Update on erosion experiments at CIEMAT

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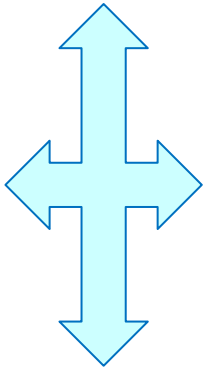
CIEMAT laboratory experiments

Benchmark tests results — **Nanocor®** ⇔ **FEBEX**

EROSION Experiments

Clays Characterization COMPARISON PROCESSES UNDERSTANDING



Laboratory prepared colloids Characterization: Size, charge, stability

Stability

- Mixtures behavior

EROSION In-situ FEBEX site – GTS (POSTER)

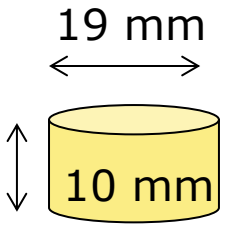
Benchmark Set-Up

Erosion Benchmark test (configuration Tim Schatz)

- **Comparison:** **Nanocor®: Na purified montmorillionite**

  FEBEX (Spain): Ca- Mg bentonite

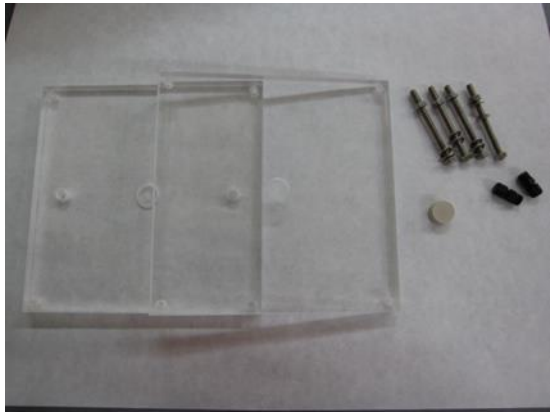
- **Compacted clay at 1400 kg/m^3**
- **Pre-saturated in NaCl 10^{-3} M**

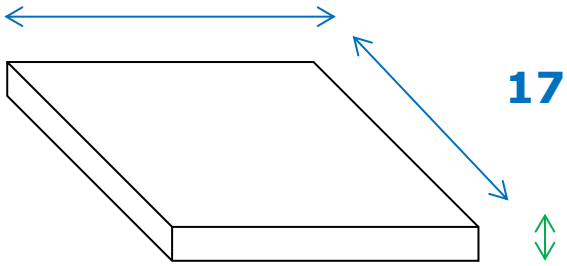


Nanocor®: 4.64 g ; H 16.9%

FEBEX: 4.52 g; H 13.9%

Artificial fracture

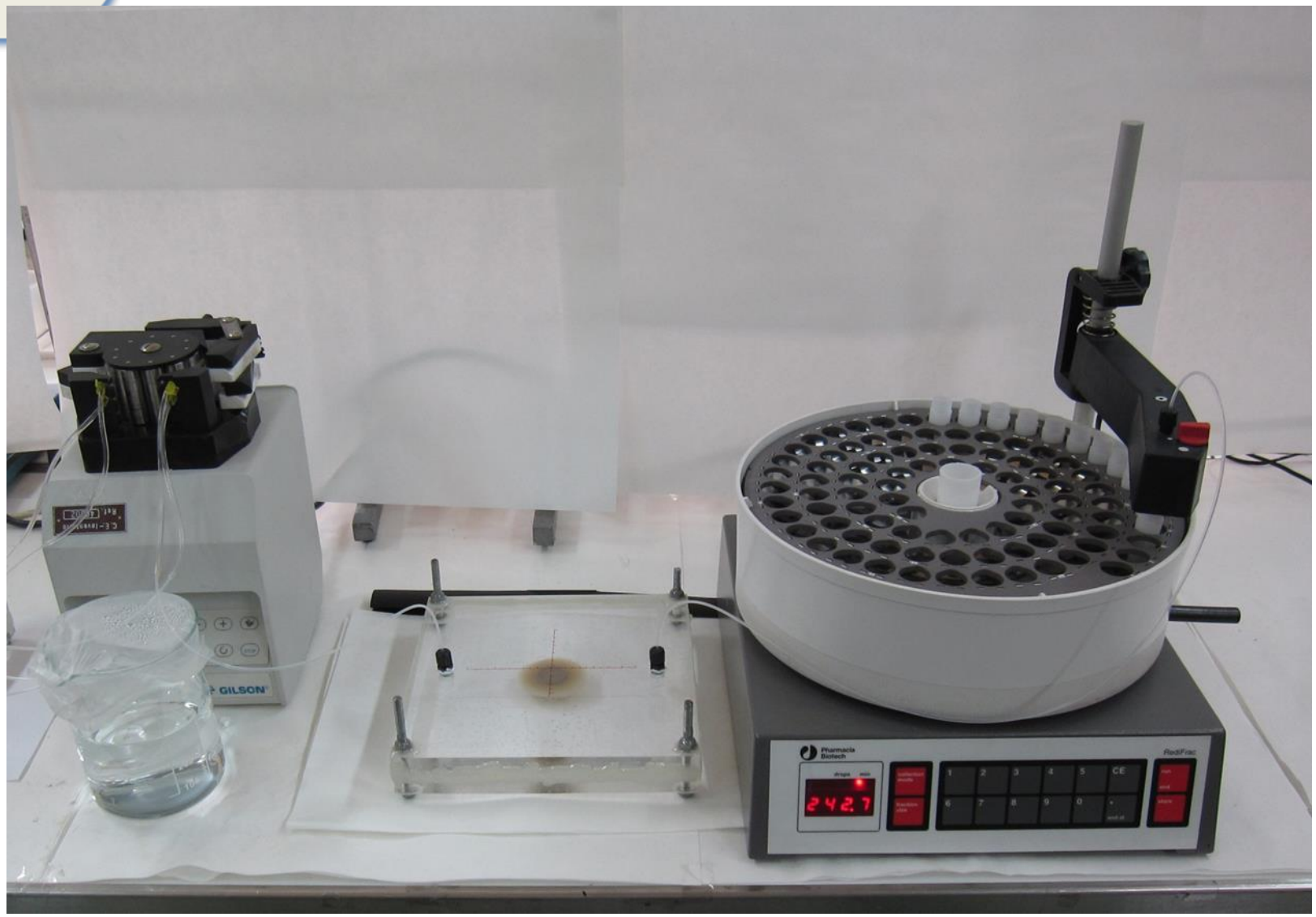




17 x 17 cm^2

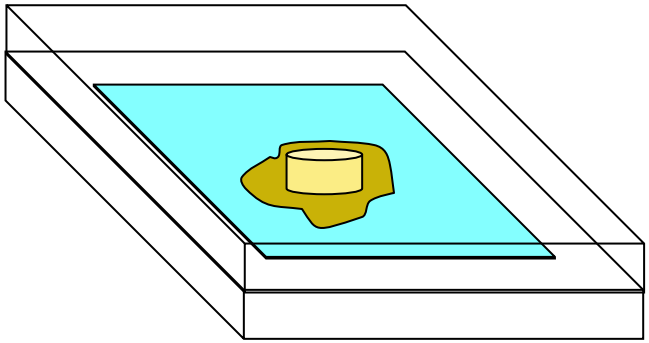
Aperture: 0.1 mm

Benchmark Set-Up



Benchmark Set-Up

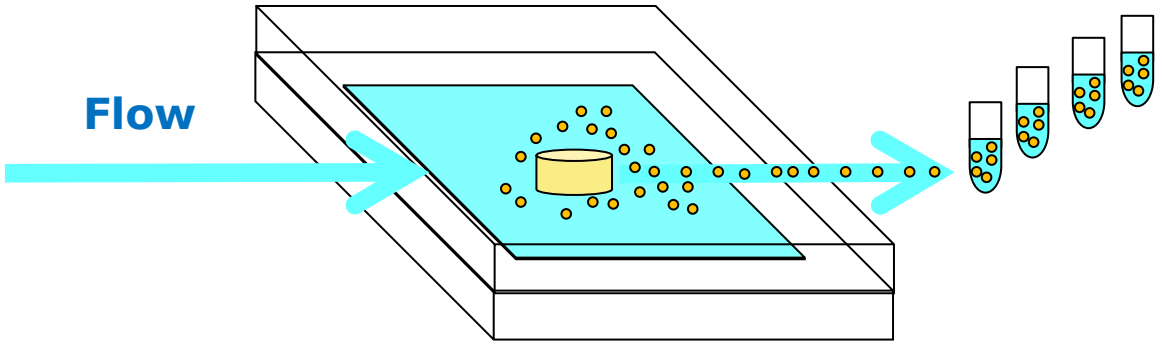
Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)



- **Pictures**
- **Extrusion distance as a function of time**
- **Diameter increment (t)**

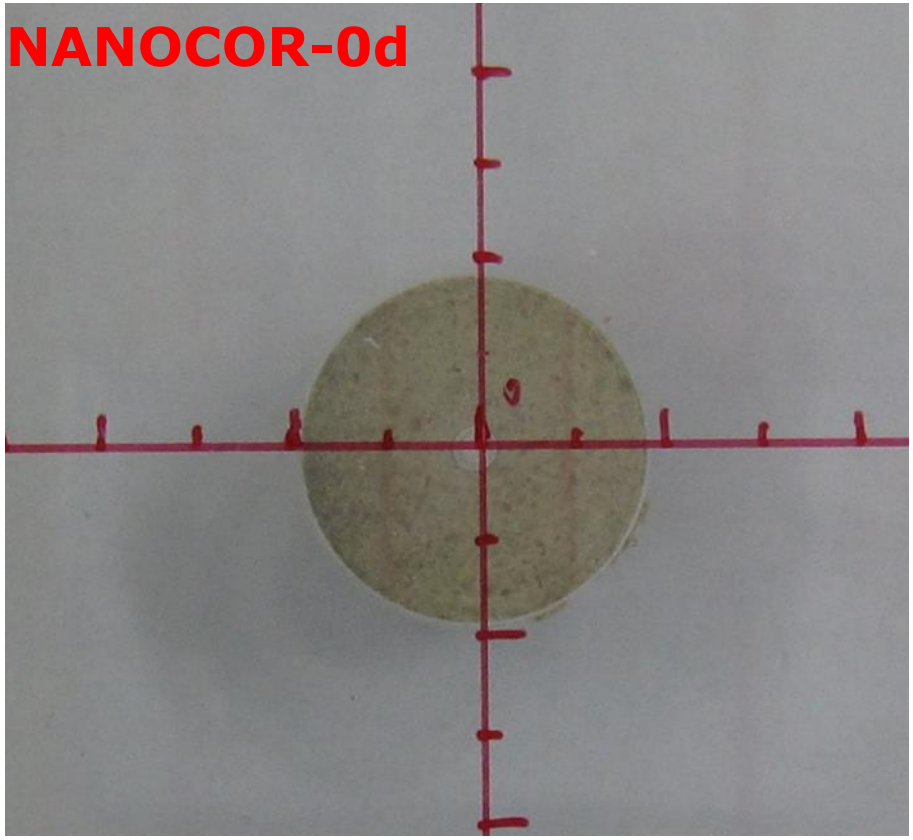
Phase 2: Low Flow conditions (14 days) 10^{-6} m/s with NaCl 10^{-3} M

