

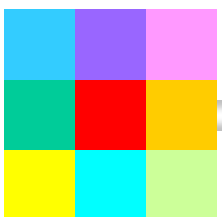
*BELBaR*



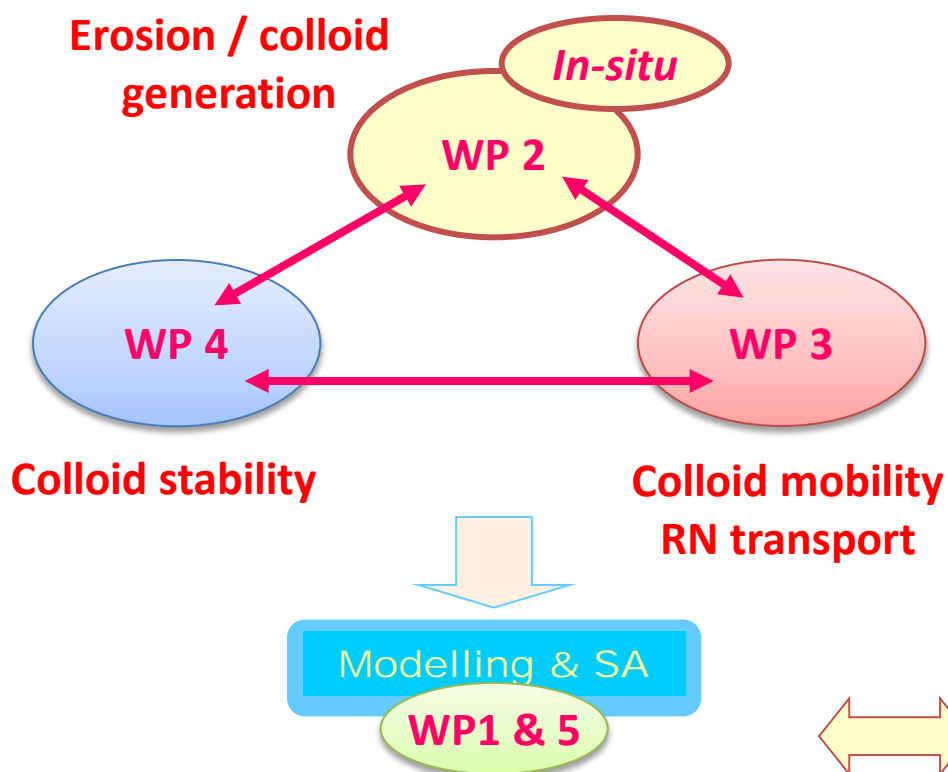
Helsinki, March 6, 2013

## **CIEMAT's activities in BELBAR: overview**

**T. Missana, U.Alonso, M.Garcia-Gutierrez,  
A.M. Fernandez, M.Mingarro  
(CIEMAT)**



## CIEMAT main effort in BELBaR: Experimental Work

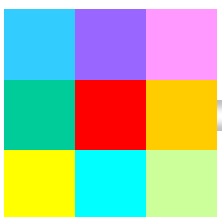


Work packages are totally **inter-dependent**. Collaboration and result transfer between them is needed.

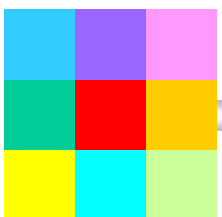
**Coherence in the selection of experimental conditions** needed even the experimental approach is different.

**Final aim:** to understand realistic scenarios; input of data for qualitative and quantitative models description in SA.

CIEMAT work is planned under these premises, taking advantage also on the experience and knowledge gathered in previous projects .



- Characteristics of the bentonite clay: smectite content; presence of certain accessory minerals (calcite, gypsum); nature of the cations present in the interlayer; total charge and charge distribution between the tetrahedral and octahedral sheets; compaction density;
- 2. Chemistry of the groundwater: ionic strength, pH, chemical composition (concentration of monovalent vs. divalent cations, potassium content);
- 3. Clay – groundwater interactions: dissolution processes and ionic exchange; kinetics of the interactions; effects of the solid to-liquid ratio; effects of hydrodynamic conditions;
- 4. Groundwater velocity at the bentonite surface: the presence of a hydraulically active fracture may play a role in bentonite erosion and has to be accounted for.
- 5. Characteristic of clay extrusion paths: porosity of the rock, fracture dimensions.



