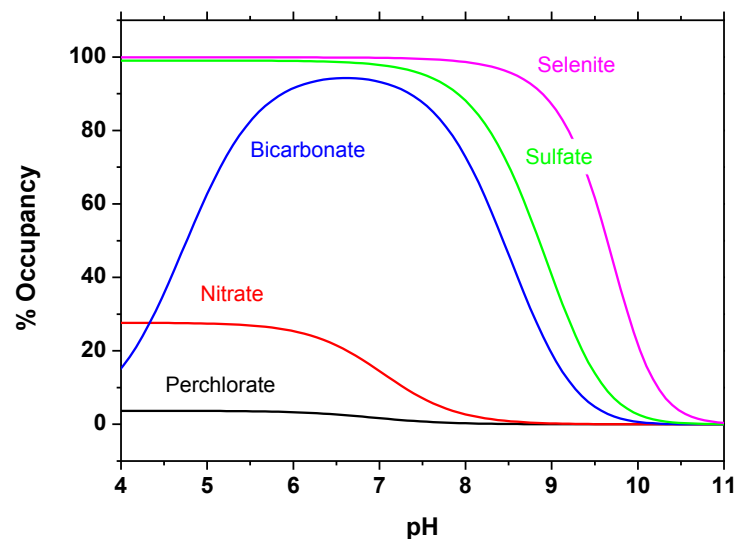




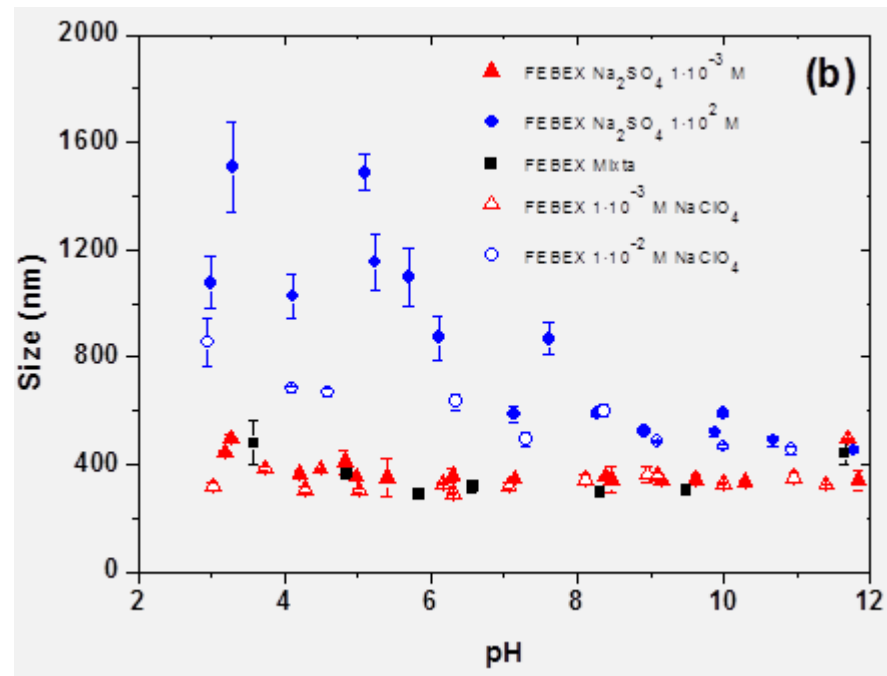
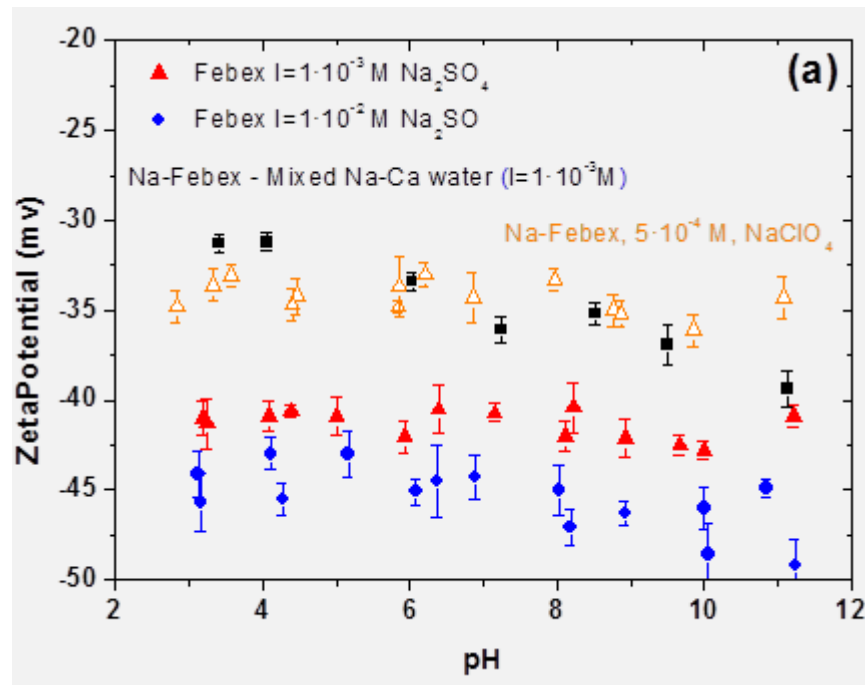
a) Zetapotential and (b) mean size of alumina as a function of pH suspended in different electrolytes at $I=1 \cdot 10^{-3} \text{ M}$. Stability ?



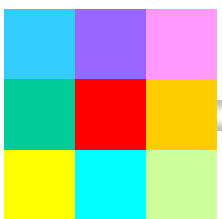
(a) Zetapotential and (b) mean size of alumina NPs suspended in NaClO_4 $5 \cdot 10^{-4}$ and pH 4.5 as a function of the $[\text{Se(IV)}]$ concentration. In the inset: alumina surface coverage.



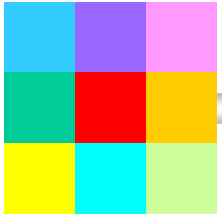
Calculated surface occupancy, for each anion, as a function of the pH after the adsorption.



(a) Zetapotential and (b) mean size of Na-FEBEX smectite prepared in Na₂SO₄, NaClO₄ or mixed water.



- Highly sorbing anions like selenium and sulphate affect Al_2O_3 colloids stability at relatively low concentrations ($1 \cdot 10^{-4}$ M). At ionic strength of $1 \cdot 10^{-3}$ M and below $\text{pH} < 7$ a different aggregation state is observed depending on the electrolyte ($\text{ClO}_4^- < \text{NO}_3^- < \text{HCO}_3^- < \text{SO}_4^{2-} \sim \text{SeO}_3^{2-}$).
- This aggregation state is related to the adsorption of the anion and the sorbate surface coverage.
- Upon anion adsorption, particles aggregation was evident, but a clear change in ζ -potential, was only observed with very high surface occupancies. Zetapotential is not sensitive for assessing stability.
- Na-smectite prepared in Na_2SO_4 present more negative zetapotentials. In spite of the higher (in absolute value) zetapotential value, the smectite was slightly less stable at acidic pH in the presence of the sulphate. Sorption of sulphates on the edge $=\text{SOH}$ sites of the smectite, decreases the edge-edge repulsions (?). Under alkaline conditions, the results are quite similar (in the presence or absence of sulphate).



BELBaR



Thanks for your attention !!