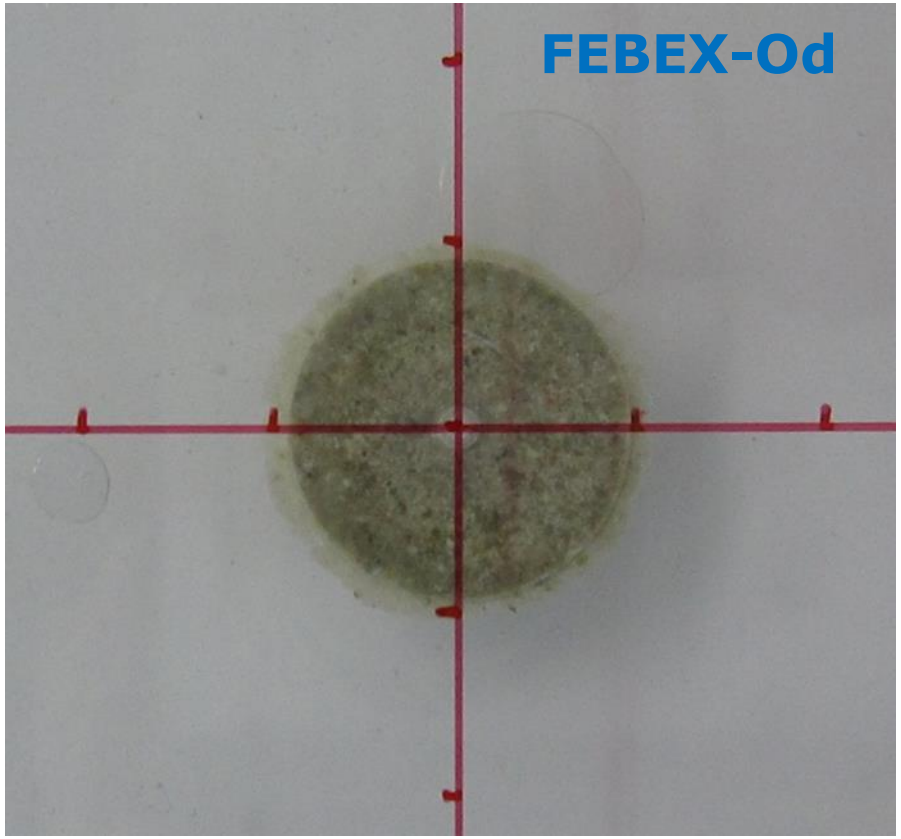
Phase 3: High Flow conditions (14 days) 10^{-4} m/s



Benchmark Test Results: Ph1

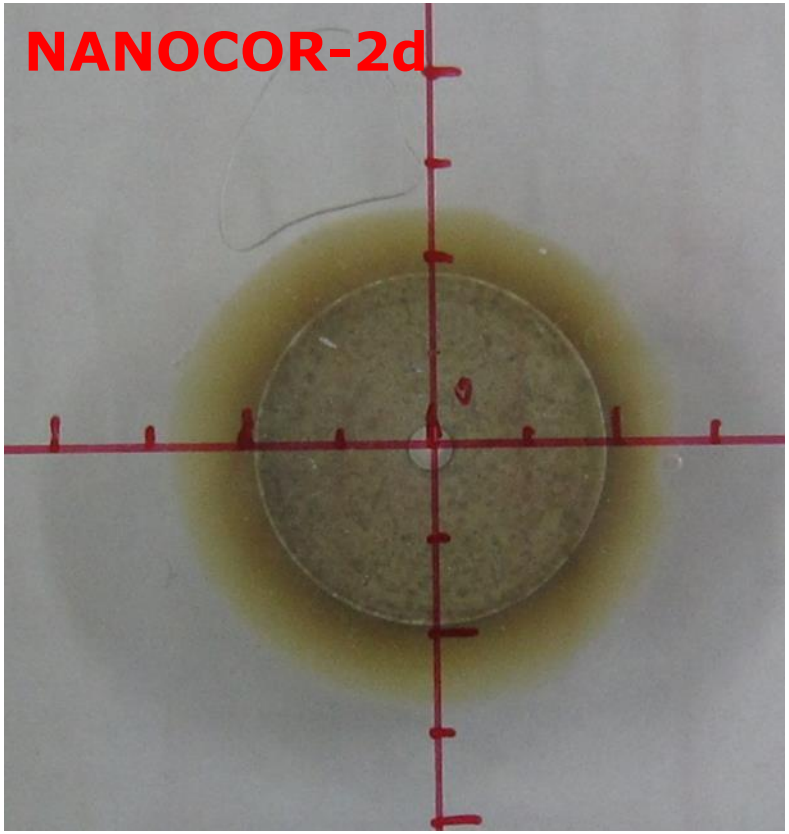
Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

