

Update on erosion experiments at CIEMAT

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Manuel Mingarro, Trinidad López, Jesús Morejón, Petri Gil

Benchmark tests results

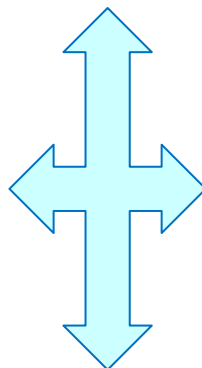
Nanocor®



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)

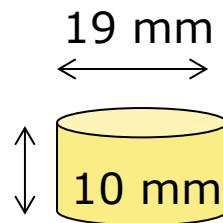
Erosion Benchmark test (configuration Tim Schatz)

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

FEBEX (Spain): Ca- Mg bentonite

- Compacted clay at 1400 kg/m³**

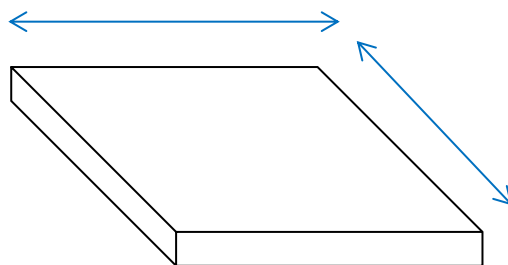
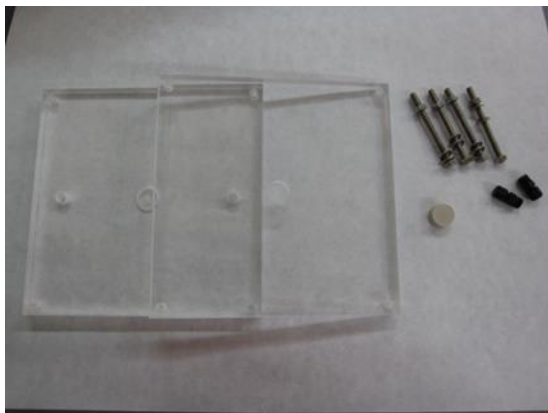
- Pre-saturated in NaCl 10⁻³ M**



Nanocor®: 4.64 g ; H 16.9%

FEBEX: 4.52 g; H 13.9%

Artificial fracture

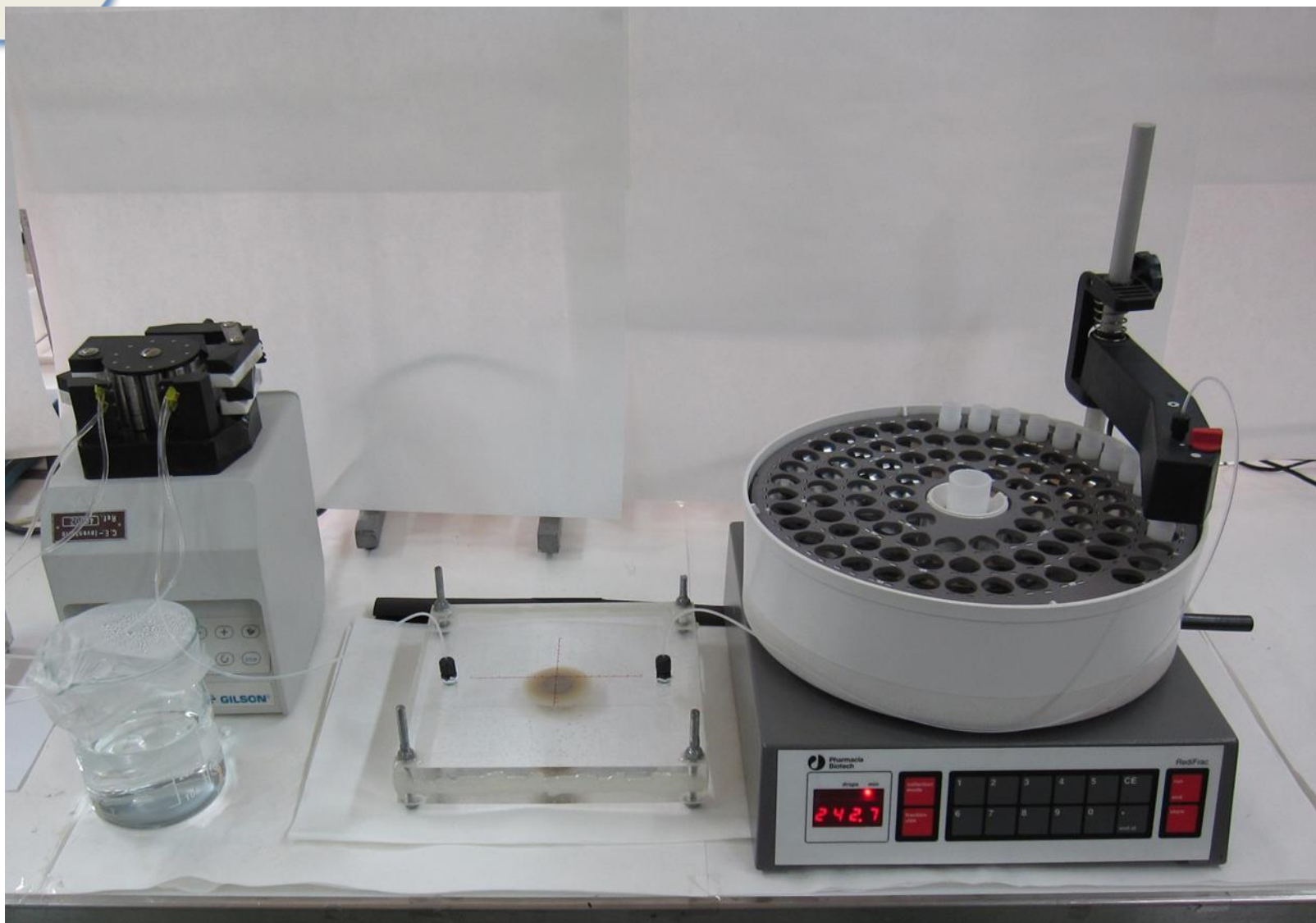


17 x 17 cm²

Aperture: 0.1 mm

Benchmark Set-Up

BELBaR



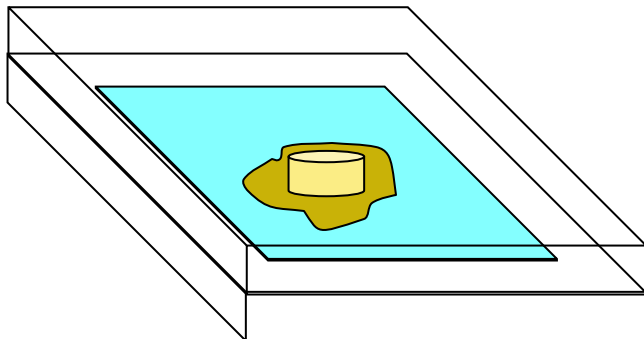
Physico-Chemistry of Actinides and Fission Products Unit



GOBIERNO
DE ESPAÑA

MINISTERIO
DE ECONOMÍA
Y COMPETITIVIDAD

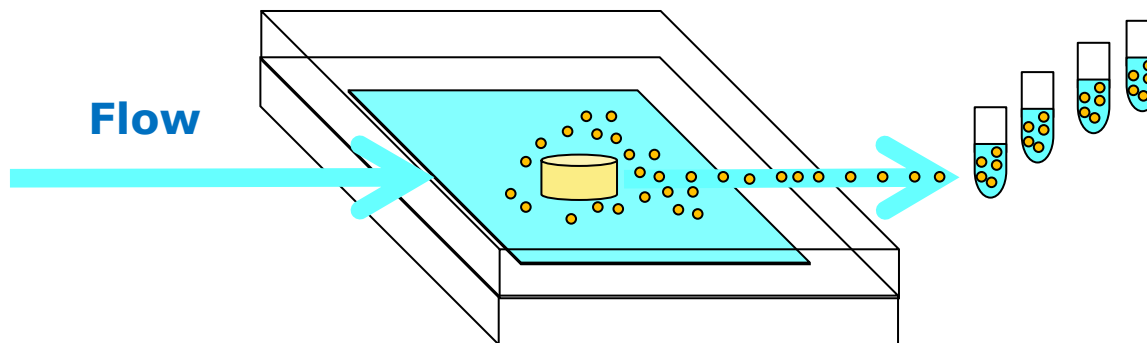
Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)



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

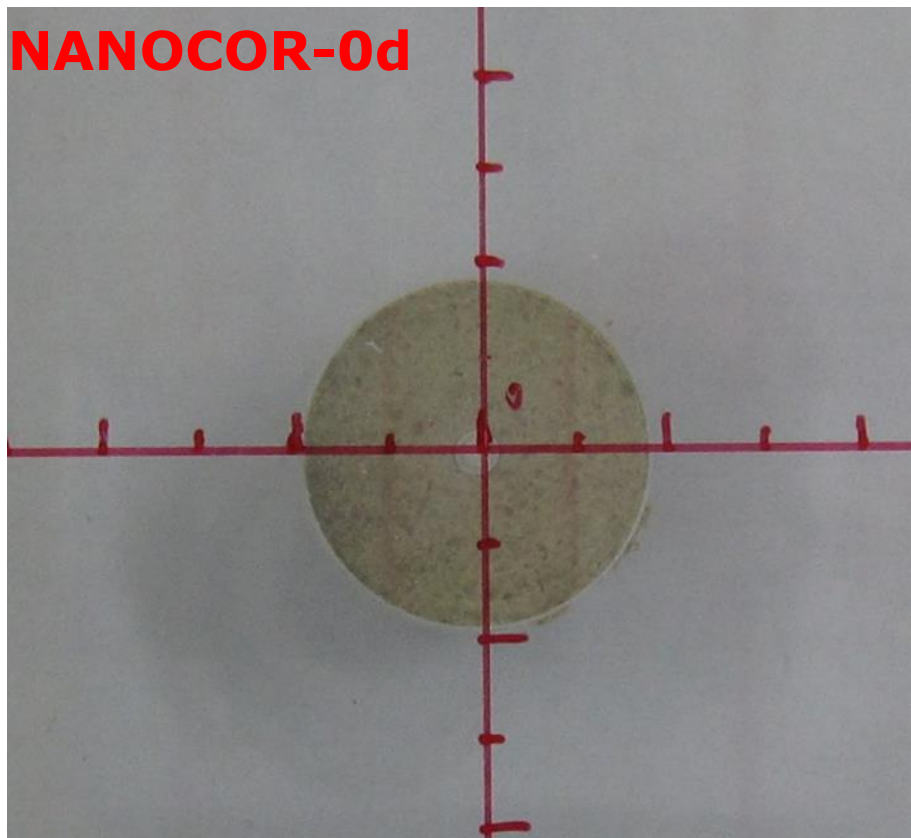
Phase 2: Low Flow conditions (14 days) 10^{-6} m/s with NaCl 10^{-3} M