**Ursula's talk (tomorrow):**

*Summary of results already obtained with the "old" configuration :*

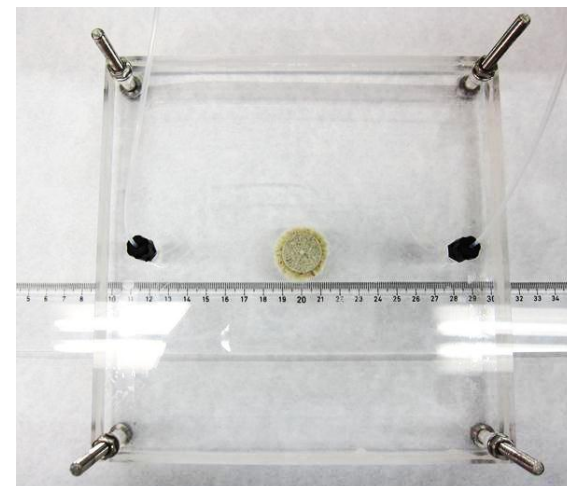
- Different clay density;
- Different clay type: raw, Ca, Na;
- Different flow rates;
- Different water chemistry;
- Bentonite/electrolyte contact area.

**Static approach**

**CHEMISTRY**

**Dynamic approach**

**CHEMISTRY  
+ FLOW**

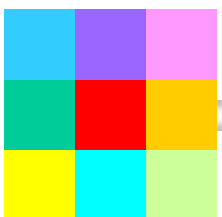


**New "radial" cells:**

**CHEMISTRY**

**+ FLOW**

**+ fracture**



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## WP 2: EROSION



FEBEX CLAY

Electrolyte

PCS analyses:  
colloid concentration  
and size

## WP2: NEW EROSION TESTS



1. Emphasis on water chemistry effects

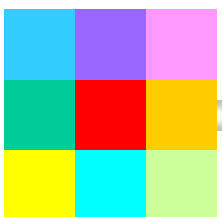


Sorption, Migration and Colloid Lab



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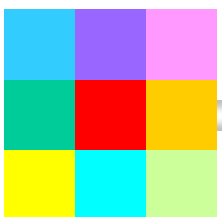


## FEBEX CLAY:

Bentonite used in the FEBEX project. Comes from the Cortijo de Archidona deposit in Spain.

The CEC is 102 meq/100 g; Main exchangeable cations: Ca (42 %); Mg (33 %); Na (23 %); K (2 %).

Mineral	(%)
Smectite	92±3
Quartz	2±1
Plagioclase (Na, Ca)	3±1
Cristobalite	2±1
K-Feldspar	Traces
Calcite	1±0.5