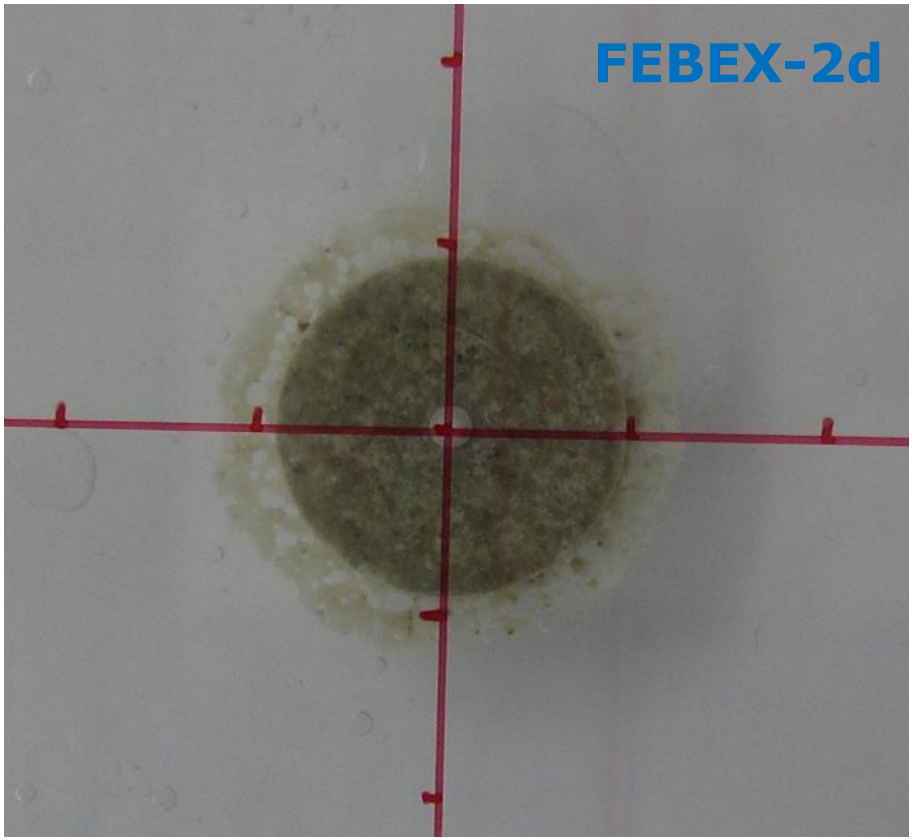




Benchmark Test Results: Ph1

Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

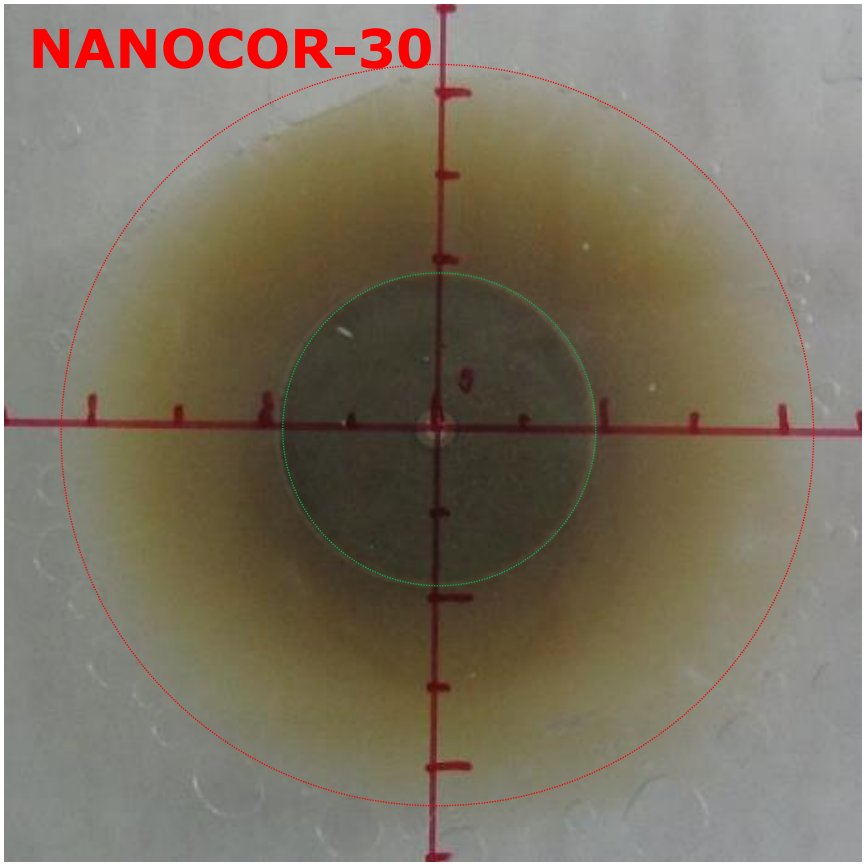


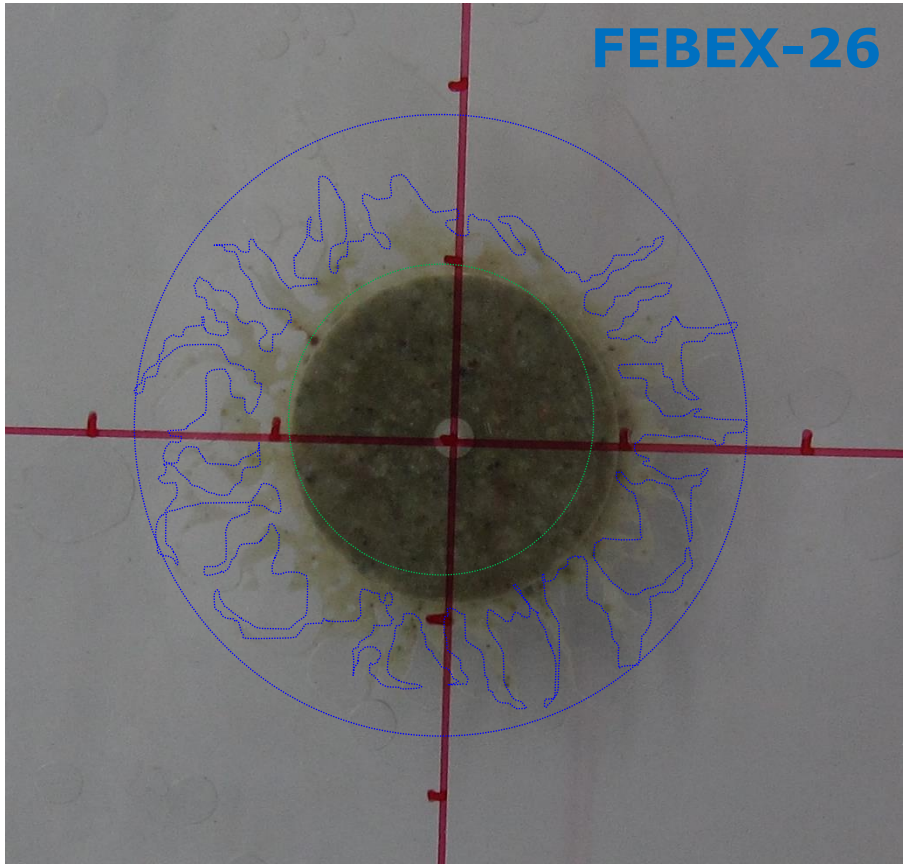


Different gel characteristics

Benchmark Test Results: Ph1

Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)



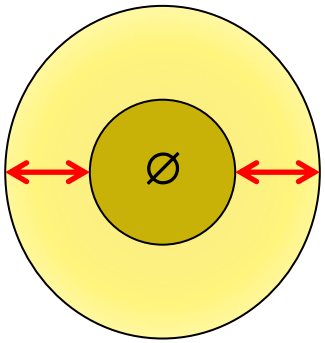


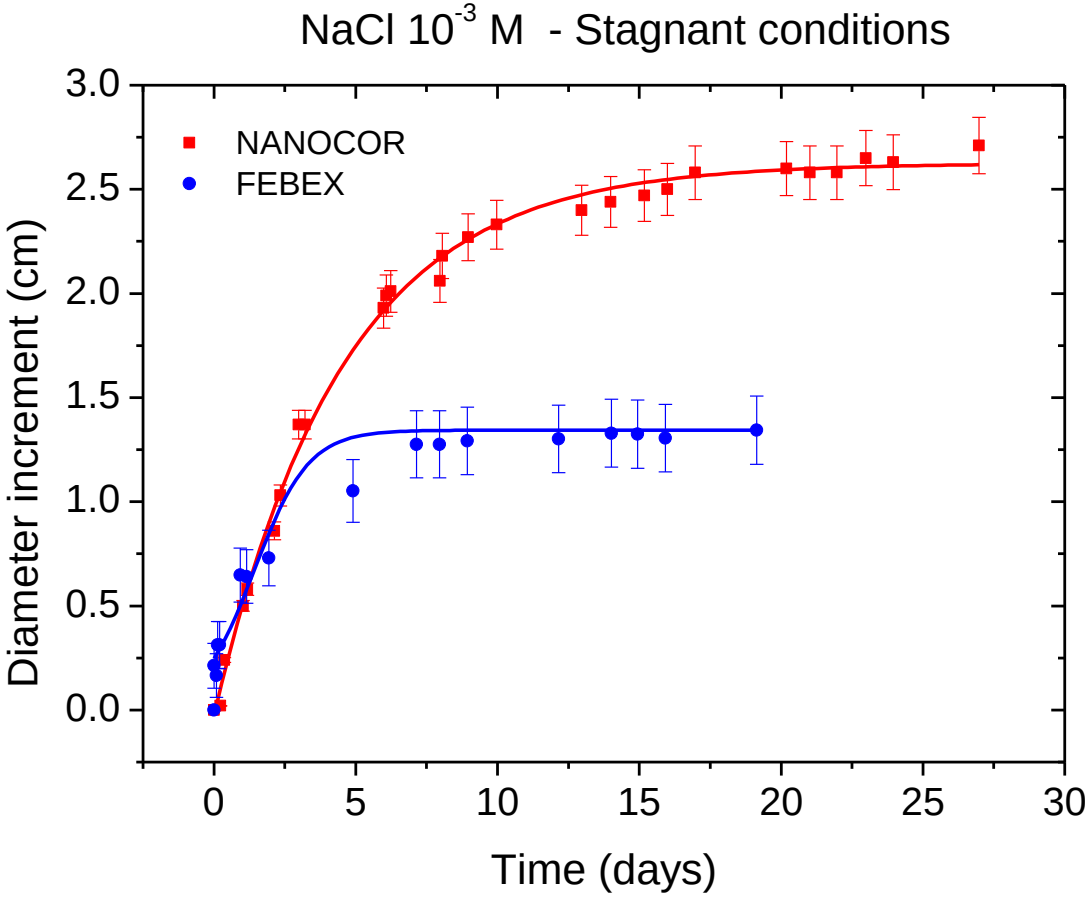
Different extrusion behavior

Benchmark Test Results

Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

Extrusion distance *Diameter increment*

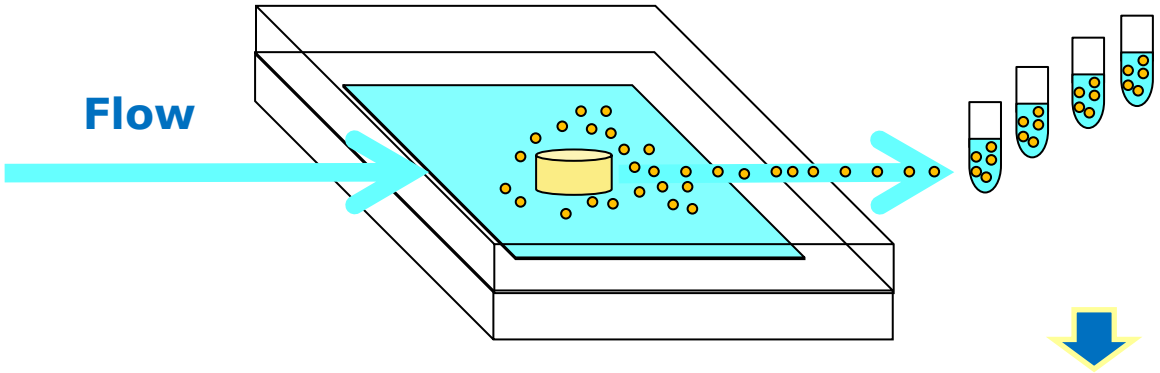




Benchmark FLOW conditions

Phase 2: Low Flow conditions (14 days)

Phase 3: High Flow conditions (14 days)

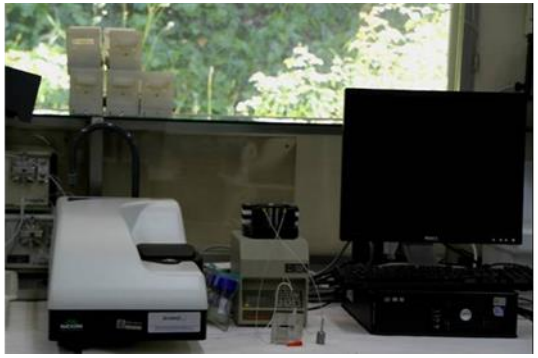


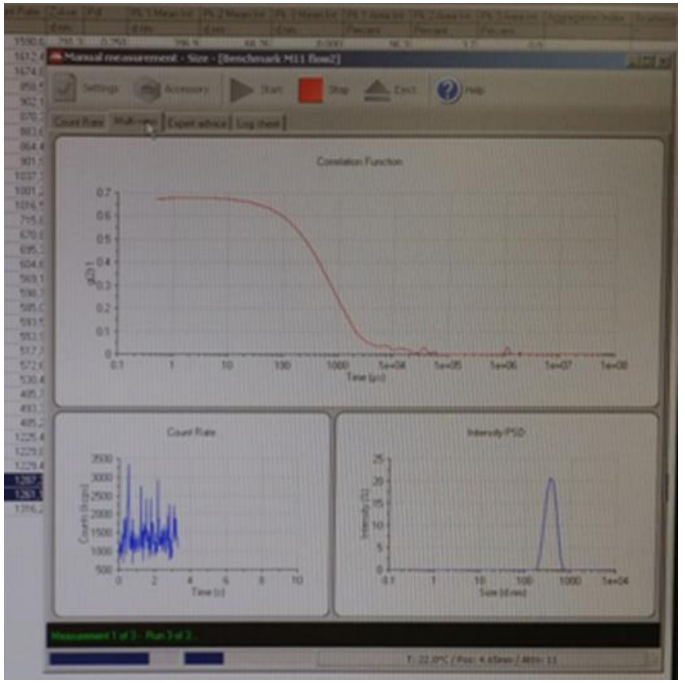
- **Periodical sampling of eluted water**
- **Analyses of mass loss (mobilised)**

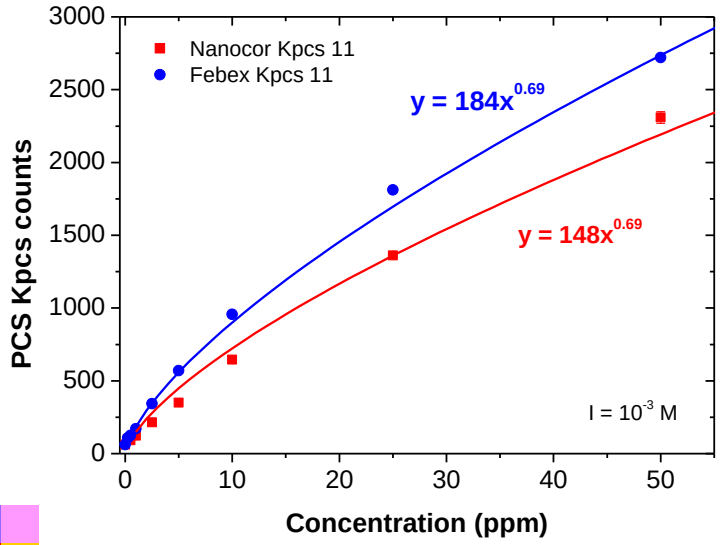
- **Photon Correlation Spectrometry (Concentration, Size)**
- **Turbidity analyses (concentration)**
- **FINAL POST MORTEM (extruded mass - mass balance)**