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

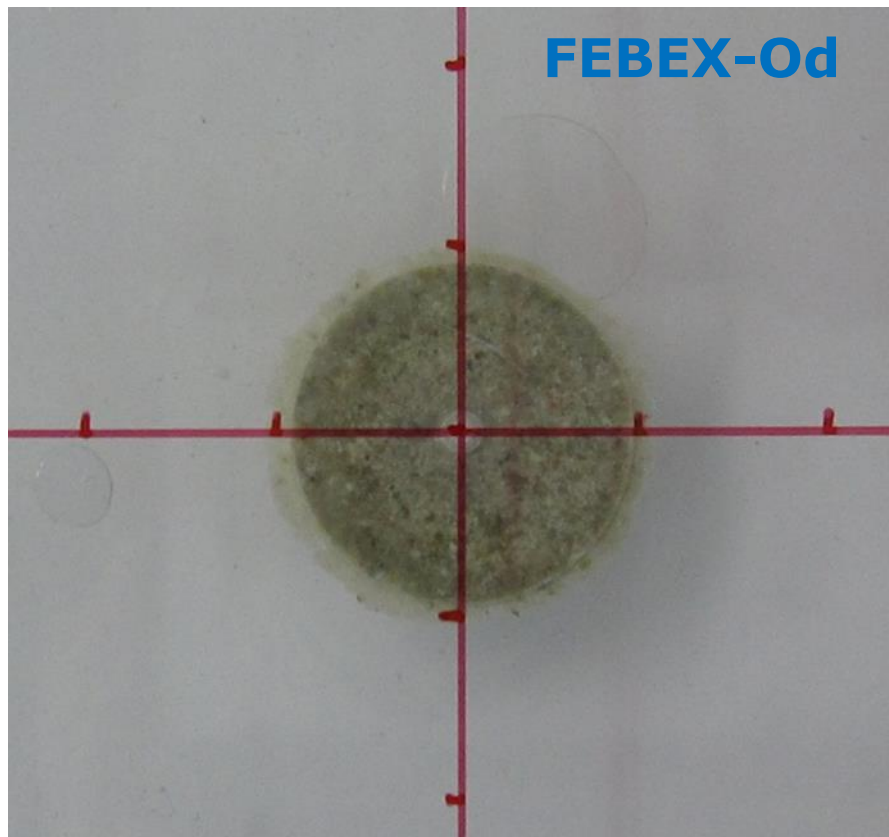


Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

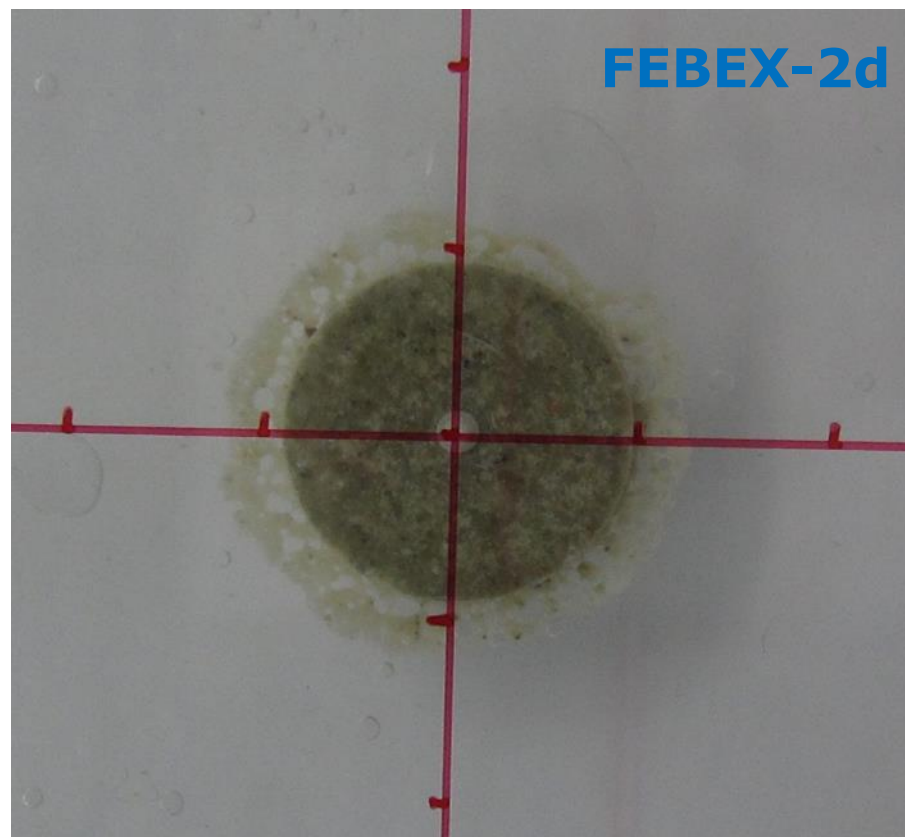
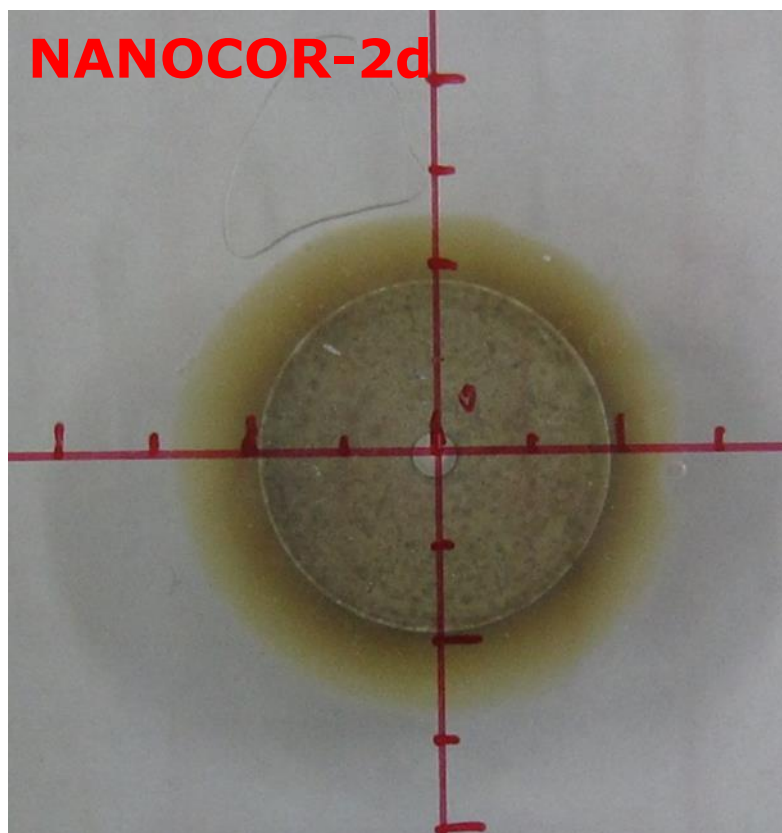
NANOCOR-0d



FEBEX-0d

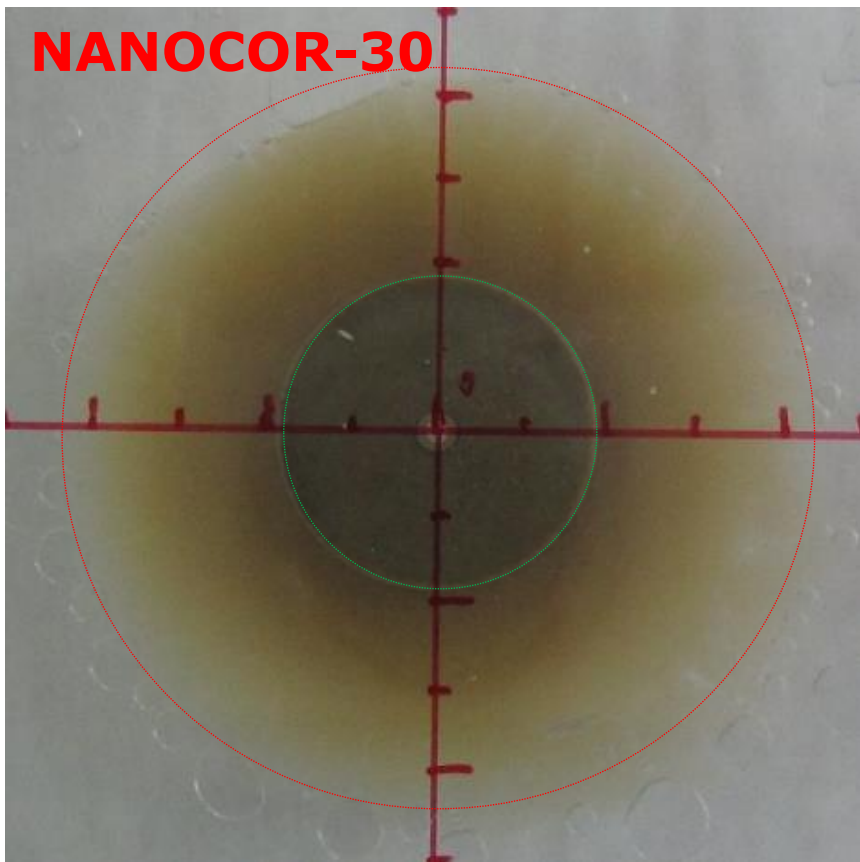
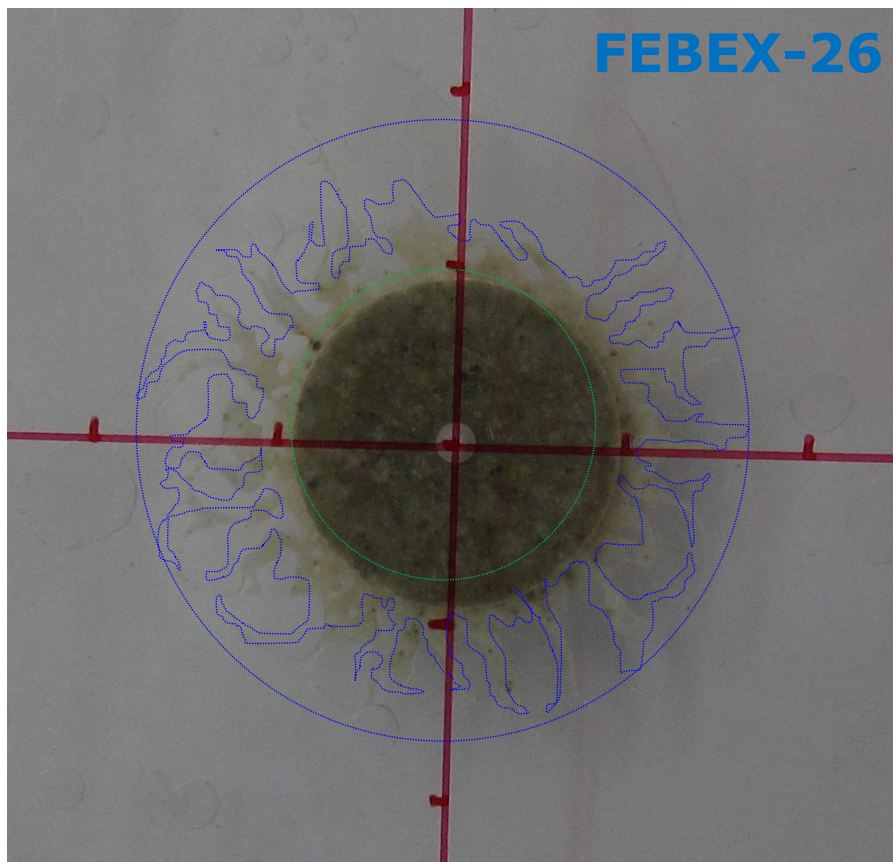


Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)



Different gel characteristics

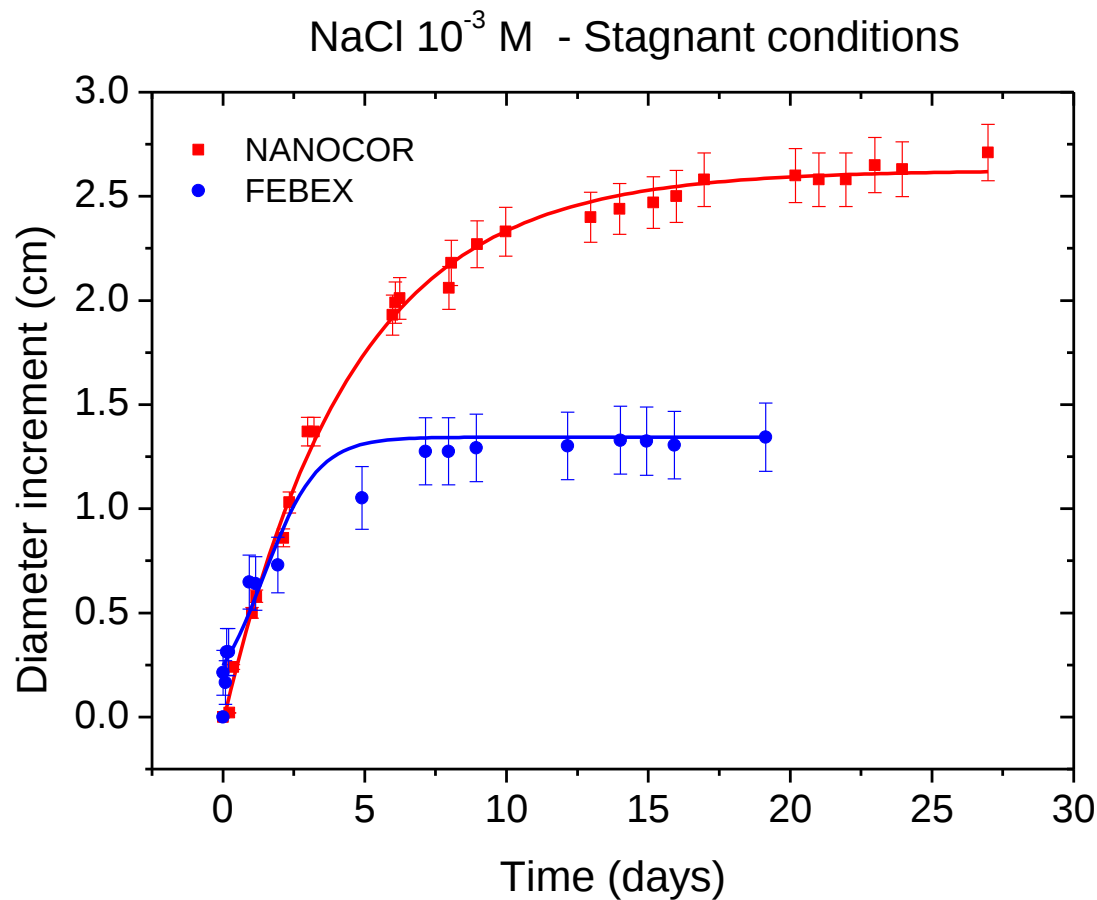
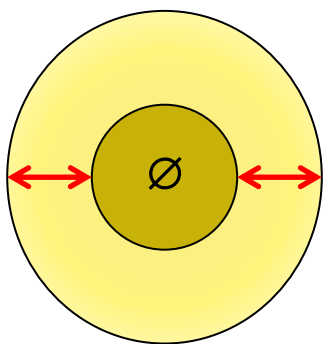
Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

NANOCOR-30**FEBEX-26**

Different extrusion behavior

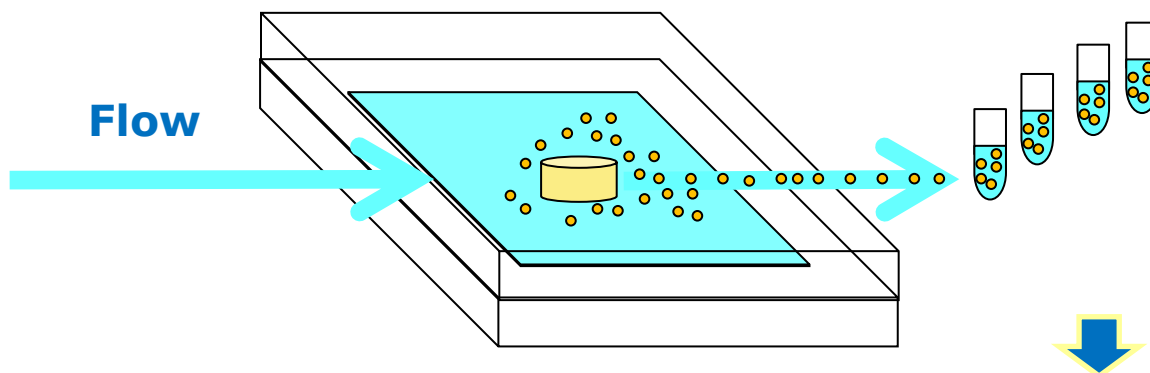
Phase 1: Stagnant conditions (30 days with NaCl 10^{-3} M)

**Extrusion
distance
Diameter
increment**



Phase 2: Low Flow conditions (14 days)

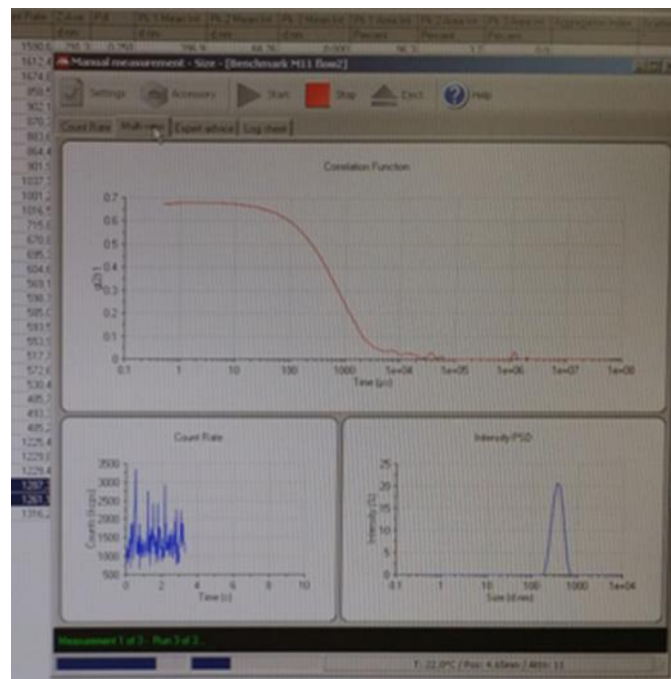
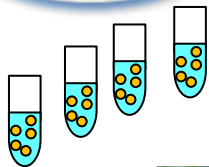
Phase 3: High Flow conditions (14 days)



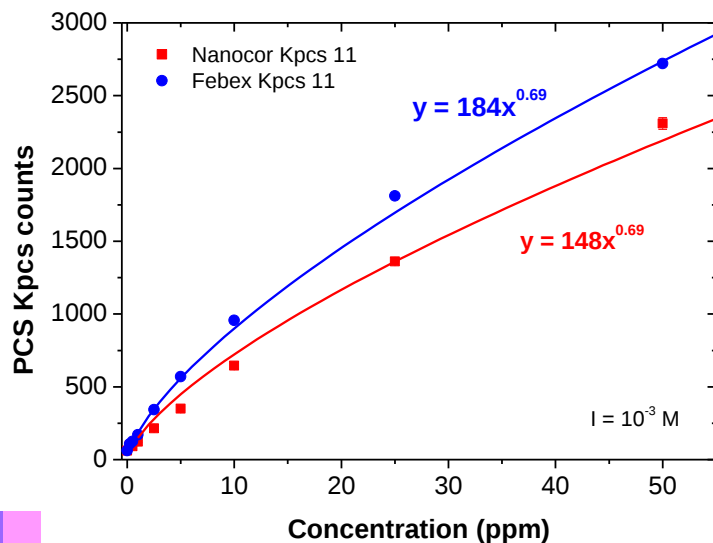
- Periodical sampling of eluted water
- **Analyses of mass loss (mobilised)**