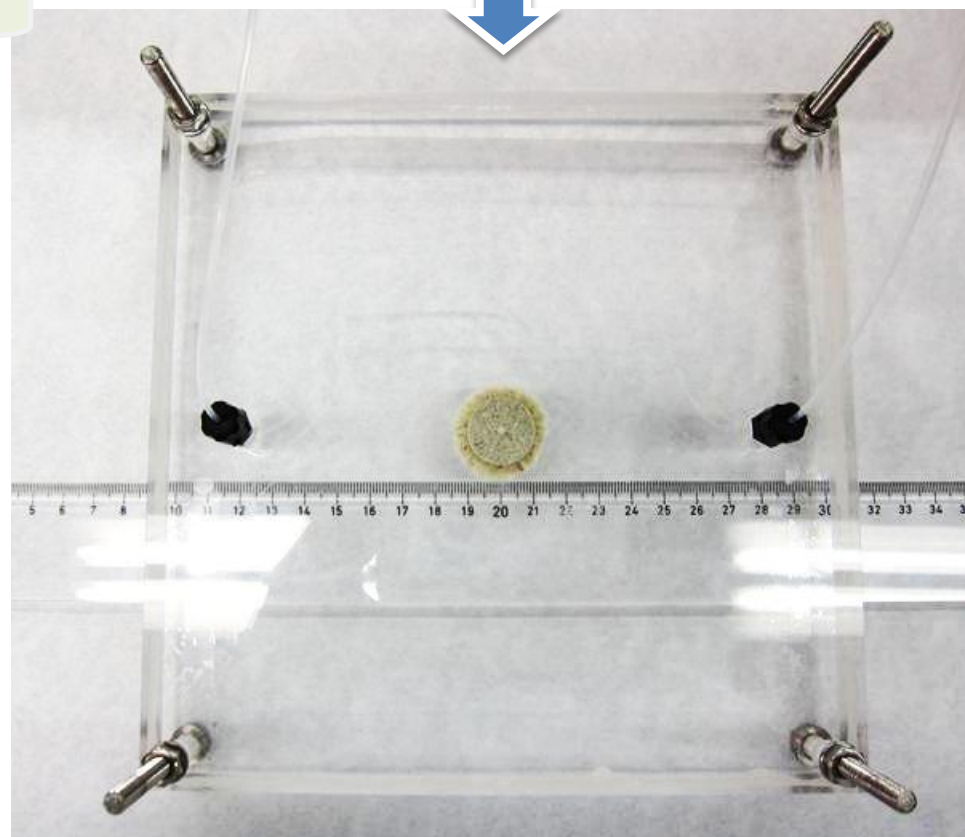
FEBEX CLAY

1.  $\text{NaClO}_4$
  2.  $\text{Ca}(\text{NO}_3)_2$
- 1E-03 M

CELL number 4 – 29/1

- FEBEX 1.65 g/cm<sup>3</sup> - 5.31 g / 19 x 9.8 mm;
- Solution: 10<sup>-3</sup> M  $\text{NaClO}_4$
- Fracture : 0.18 mm
- Q = 8.2 mL/h v=7E-05 m/s