Benchmark FLOW conditions

- **Photon Correlation Spectrometry (Concentration, Size)**



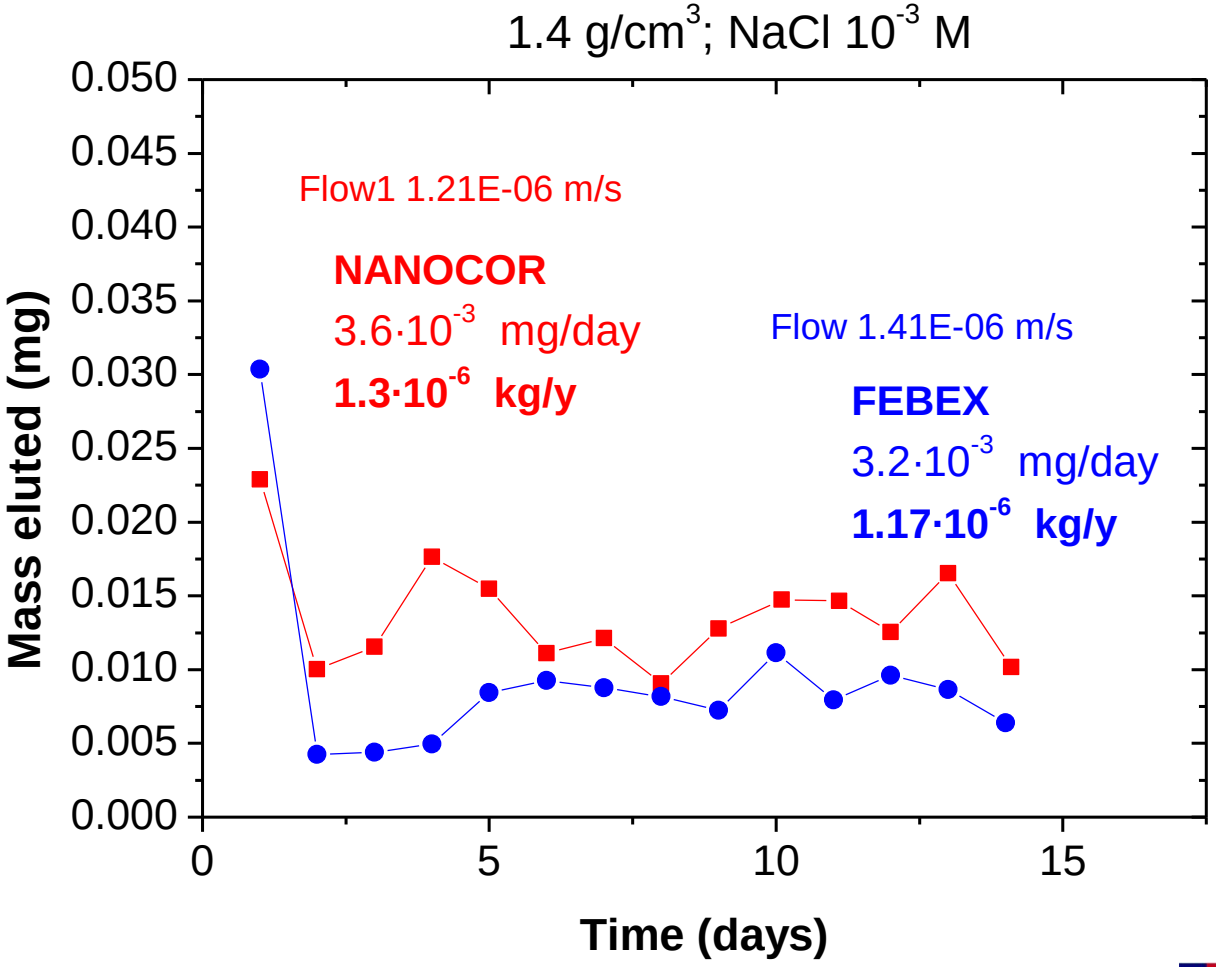




- **Calibration curves with laboratory prepared colloids in same electrolyte**

Benchmark Test Results - Flow1

Phase 2: Low Flow conditions (14 days)

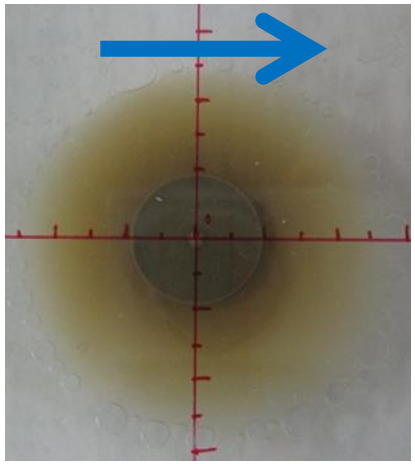


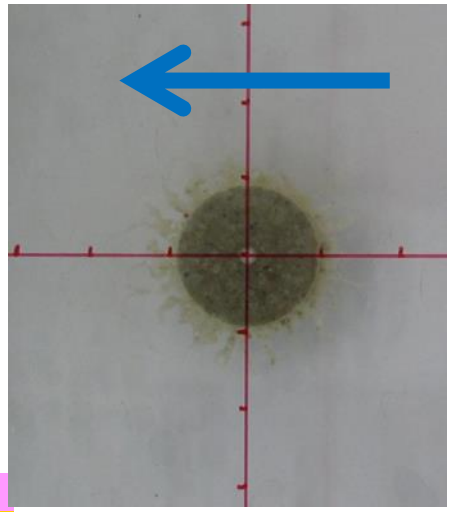
Bentonite exposed surface not corrected: S = 6 mm²

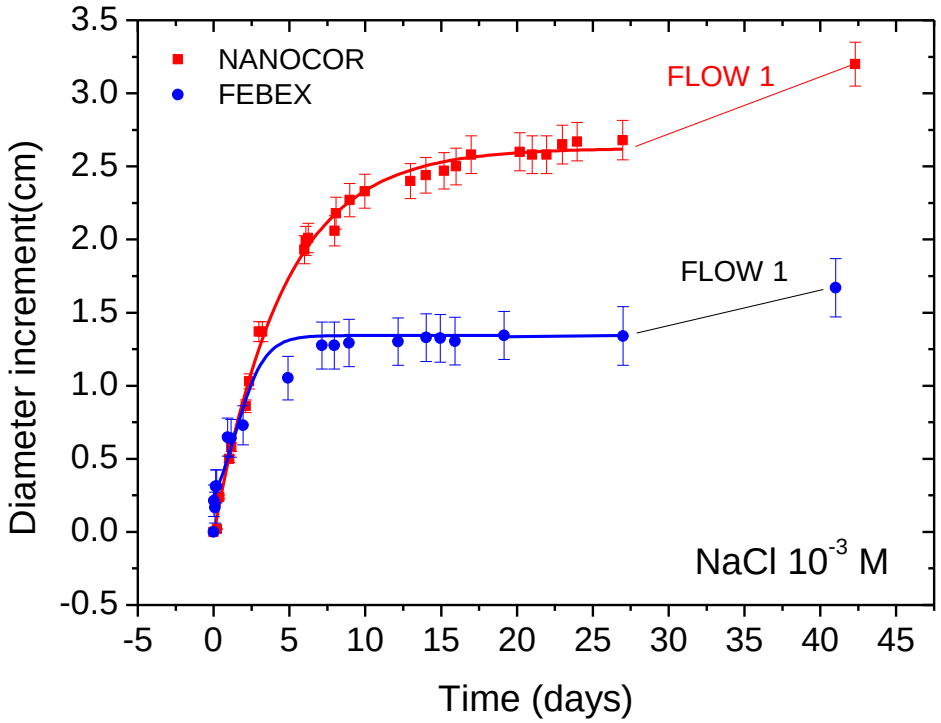
Benchmark Test Results - Flow1

NANOCOR - 30+15 days

Extrusion increment (30 + 15 days)