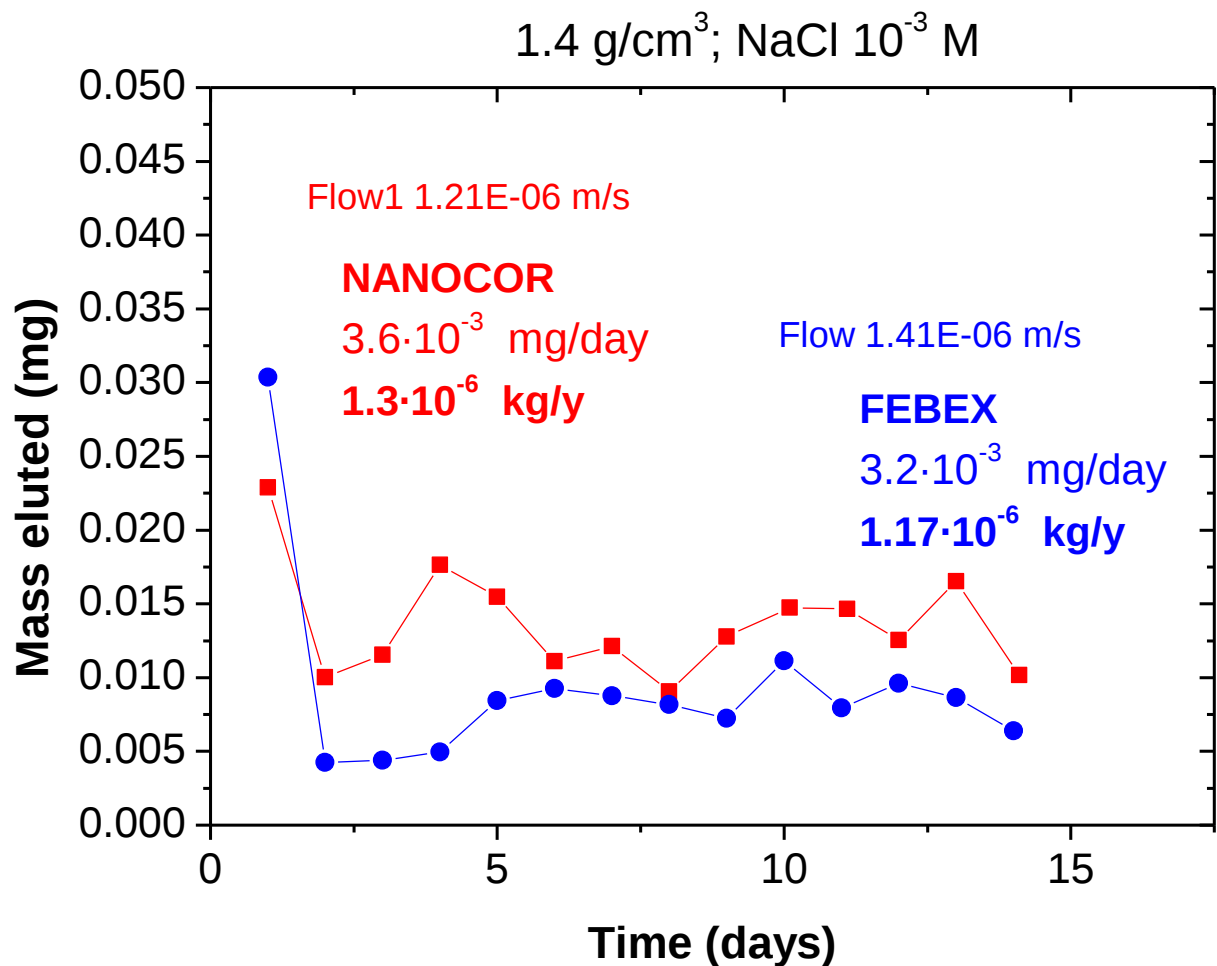
- **Photon Correlation Spectrometry (Concentration, Size)**
- **Turbidity analyses (concentration)**
- **FINAL POST MORTEM (extruded mass - mass balance)**

- Photon Correlation Spectrometry (Concentration, Size)

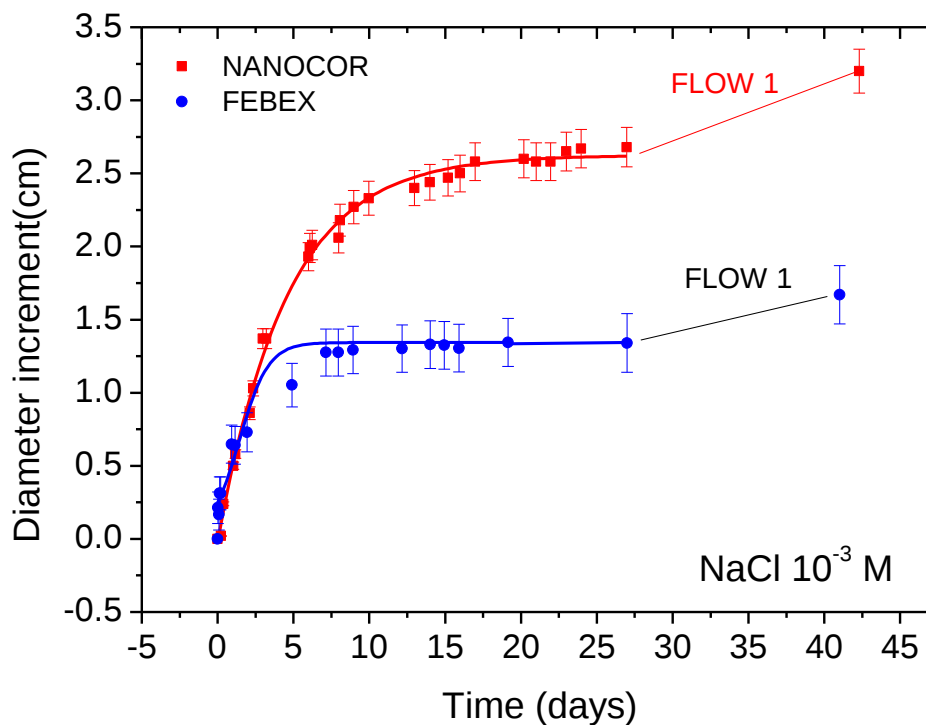
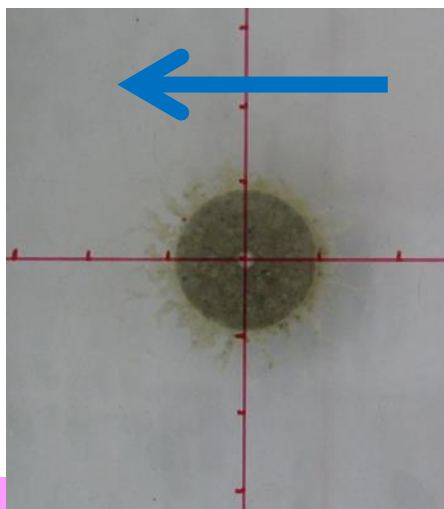
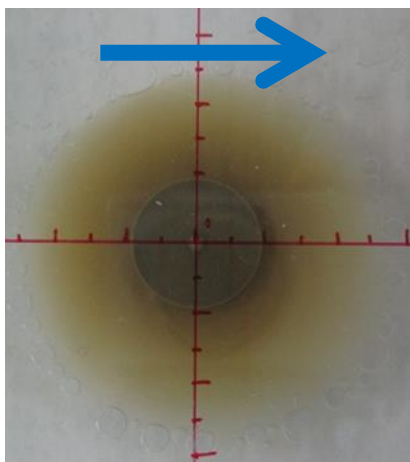


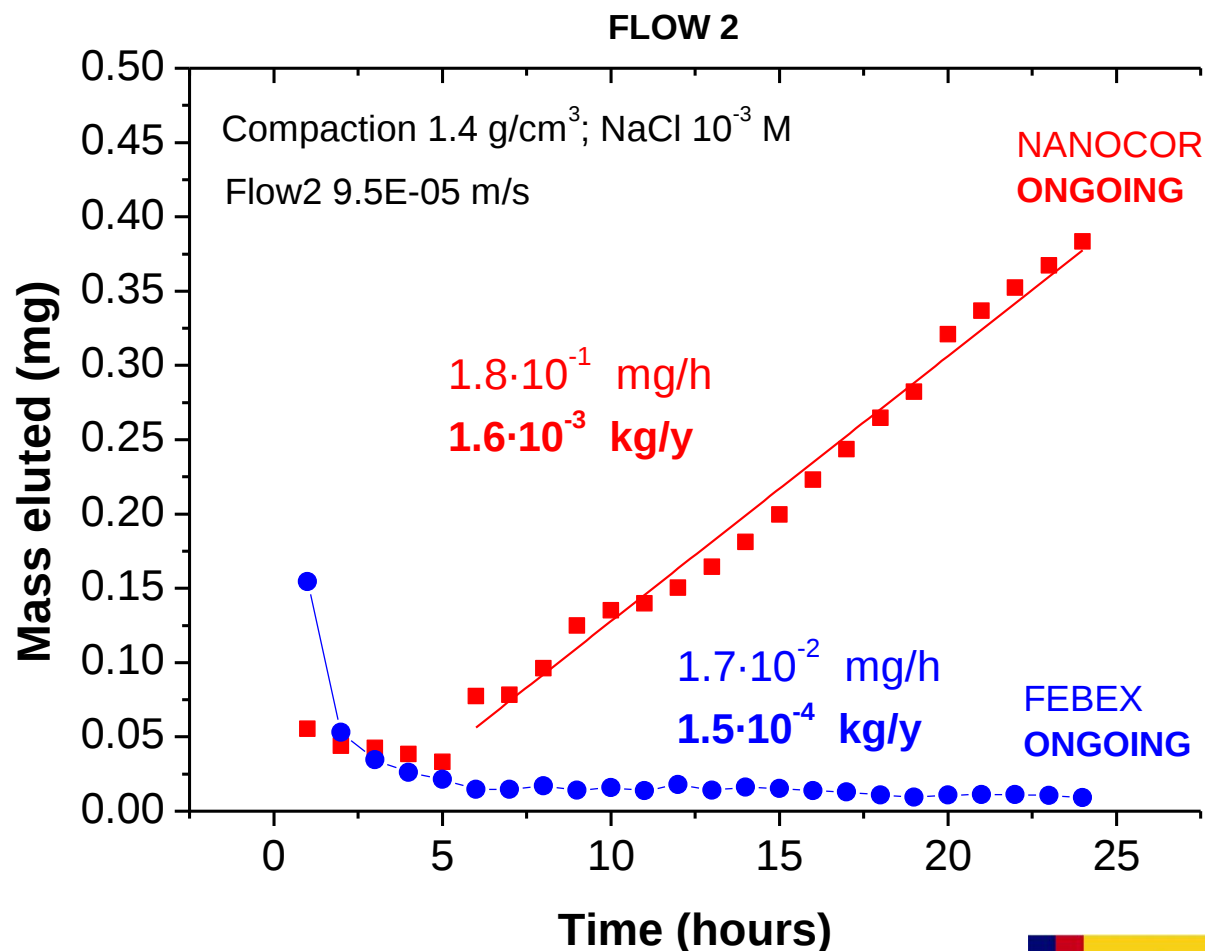
- Calibration curves with laboratory prepared colloids in same electrolyte