Experimental cell



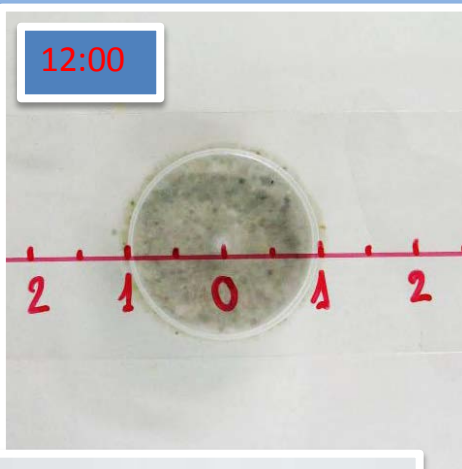


# Evolution of bentonite in the cell with $\text{NaClO}_4$

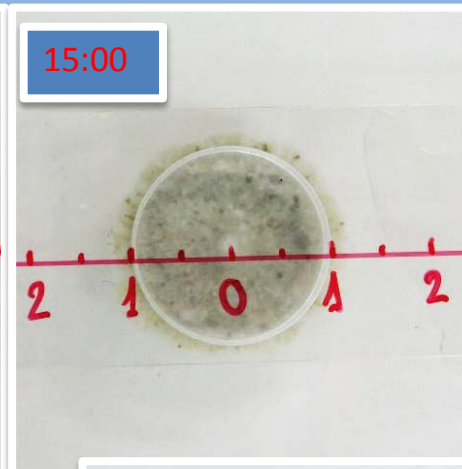
11:40



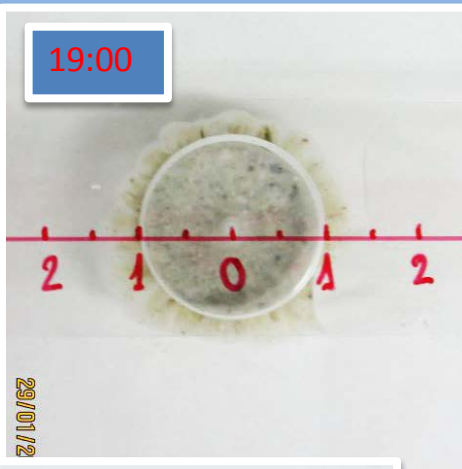
12:00



15:00



19:00



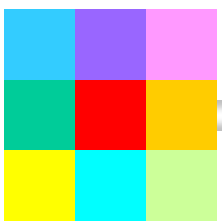
1d + 11:40



2d + 9:30



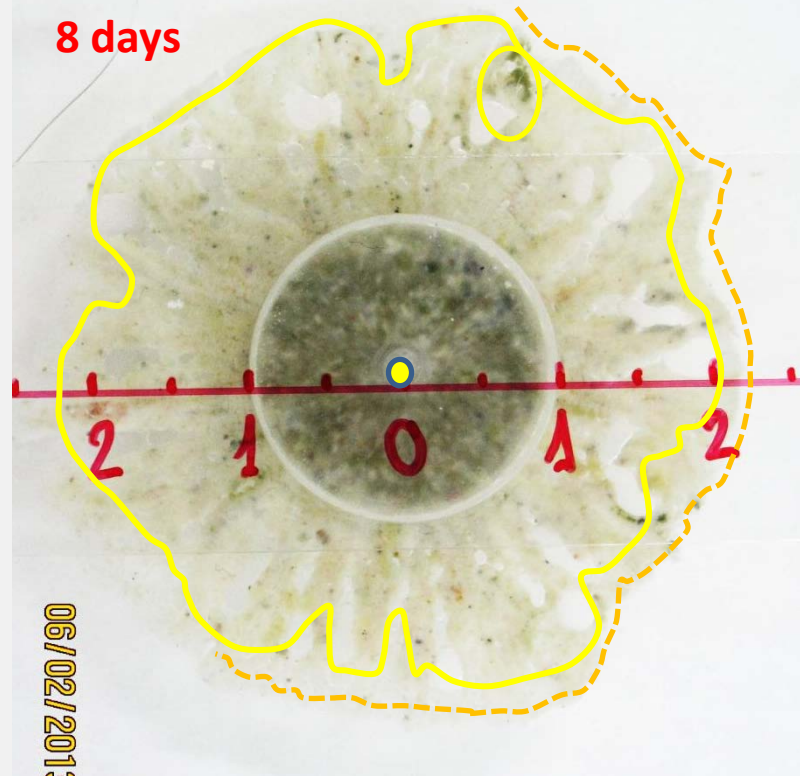




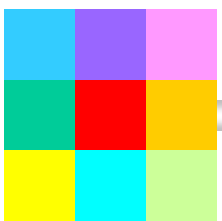