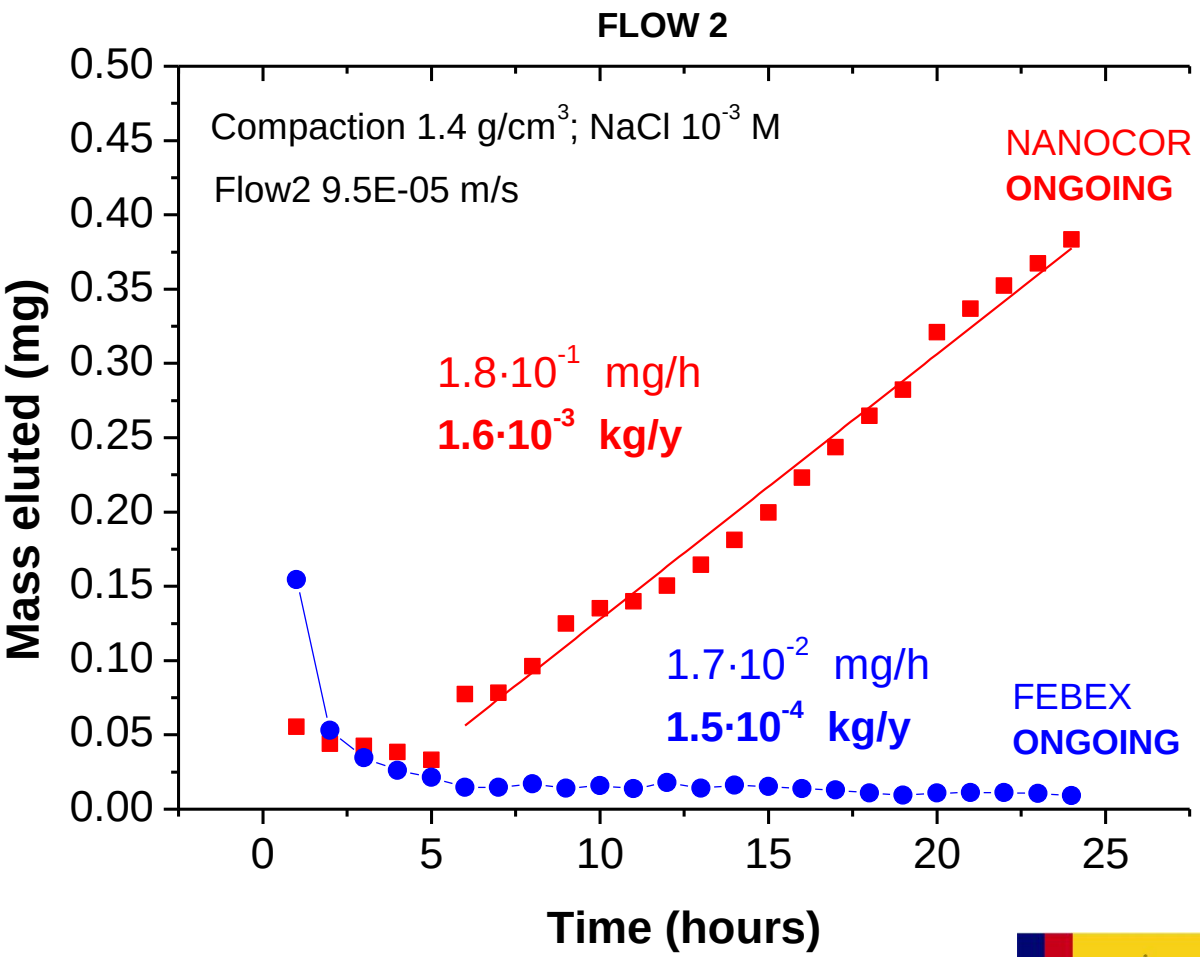






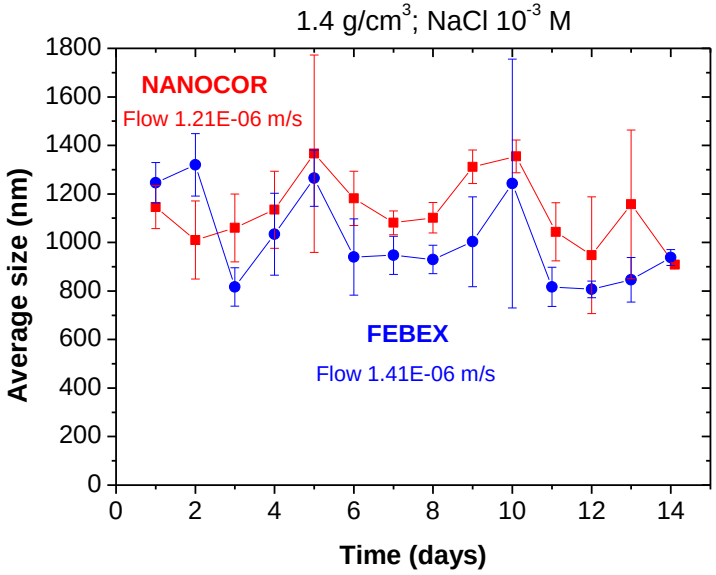
Benchmark Test Results – Flow 2

Phase 2: High Flow conditions (1 day – SO FAR)

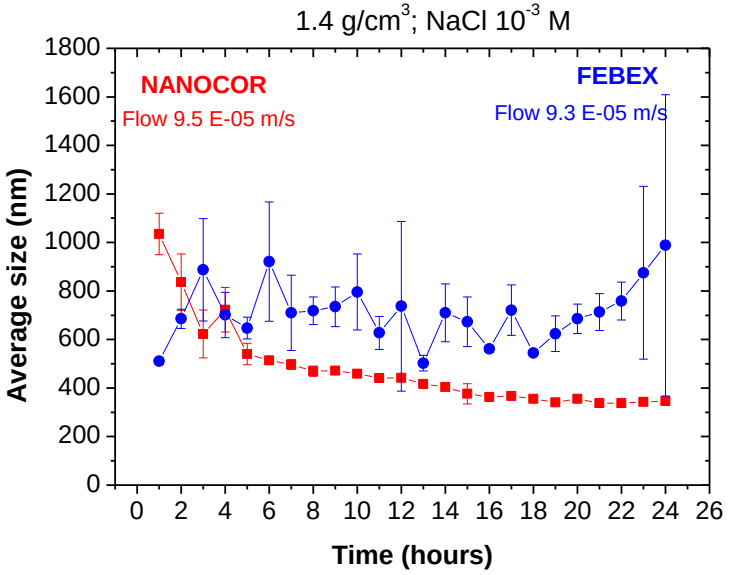


Benchmark Test Results – Size

Low Flow conditions (15 days)



High Flow conditions (1 day – SO FAR)

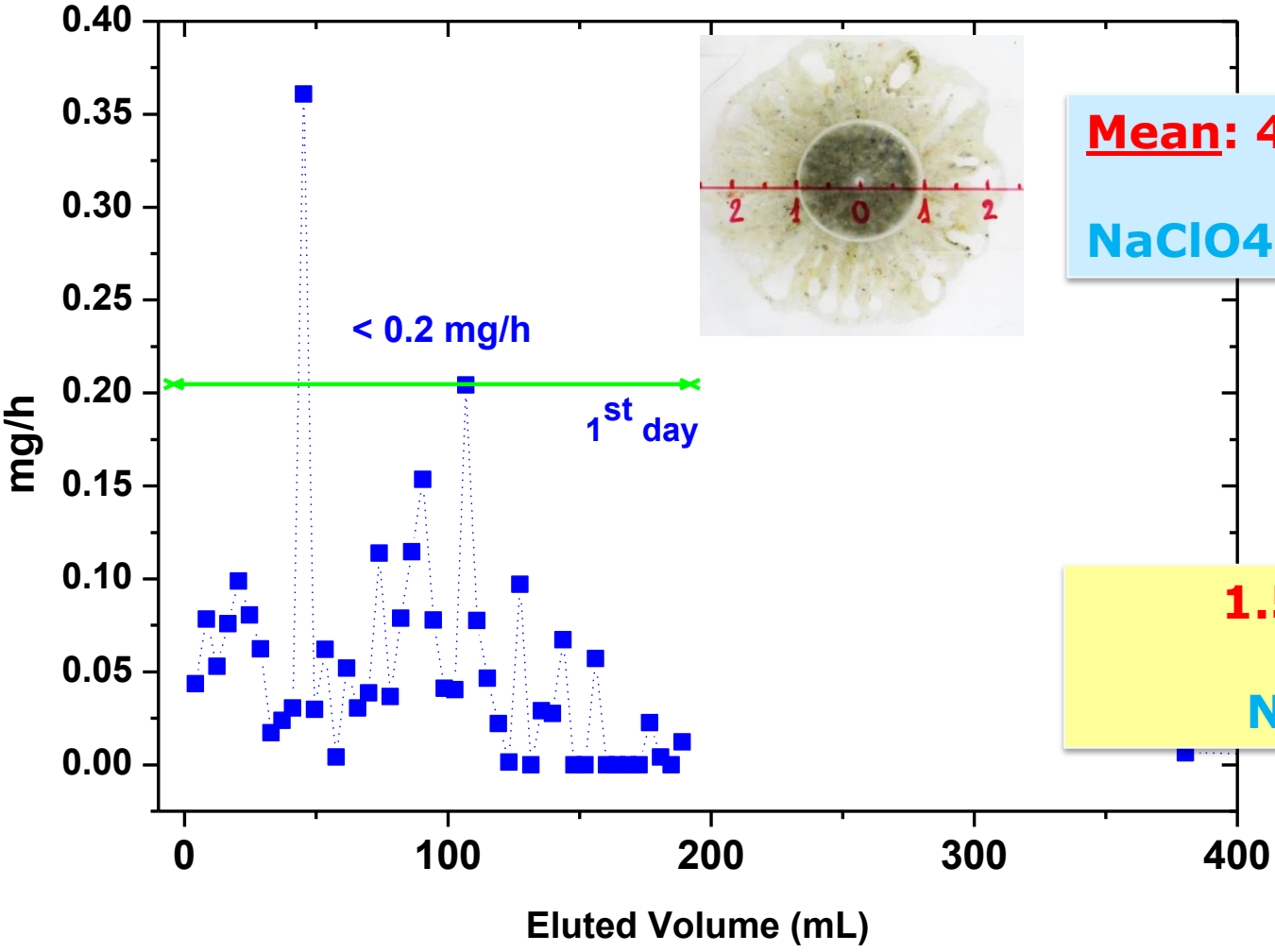


Initially bigger particles are mobilised

Colloids are released

Former Results (NaClO4 5·10^{-4} M)

High Flow conditions: FEBEX clay



Mean: 4.8E-04 Kg/y

NaClO4 5·10-4 M

1.5E-04 Kg/y

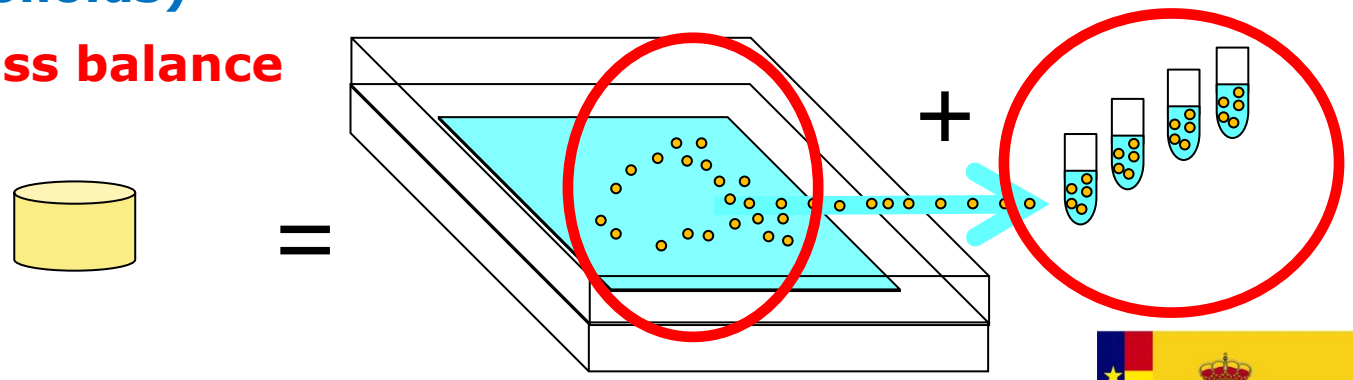
NaCl 10^{-3} M

Benchmark Test Results

- **Erosion - extrusion behavior of natural FEBEX is not fully comparable to that of purified Nanocor (Na-bentonite).**
- **At low flow rate erosion is comparable, but lower at higher flow.**
- **Colloidal particles are mobilized (size < 1 um).**

TO DO:

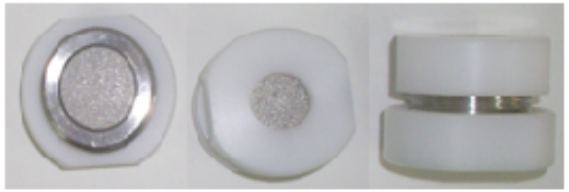
- **To finish high flow rate phase**
- **Turbidity measurements vs PCS measurements**
- **Post mortem analyses: EXTRUDED clay (+ mobilized particles /colloids)**
- **Mass balance**



Static erosion experiments

✓Static: Diffusive conditions

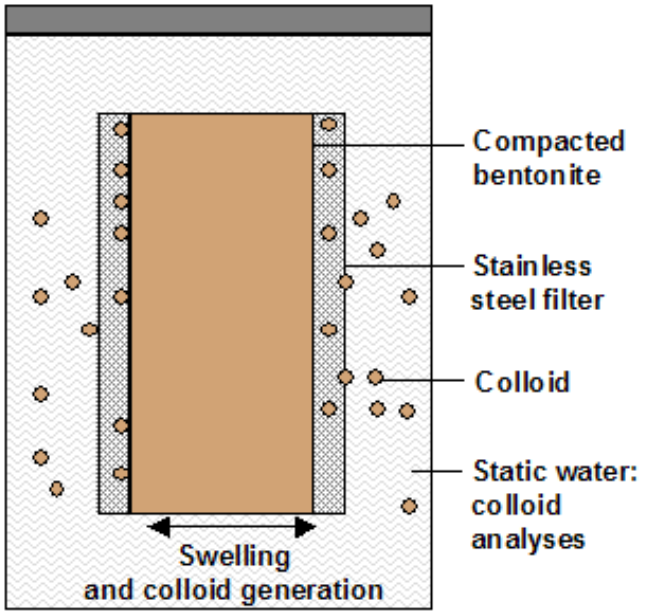
(a)