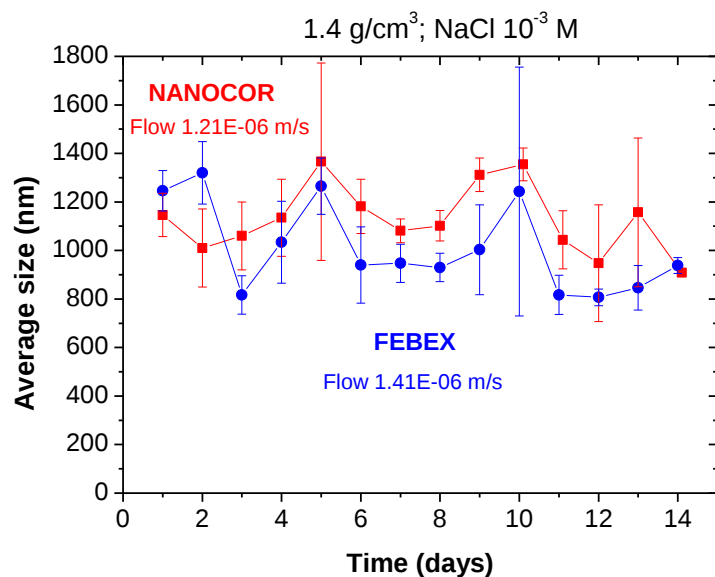


Phase 2: Low Flow conditions (14 days)

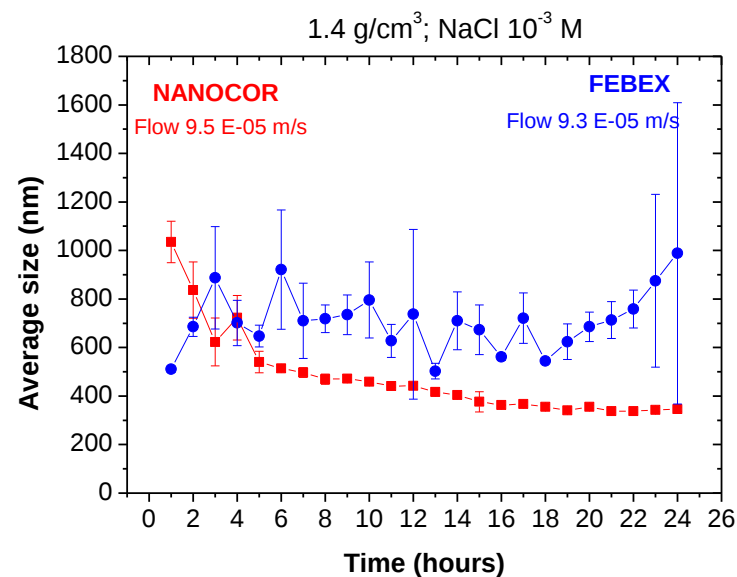
*Bentonite
exposed
surface not
corrected:
S = 6 mm²*

NANOCOR - 30+15 days**Extrusion increment (30 + 15 days)**

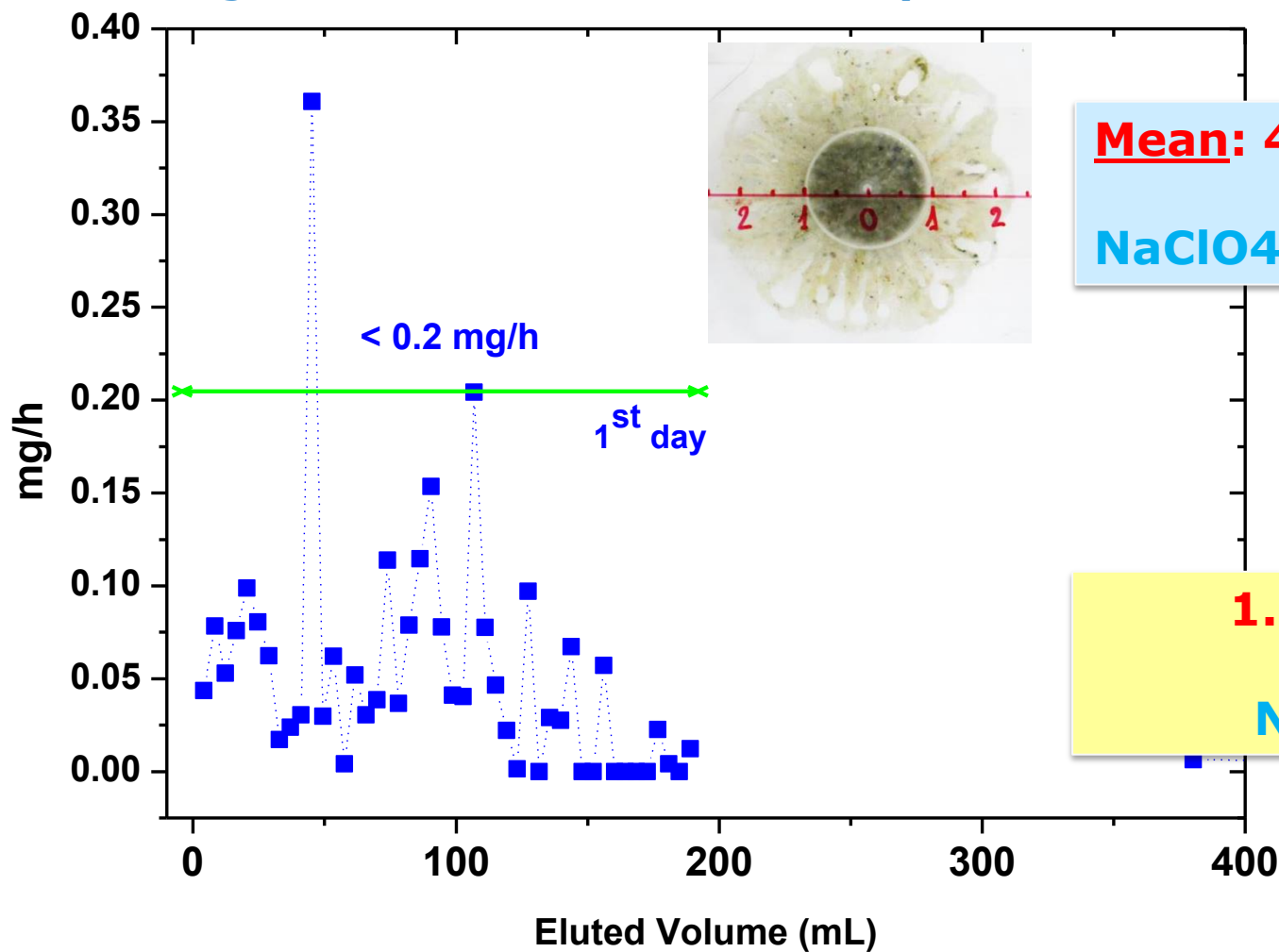
Phase 2: High Flow conditions (1 day – **SO FAR**)

Low Flow conditions (15 days)

Initially bigger particles
are mobilised

High Flow conditions (1 day – SO FAR)

Colloids are released

High Flow conditions: FEBEX clay

Mean: $4.8\text{E-}04$ Kg/y

NaClO_4 $5 \cdot 10^{-4}$ M

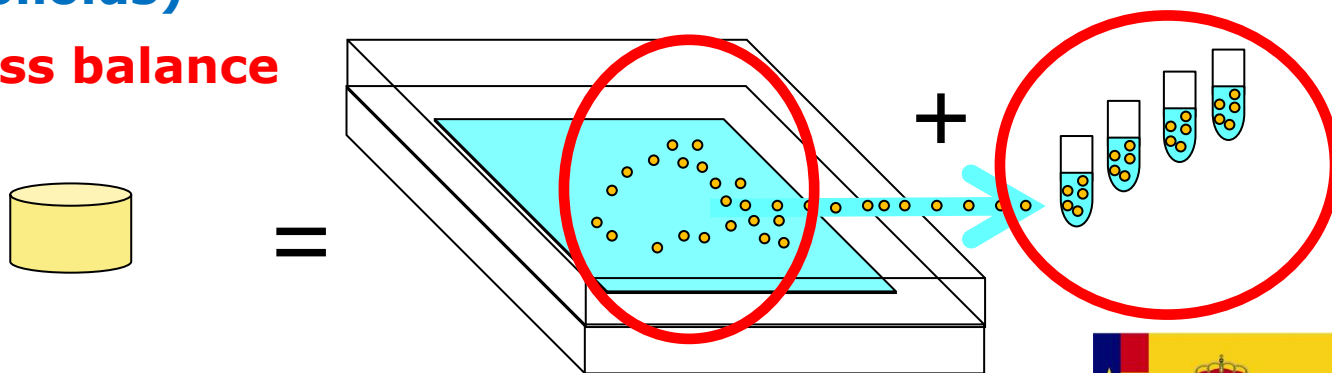
$1.5\text{E-}04$ Kg/y

NaCl 10^{-3} M

- ❖ 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 μm).