4 g clay
S = 3.5 cm^2
200 mL

FILTER PORE 100 um

(b)



Known processes

- ✓ Chemical effects (Na, Ca, ionic strength
- ✓ Homoionic clays,
- ✓ dry density
- ✓ etc

FEASIBLE SYSTEM FOR COMPARISONS

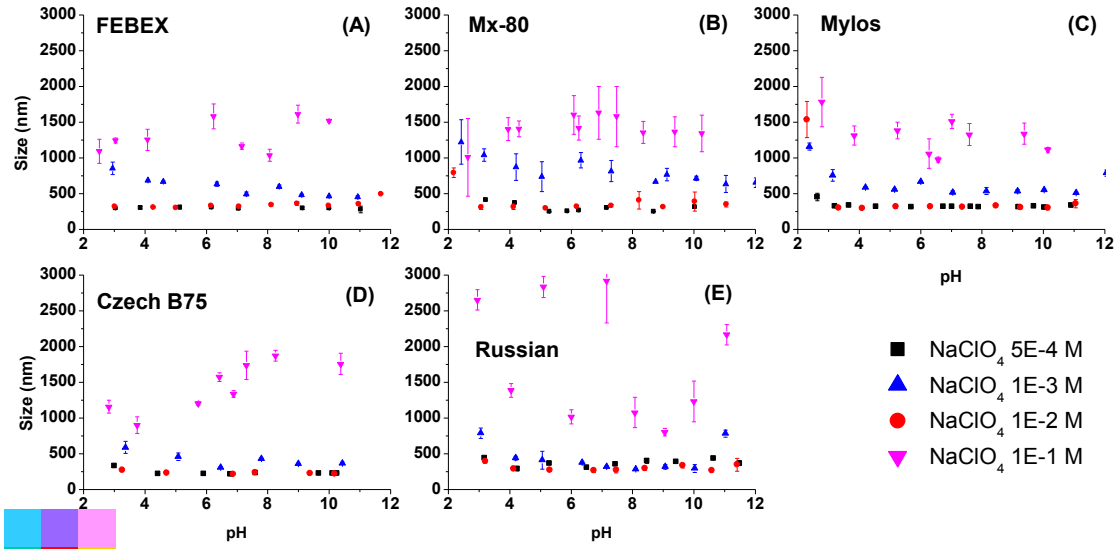
- Deionised water: Most favourable conditions.
- Quantitative analyses of contact electrolyte.
- **Photon Correlation Spectrometry.**
- Colloid concentration and size distribution

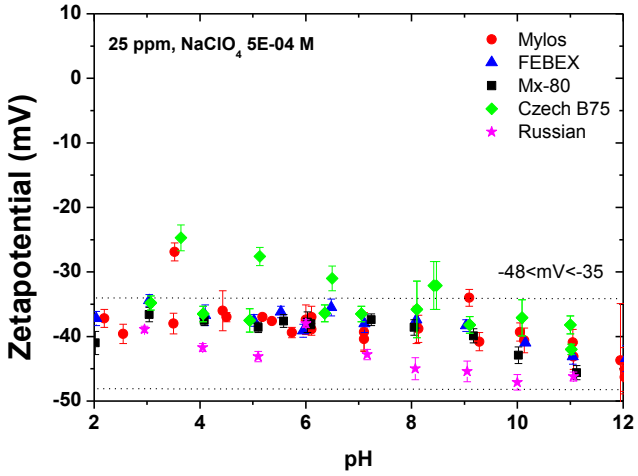
Natural bentonites

Data		MX-80	Febex	Ibeco	B75	Khakassia
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

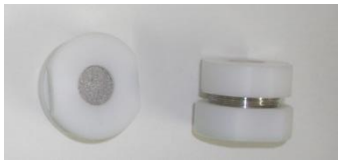
Laboratory prepared colloids: Size and charge

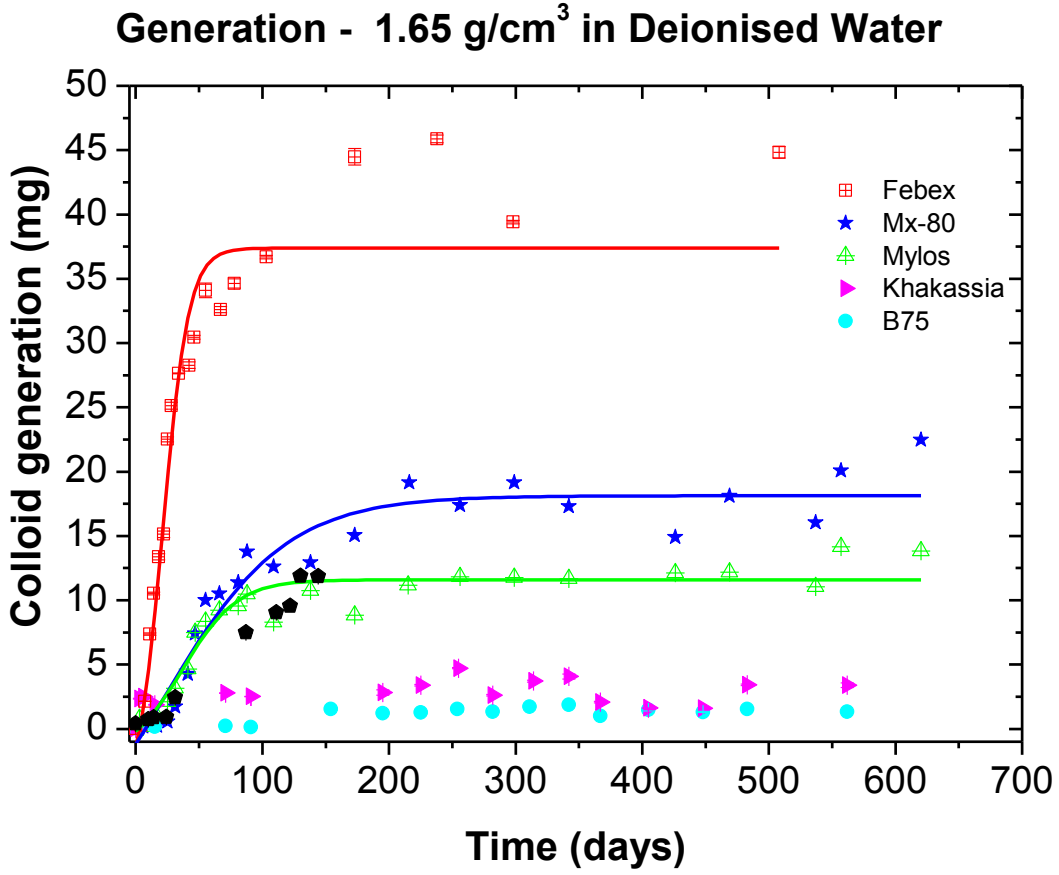
Different clays exhibited very similar colloid characteristics





Bentonite erosion experiments



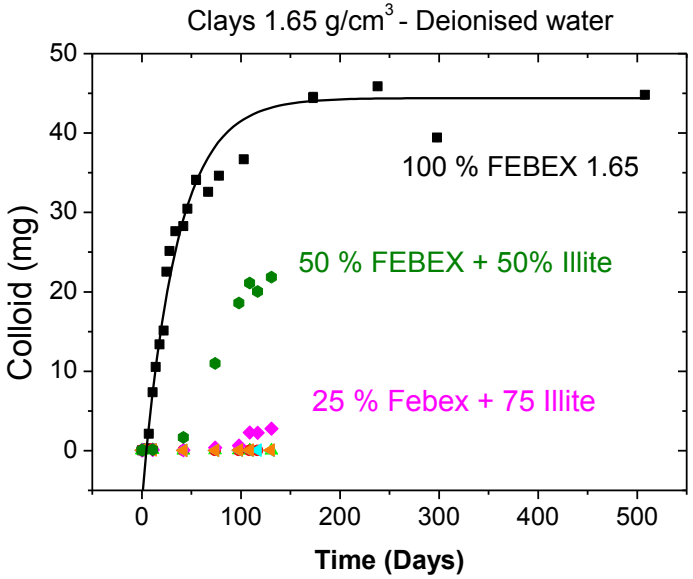


Equilibrium

Different erosion mass

Bentonite erosion: Mixtures

- **Bentonite FEBEX 100 %** ⟷ **100 % Illite**, **100 % Kaolinite**
- **Bentonite FEBEX 50 % +** **50 % Illite**, **50 % Kaolinite**
- **Bentonite FEBEX 25 % +** **75 % Illite**, **75 % Kaolinite**

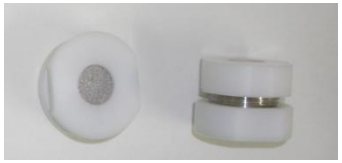


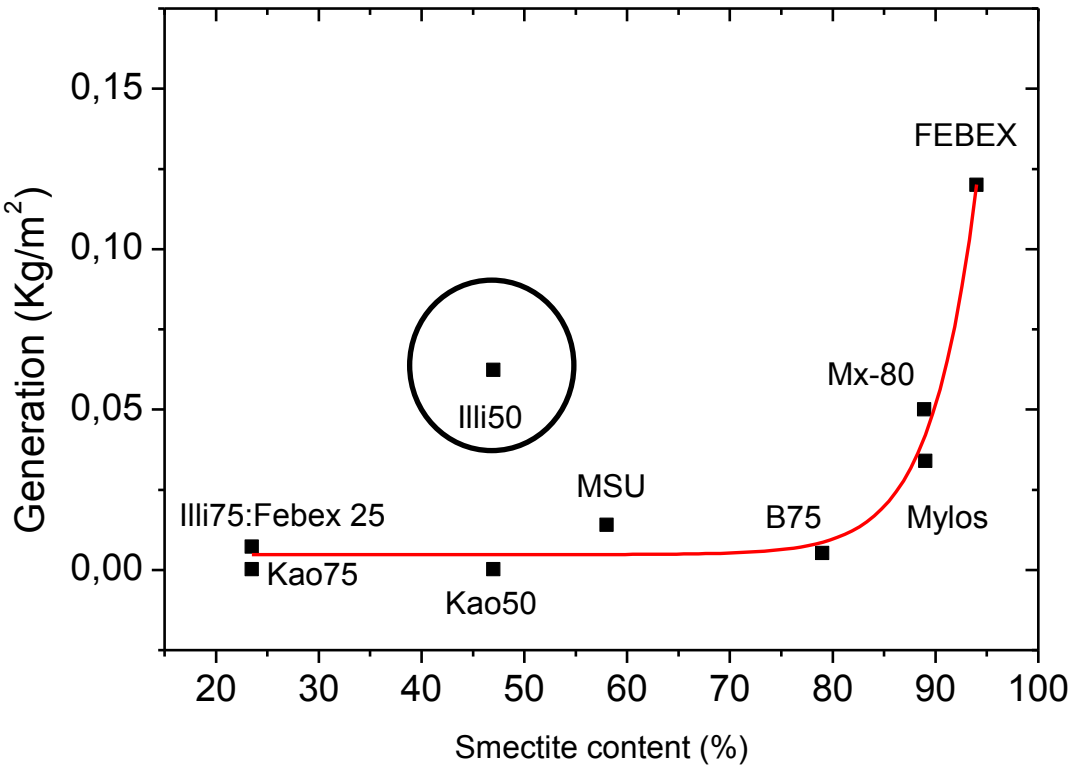
FEBEX mixed with illite still generated colloids

No generation from:

100 % Illite
100 % Kaolinite
FEBEX + Kaolinite

Erosion behaviour of different bentonites





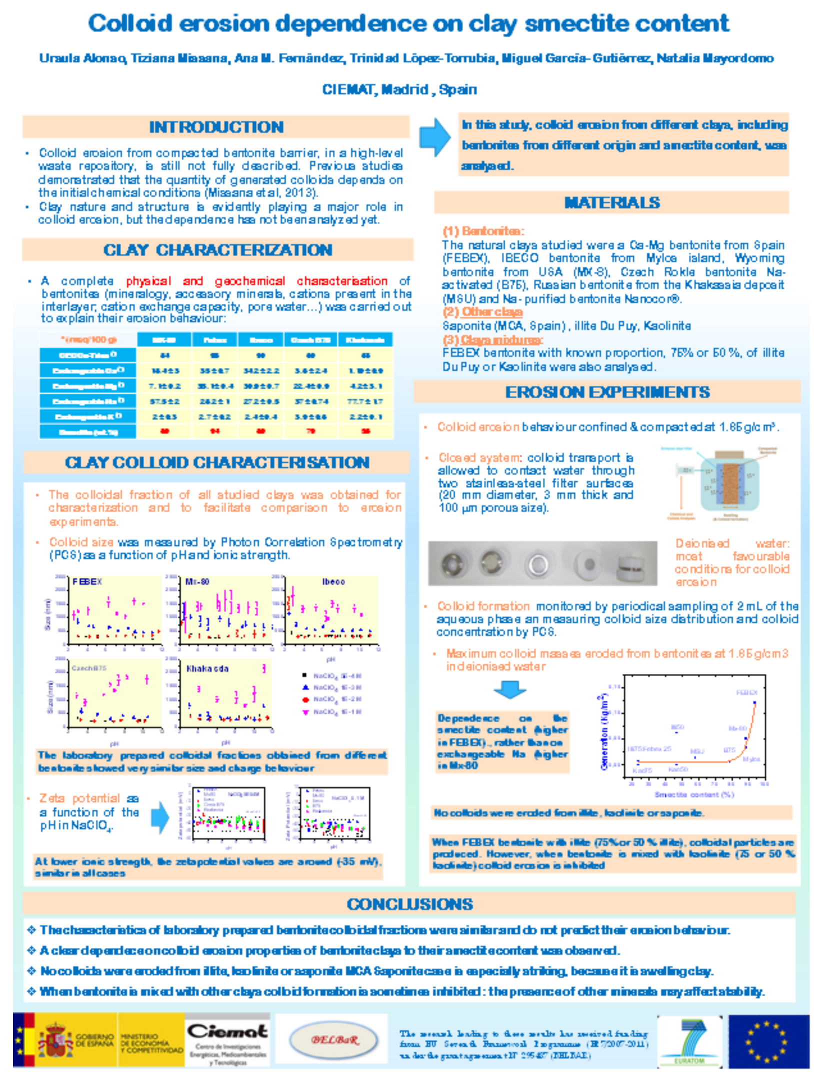
Maximun eroded masses showed dependence to the smectite content (higher in FEBEX), than to the exchangeable Na (higher in Mx-80).

When bentonite is mixed with kaolinite (75 or 50 % kaolinite) colloid erosion is inhibited.

Are other clays / oxides affecting stability??

Erosion

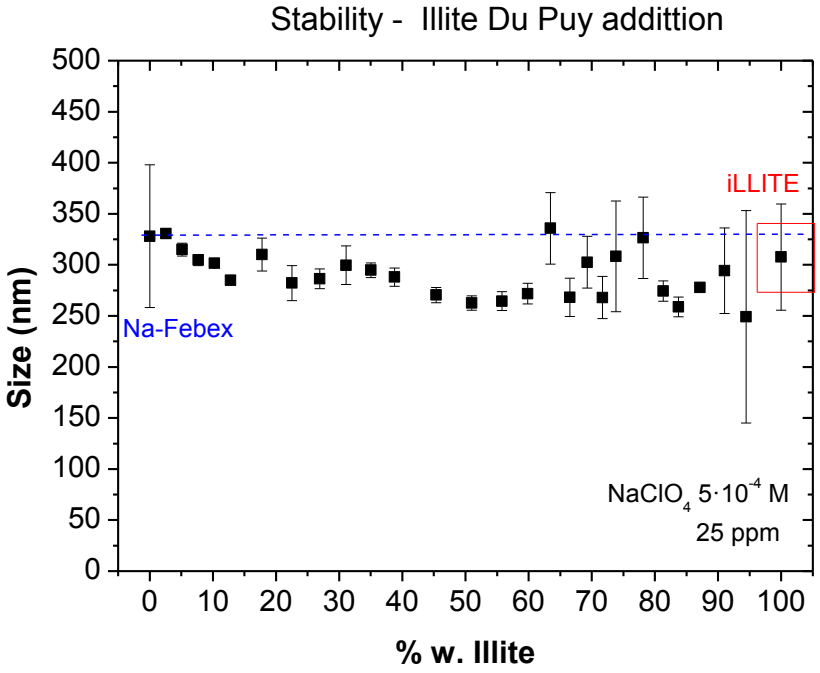
Colloid erosion dependence on clay smectite content

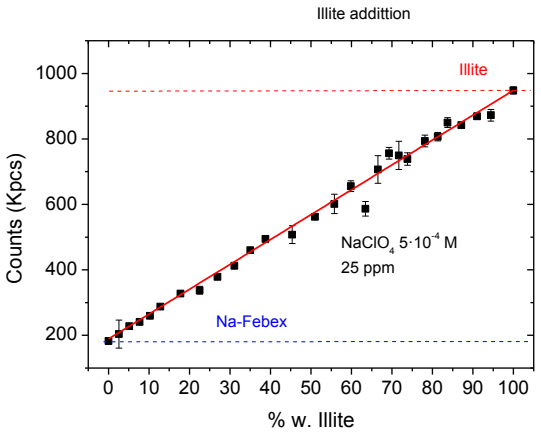


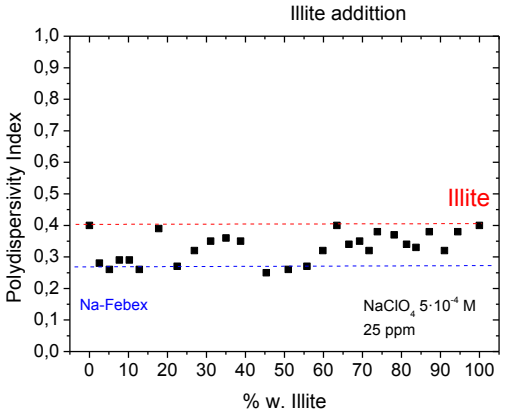
Mixtures stability

Addition of known proportions of illite to a stable suspension of FEBEX colloids

PCS measurements





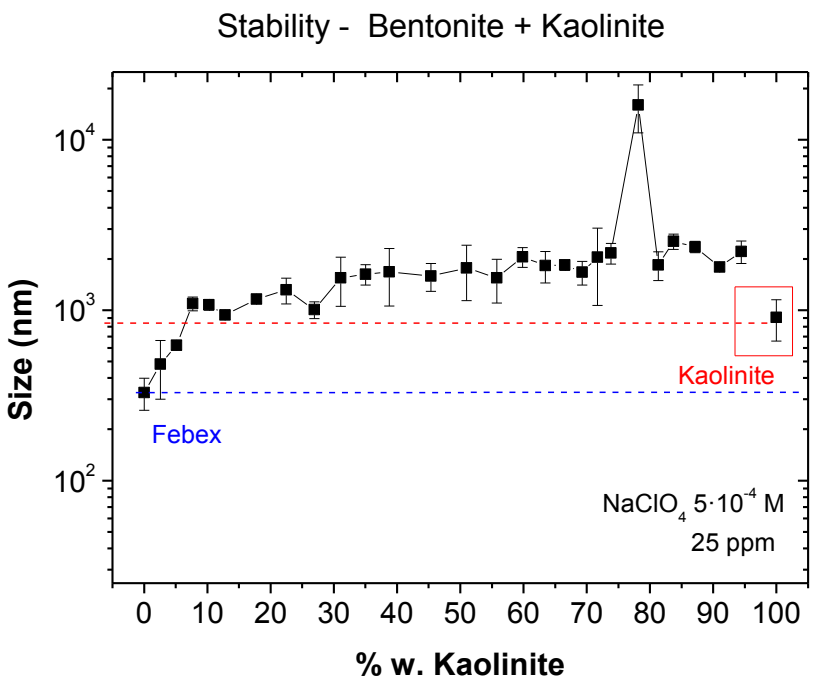


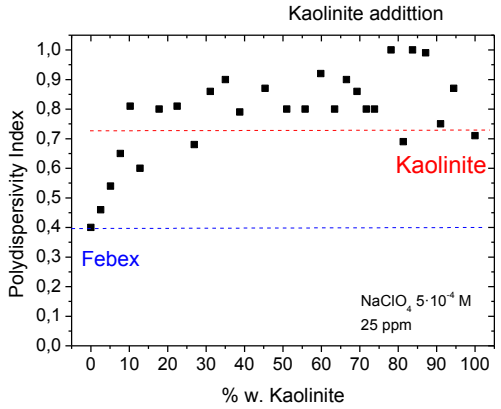
Illite does not affect bentonite colloid stability