TO DO:

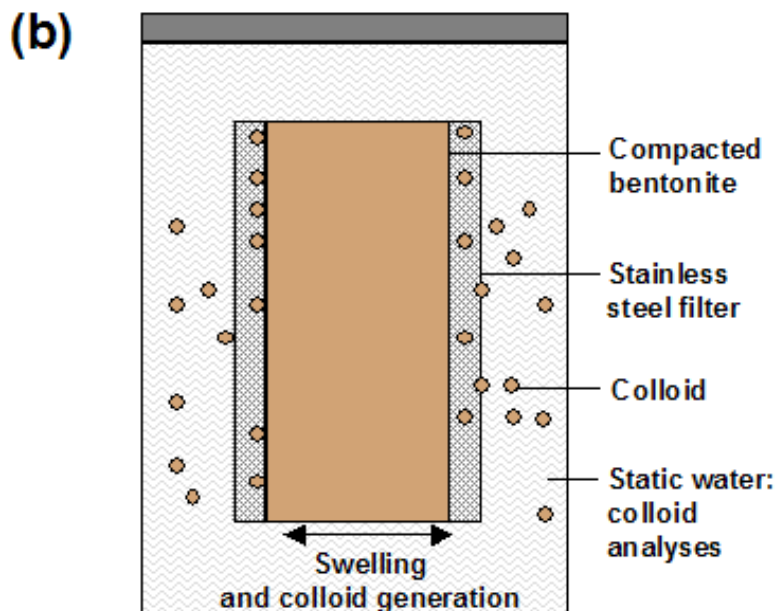
- ❖ To finish high flow rate phase
- ❖ Turbidity measurements vs PCS measurements
- ❖ Post mortem analyses: EXTRUDED clay (+ mobilized particles /colloids)
- ❖ **Mass balance**



✓ Static: Diffusive conditions



FILTER PORE 100 μm



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

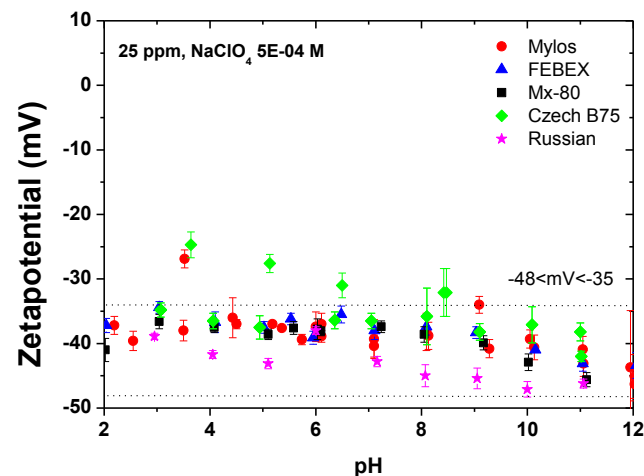
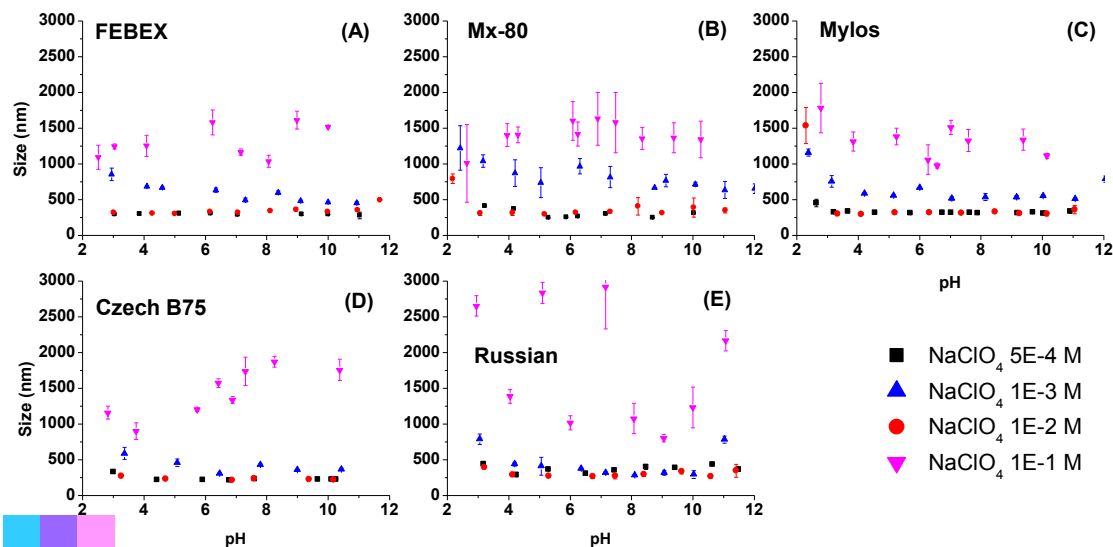


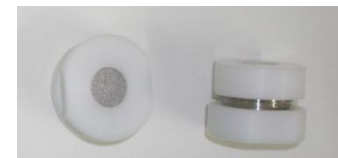
BELBaR

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

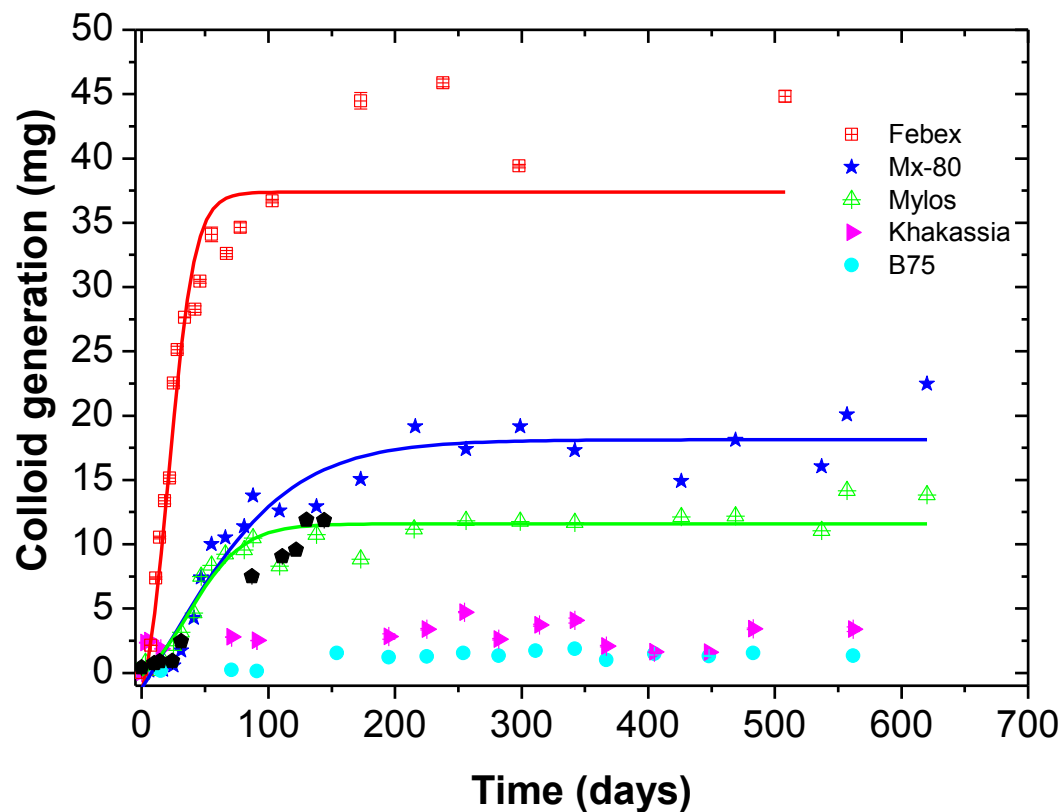
**Laboratory
prepared colloids:
Size and charge**

**Different clays
exhibited very similar
colloid characteristics**



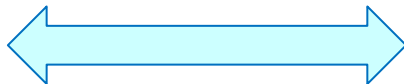


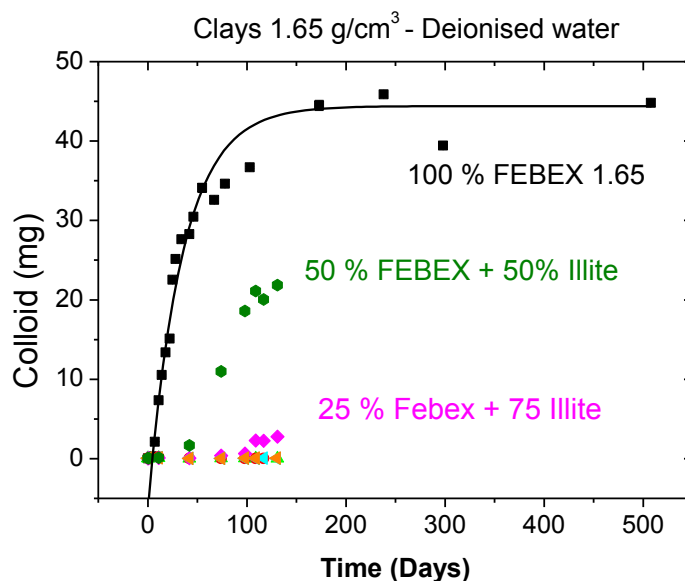
Generation - 1.65 g/cm^3 in Deionised Water



Equilibrium

Different erosion mass

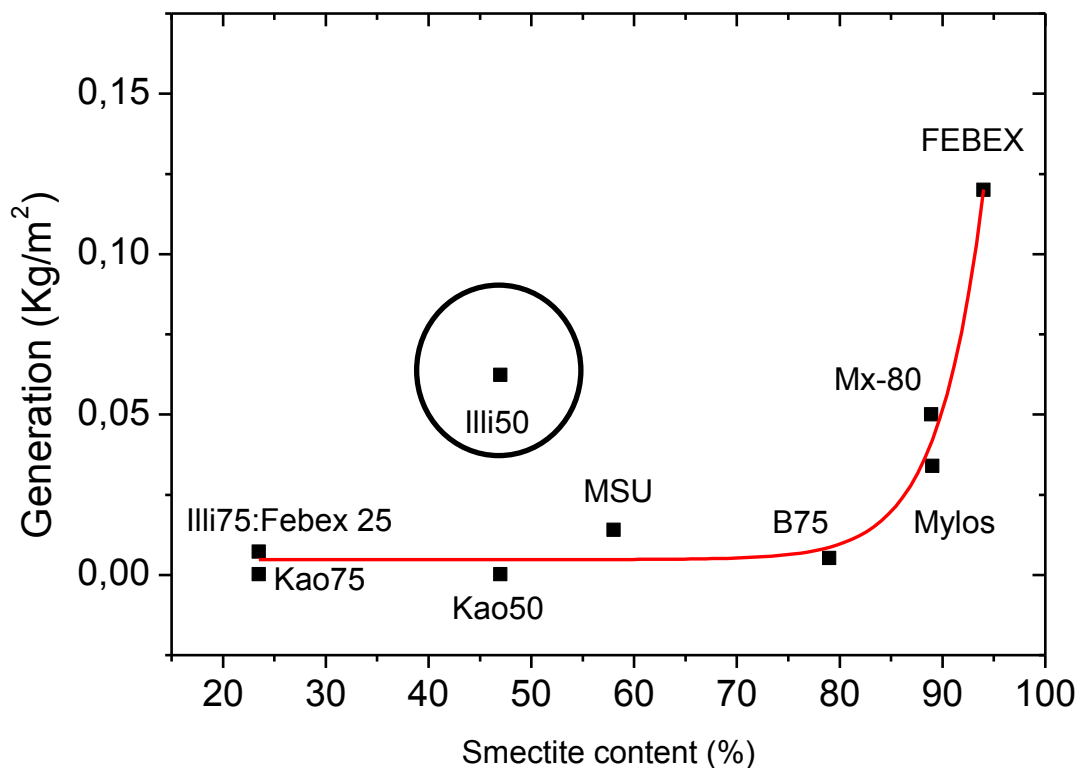
- Bentonite FEBEX 100 %  100 % Illite
100 % Kaolinite
- Bentonite FEBEX 50 % + 50 % Illite
50 % Kaolinite
- Bentonite FEBEX 25 % + 75 % Illite
75 % Kaolinite



**FEBEX mixed with illite
still generated colloids**

No generation from:
100 % Illite
100 % Kaolinite
FEBEX + Kaolinite

Erosion behaviour of different bentonites



Maximum 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??

Colloid erosion dependence on clay smectite content

Colloid erosion dependence on clay smectite content

Urula Alonaa, Tiziana Masana, Ana M. Fernández, Trinidad López-Torres, Miguel García-Gutiérrez, Natalia Mayordomo

CIEMAT, Madrid, Spain

INTRODUCTION

- Colloid erosion from compacted bentonite barrier, in a high-level waste repository, is still not fully described. Previous studies demonstrated that the quantity of generated colloids depends on the initial chemical conditions (Masana et al., 2013).
- Clay nature and structure is evidently playing a major role in colloid erosion, but the dependence has not been analyzed yet.

In this study, colloid erosion from different clays, including bentonites from different origin and smectite content, was analyzed.

MATERIALS

(1) Bentonites:

The natural clays studied were a Ca-Mg bentonite from Spain (FEBEX), IBECO bentonite from Mylos island, Wyoming bentonite from USA (MK-S), Czech Rokle bentonite Na-activated (B75), Russian bentonite from the Khakassia deposit (M8U) and Na-purified bentonite Nanoco®.

(2) Other clays

Saponite (MCA, Spain), Illite Du Puy, Kaolinite

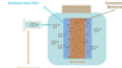
(3) Clay mixtures

FEBEX bentonite with known proportion, 75% or 50% of illite Du Puy or Kaolinite were also analyzed.

EROSION EXPERIMENTS

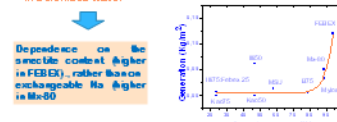
- Colloid erosion behaviour confined & compacted at 1.65 g/cm³.

- Closed system: colloid transport is allowed to contact water through two stainless-steel filter surfaces (20 mm diameter, 3 mm thick and 100 µm porous size).



- Colloid formation monitored by periodical sampling of 2 mL of the aqueous phase and measuring colloid size distribution and colloid concentration by PCS.

- Maximum colloid mass as eroded from bentonites at 1.65 g/cm³ in deionised water



No colloids were eroded from illite, kaolinite or saponite.

When FEBEX is mixed with illite (75% or 50% illite), colloidal particles are produced. However, when bentonite is mixed with kaolinite (25 or 50% kaolinite) colloid erosion is inhibited.

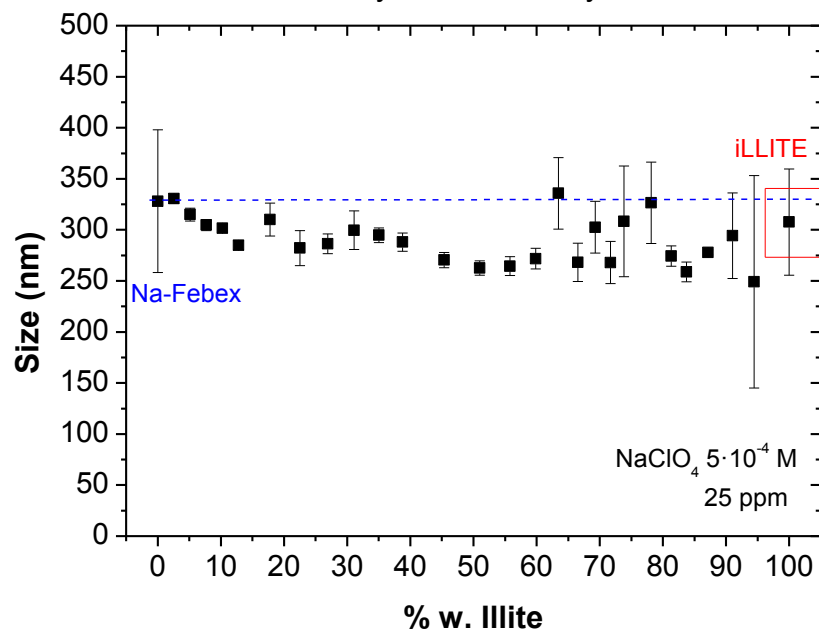
CONCLUSIONS

- The characteristics of laboratory prepared bentonite colloidal fractions were similar and do not predict their erosion behaviour.
- A clear dependence on colloid erosion properties of bentonite clays to their smectite content was observed.
- No colloids were eroded from illite, kaolinite or saponite. MCA Saponite case is especially striking, because it is swelling clay.
- When bentonite is mixed with other clays colloid formation is sometimes inhibited: the presence of other minerals may affect stability.

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

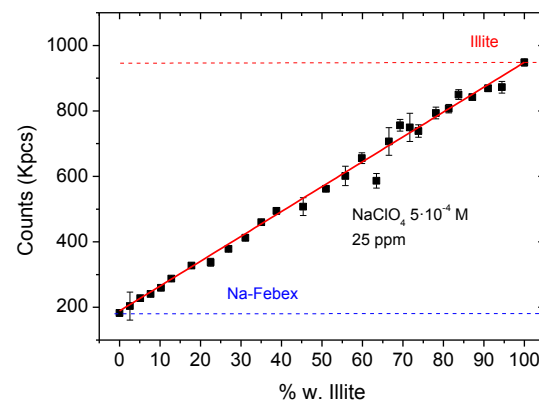
PCS measurements

Stability - Illite Du Puy addition

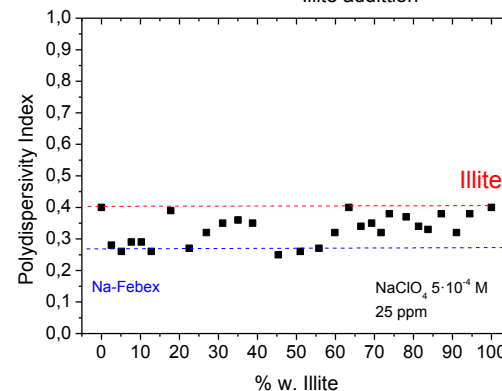


**Illite does not affect
bentonite colloid stability**

Illite addition

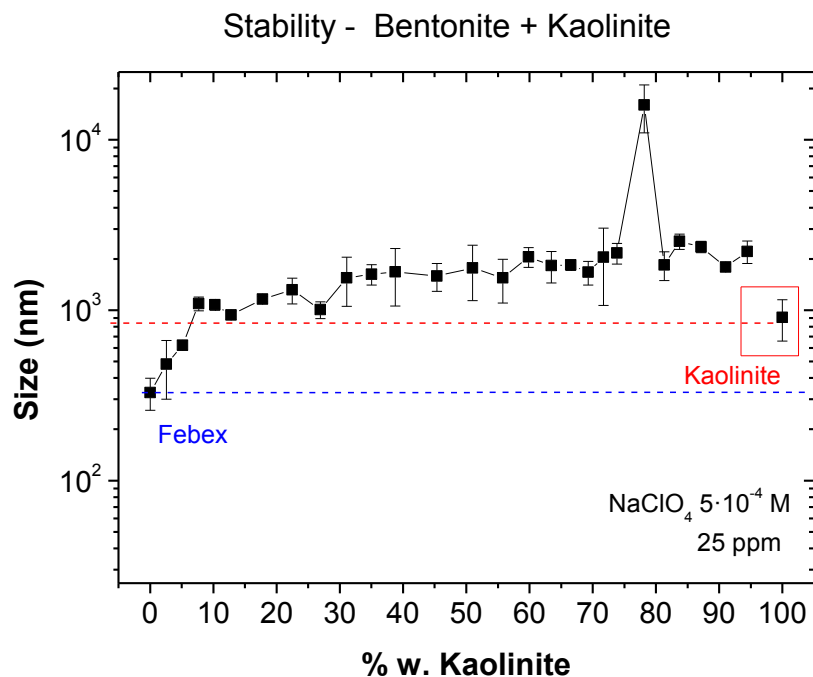


Illite addition

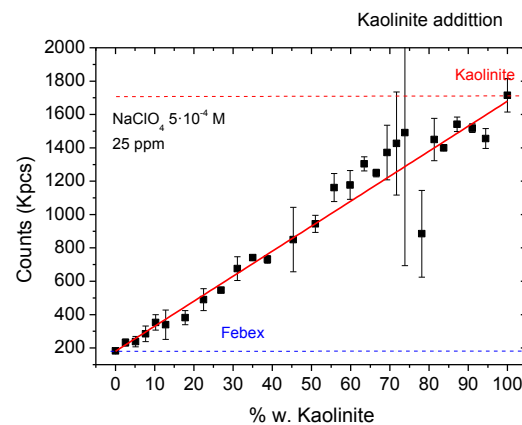
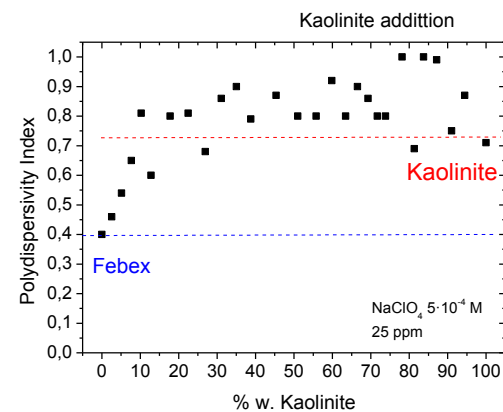