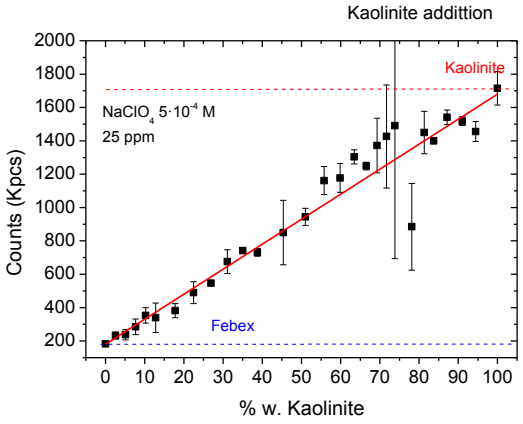
Mixtures stability

Addition of known proportions of Kaolinite to a stable suspension of FEBEX colloids

PCS measurements







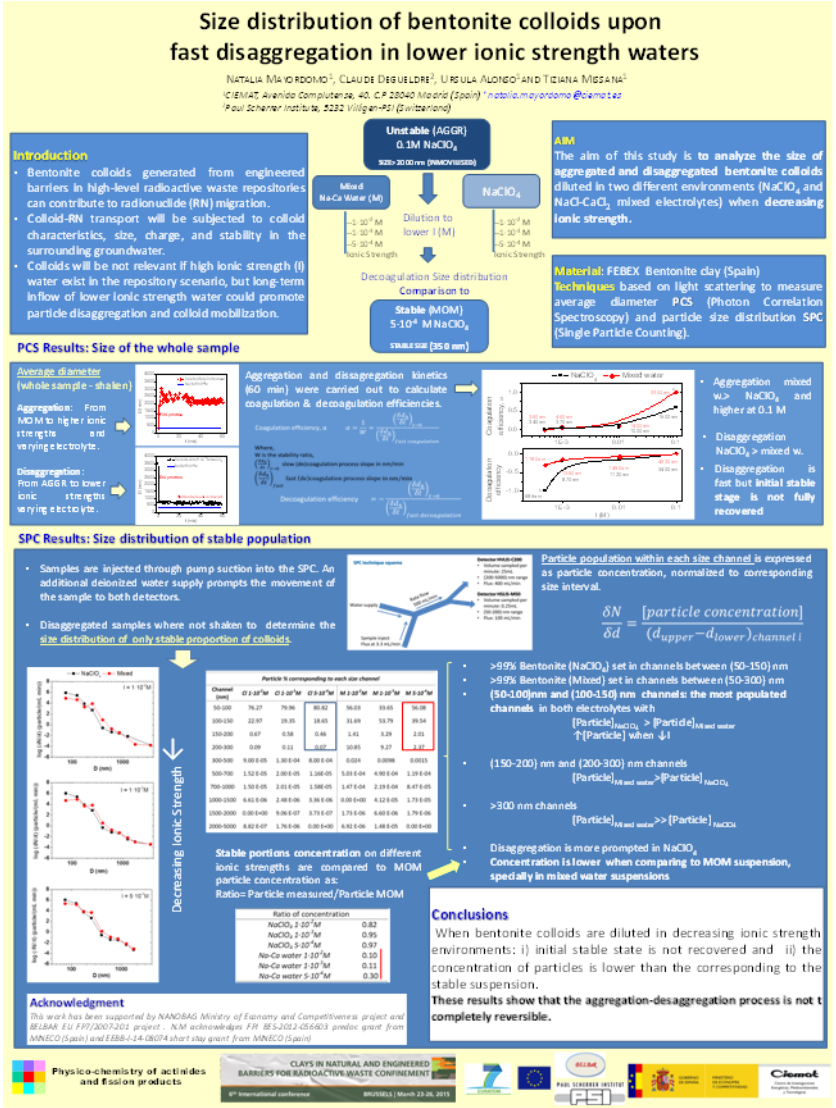
Kaolinite destabilized bentonite colloid!

Colloid stability

Colloid disaggregation in lower strength waters

Size distribution of bentonite colloids upon fast disaggregation in lower strength waters

Natalia Mayordomo (Talk)



Conclusions

BENCHMARK TEST

- **Erosion behavior of natural bentonites is not fully comparable to that of purified /simplified systems.**

Clay	Extrusion (cm)	Rate at flow 10^{-6} m/s	Preliminar Rate at flow 10^{-4} m/s
NANOCOR	2.7 ± 0.2	1,3E-06 kg /y	1,6E-03 kg /y
FEBEX	1,4 ± 0.2	1,2E-06 kg /y	1,5E-04 kg /y

STATIC EXPERIMENTS

- **Colloid erosion related to clay smectite content.**

STABILITY

- **Some clays and oxides affect bentonite colloid stability and inhibit bentonite erosion.**

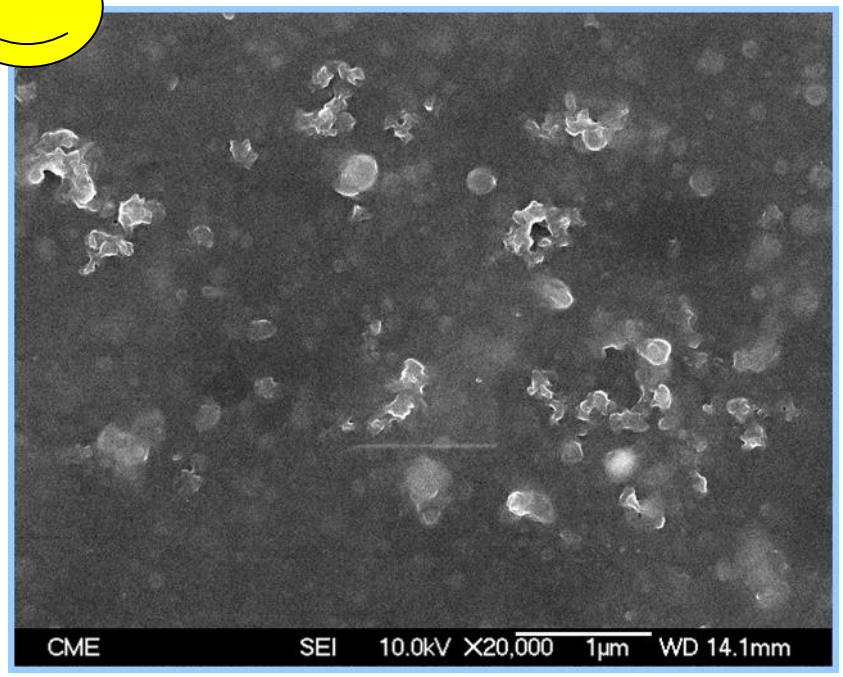
GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMIA Y COMPETITIVIDAD

Erosion FEBEX In-situ – GTS

BELBaR

FEBEX

Bentonite colloids In-situ



Overview of results from colloid samplings at the Grimsel Test Site (Switzerland) from 2006 to 2014.

T. Missana, U. Alonso, M. García-Gutiérrez (CIEMAT)

INTRODUCTION

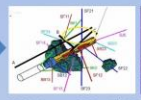
In-situ studies on clay colloid generation from compacted bentonite were carried out by CIEMAT since 2006 in the FEBEX gallery at the Grimsel Test Site (GTS, Switzerland). The FEBEX experiment represented a good opportunity to perform studies on bentonite erosion under realistic and favourable conditions. These investigations started in the frame of the FUNMIG (Fundamental of Radionuclide Migration, 2004-2008) Project and continued within the BELBAR (Bentonite Erosion: effects on the Long term performance of the engineered Barrier and Radionuclide transport, 2012-2016) Project.


Grimsel Test Site, GTS

The FEBEX Experiment at GTS

MAIN AIMS: Processes understanding / Comparison with laboratory data/ Evaluation of colloid formation and mobility in a very favourable case: Grimsel Water is alkaline and with low salinity. Different boreholes analysed: parallel and radial to the tunnel. FUN 1 and FUN 2 are relatively near to the bentonite surface (30 and 60 cm).

"Old" Radial boreholes



"New" parallel boreholes Fun1 and Fun2 drilled in 2005

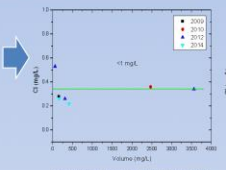
EXPERIMENTAL

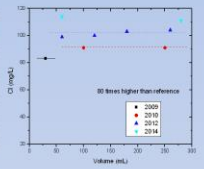
Samplings: September 2006; March, May and September 2007, April and July 2008, May 2009, August 2010, July 2012 and October 2014. *In-situ* measurement of conductivity, pH and turbidity (from May 2009 on). Photon Correlation Spectroscopy, PCS, for colloid concentration and size; Laser Doppler Electrophoresis for surface potential; Electron microscopy (SEM, FESEM) and AFM for microstructure; EDX and ICP-MS for chemical characterisation.

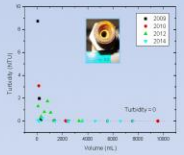
RESULTS

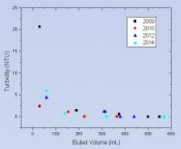
The effect of the bentonite on the groundwater is clearly observed in some borehole (for example: increase of the conservative ion Cl or conductivity). "Reference water" (SJ5-3) borehole is unaffected.

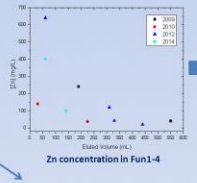
Transient behaviour of turbidity (related with the presence of particles) is often seen: it is related to different types of CONTAMINATION (iron oxides, heavy metals, organics, rock particles, ...). Tend to decrease as the water is eluted.

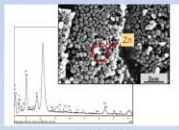

Chlorine in SJ5-3 (Reference Water). Unaffected.


Chlorine in FUN1-4 (30 cm. far from the bentonite): Increases with time.


Ej: Turbidity in SJ5-3 (Reference Water). Tap Oxides.

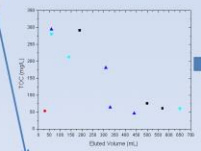

Ej: Turbidity in FUN1-4 (30 cm. far from the bentonite).


Zn concentration in Fun1-4


Zn colloids

CONCLUSIONS

- In different boreholes, concentrations significantly higher than expected in Grimsel water (around 0.2 ppm) were found.
- Evidences of the existence of colloids others than natural. Main contribution is from artefacts produced by drilling of new experimental boreholes: small pieces of rock, heavy metals and organic matter were clearly identified. They are difficult to get over, for the very low transmissivity of the fractures in the tunnel.
- The possible presence of bentonite colloids is masked and cannot be evaluated with technique like PCS.
- The aluminum signal, necessary condition to prove the existence of bentonite colloids in the water, is still quite low. The maximum concentration of bentonite colloids (considering the Al concentration) is around 0.5-0.8 ppm.
- The highest Al concentration values are observed in the intervals more chemical affected by bentonite.


TOC concentration in Fun1-4


Residue after sample ultracentrifugation

But... Al signal still quite low

ACKNOWLEDGEMENTS
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GOBIERNO DE ESPAÑA MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Acknowledgments

Thank you for your attention!

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