Addition of known proportions of Kaolinite to a stable suspension of FEBEX colloids

PCS measurements



**Kaolinite destabilized
bentonite colloid!**



Colloid stability



BELBA

Colloid disaggregation in lower strength waters



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



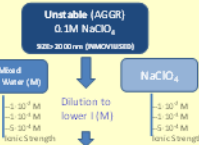
Natalia Mayordomo (Talk)

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

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²Paul Scherrer Institute, 5232 Villigen-PSI (Switzerland)

Introduction

- Bentonite colloids generated from engineered barriers in high-level radioactive waste repositories can contribute to radionuclide (RN) migration.
- Colloid-RN transport will be subjected to colloid characteristics, size, charge, and stability in the surrounding groundwater.
- Colloids will be not relevant if high ionic strength (I) water exist in the repository scenario, but long-term inflow of lower ionic strength water could promote particle disaggregation and colloid mobilization.



AIM

The aim of this study is to analyze the size of aggregated and disaggregated bentonite colloids diluted in two different environments (NaClO₄ and NaCl-CaCl₂ mixed electrolytes) when decreasing ionic strength.

Material: FEBEX Bentonite clay (Spain)

Techniques based on light scattering to measure average diameter PCS (Photon Correlation Spectroscopy) and particle size distribution SPC (Single Particle Counting).

PCS Results: Size of the whole sample

Average diameter (whole sample - shaken)

Aggregation: From MOM to higher ionic strength and varying electrolyte.

Disaggregation: From AGG to lower ionic strength and varying electrolyte.

Aggregation and disaggregation kinetics (60 min) were carried out to calculate aggregation & disaggregation efficiencies.

$$\text{Aggregation efficiency} = 1 - \left(\frac{[C]_{t=60}}{[C]_{t=0}} \right)$$

$$\text{Disaggregation efficiency} = 1 - \left(\frac{[C]_{t=60}}{[C]_{t=0}} \right)$$

Disaggregation efficiency



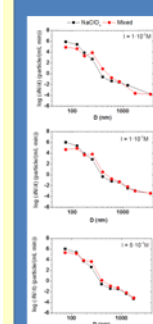
Aggregation mixed w. > NaClO₄ and higher at 0.1 M

Disaggregation NaClO₄ > mixed w.

Disaggregation is fast but initial stable state is not fully recovered

SPC Results: Size distribution of stable population

- Samples are injected through pump suction into the SPC. An additional deionized water supply prompts the movement of the sample to both detectors.
- Disaggregated samples were not shaken to determine the size distribution of only stable proportion of colloids.



Particle population within each size channel is expressed as particle concentration, normalized to corresponding size interval.

$$\frac{\delta N}{\delta d} = \frac{[\text{particle concentration}]}{(d_{upper} - d_{lower})_{channel}}$$

Channel (nm)	1e-3 M	1e-4 M	1e-5 M	1e-6 M	1e-7 M	1e-8 M
10-200	0.07	0.05	0.03	0.02	0.01	0.01
200-300	0.07	0.05	0.03	0.02	0.01	0.01
300-500	0.07	0.05	0.03	0.02	0.01	0.01
500-700	0.07	0.05	0.03	0.02	0.01	0.01
700-1000	0.07	0.05	0.03	0.02	0.01	0.01
1000-1500	0.07	0.05	0.03	0.02	0.01	0.01
1500-2000	0.07	0.05	0.03	0.02	0.01	0.01
2000-3000	0.07	0.05	0.03	0.02	0.01	0.01
3000-5000	0.07	0.05	0.03	0.02	0.01	0.01
5000-10000	0.07	0.05	0.03	0.02	0.01	0.01

Stable portions concentration on different ionic strengths are compared to MOM particle concentration as:

Ratio: Particle measured/Particle MOM

Ratio of concentration	NaClO ₄ 2.10 ⁻⁴ M	NaClO ₄ 5.10 ⁻⁴ M	NaClO ₄ 1.10 ⁻³ M	NaCl-CaCl ₂ 2.10 ⁻⁴ M	NaCl-CaCl ₂ 5.10 ⁻⁴ M	NaCl-CaCl ₂ 1.10 ⁻³ M
Ratio of concentration	0.82	0.95	0.97	0.10	0.11	0.30

- >99% Bentonite (NaClO₄) set in channels between (50-150) nm
- >99% Bentonite (Mixed) set in channels between (50-300) nm
- (50-100)nm and (100-150) nm channels the most populated channels in both electrolytes with $\frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}} > \frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}}$
- (150-200) nm and (200-300) nm channels $\frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}} > \frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}}$
- >300 nm channels $\frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}} > \frac{[Particle]_{NaClO_4}}{[Particle]_{Mixed}}$
- Disaggregation is more prompted in NaClO₄
- Concentration is lower when comparing to MOM suspension, specially in mixed water suspensions

Conclusions

When bentonite colloids are diluted in decreasing ionic strength environments: i) initial stable state is not recovered and ii) the concentration of particles is lower than the corresponding to the stable suspension. These results show that the aggregation-disaggregation process is not completely reversible.

Acknowledgment

This work has been supported by NANOBAG Ministry of Economy and Competitiveness project and BELBA EU FP7/2007-2013 project - R&D activities for FP 85-2002-2013-2014 project grant from MINECO (Spain) and EBB-14-18074 short stay grant from MINECO (Spain).



Conclusions

BENCHMARK TEST

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

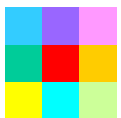
Clay	Extrusion (cm)	Rate at flow 10^{-6} m/s	Preliminar Rate at flow 10^{-4} m/s
NANOCOR	2.7 ± 0.2	$1,3E-06$ kg /y	$1,6E-03$ kg /y
FEBEX	$1,4 \pm 0.2$	$1,2E-06$ kg /y	$1,5E-04$ kg /y

STATIC EXPERIMENTS

- ❖ Colloid erosion related to clay smectite content.

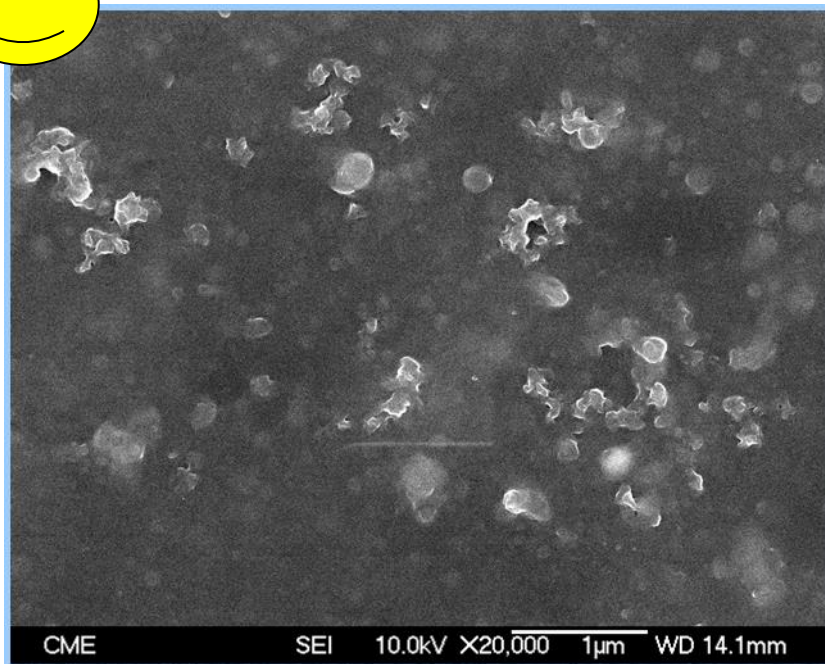
STABILITY

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





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.

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).

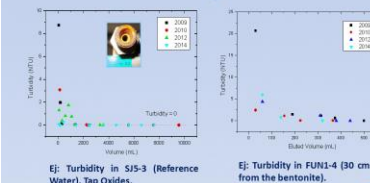
EXPERIMENTAL

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 2008 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" (SJS-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.

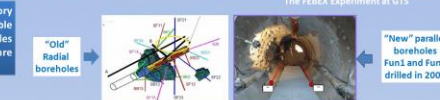


CONCLUSIONS

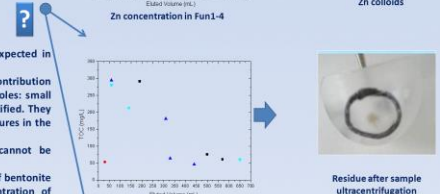
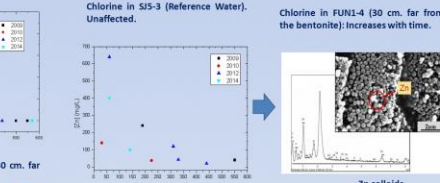
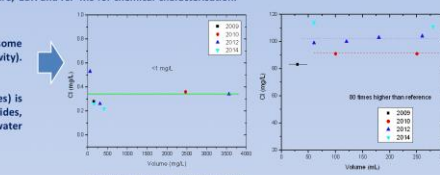
- In different boreholes, concentrations significantly higher than expected in Grimsel water (around 0.2 ppm) were found.
- Evidences of the existence of colloids other than natural. Main contribution is from artefacts produced by drilling of new experimental boreholes: small pieces of rock, heavy metals 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 chemically affected by bentonite.

ACKNOWLEDGEMENTS

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But... Al signal still quite low

Acknowledgments

BELBAR



Thank you for your attention!

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