2 days



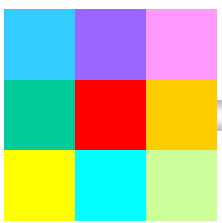
8 days



Gel front velocity decreases significantly after the first day

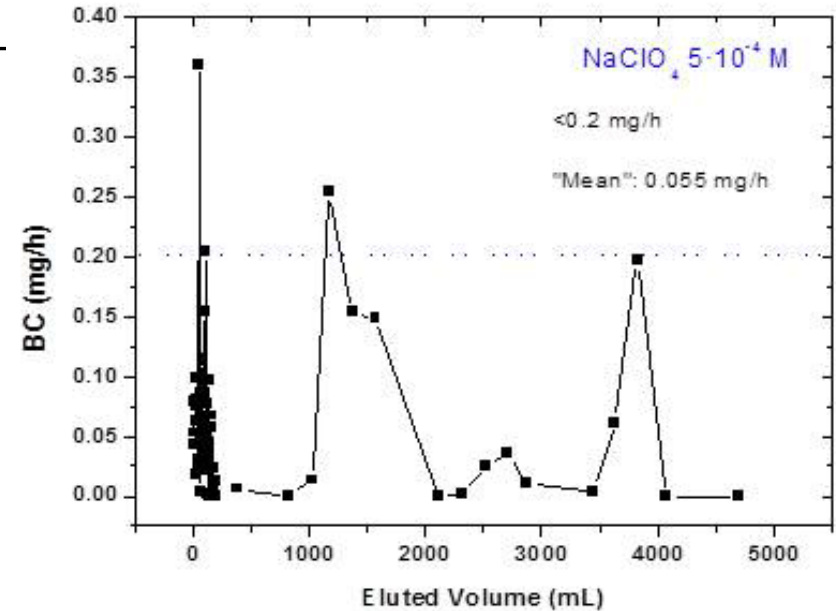
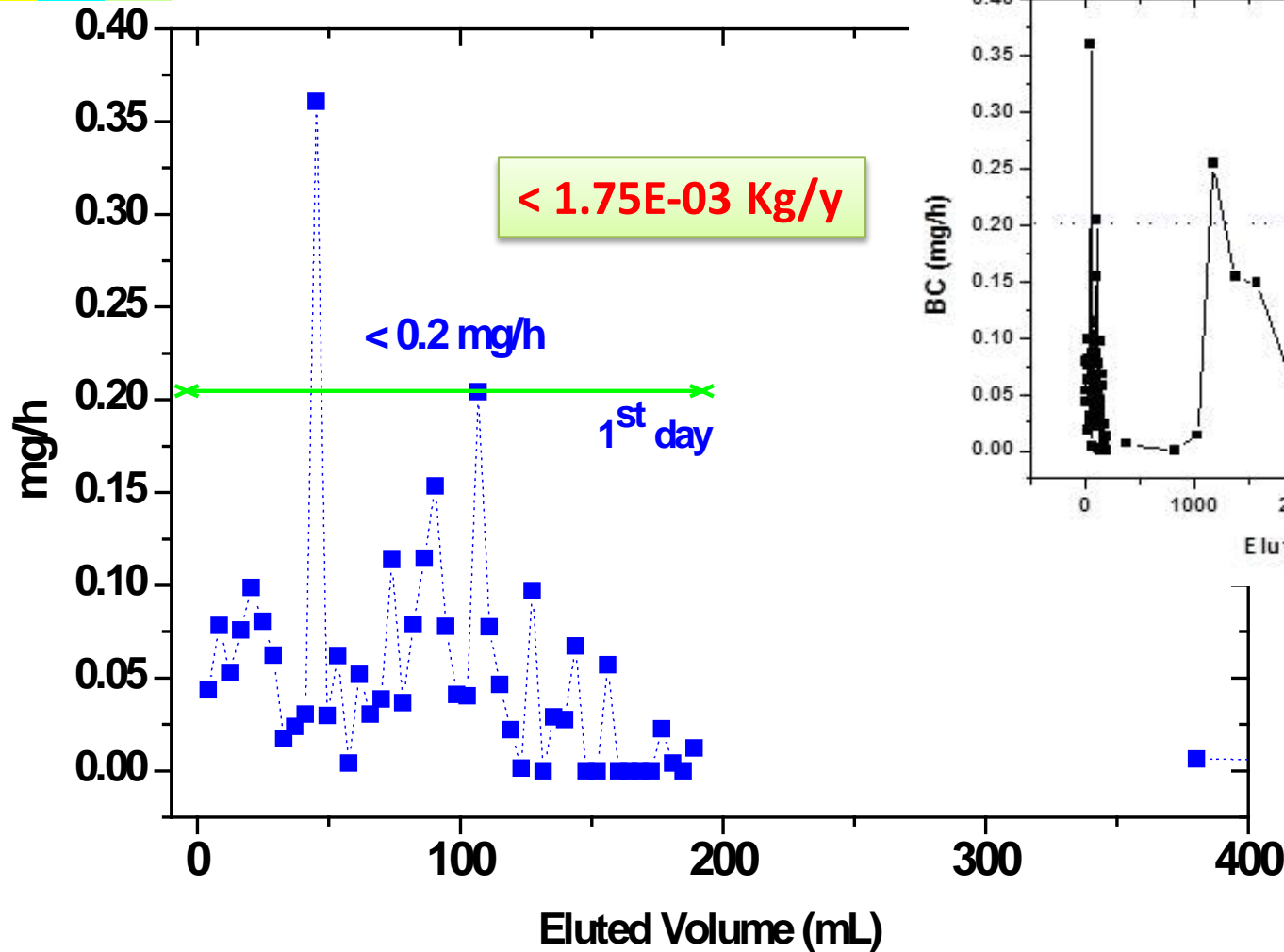


Gel is depleting: source of particles



BELBaR

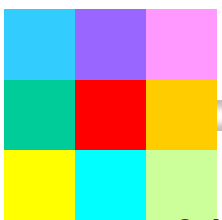
FEBEX,  $\text{NaClO}_4$



$< 1.7\text{E-}03 \text{ Kg/y}$

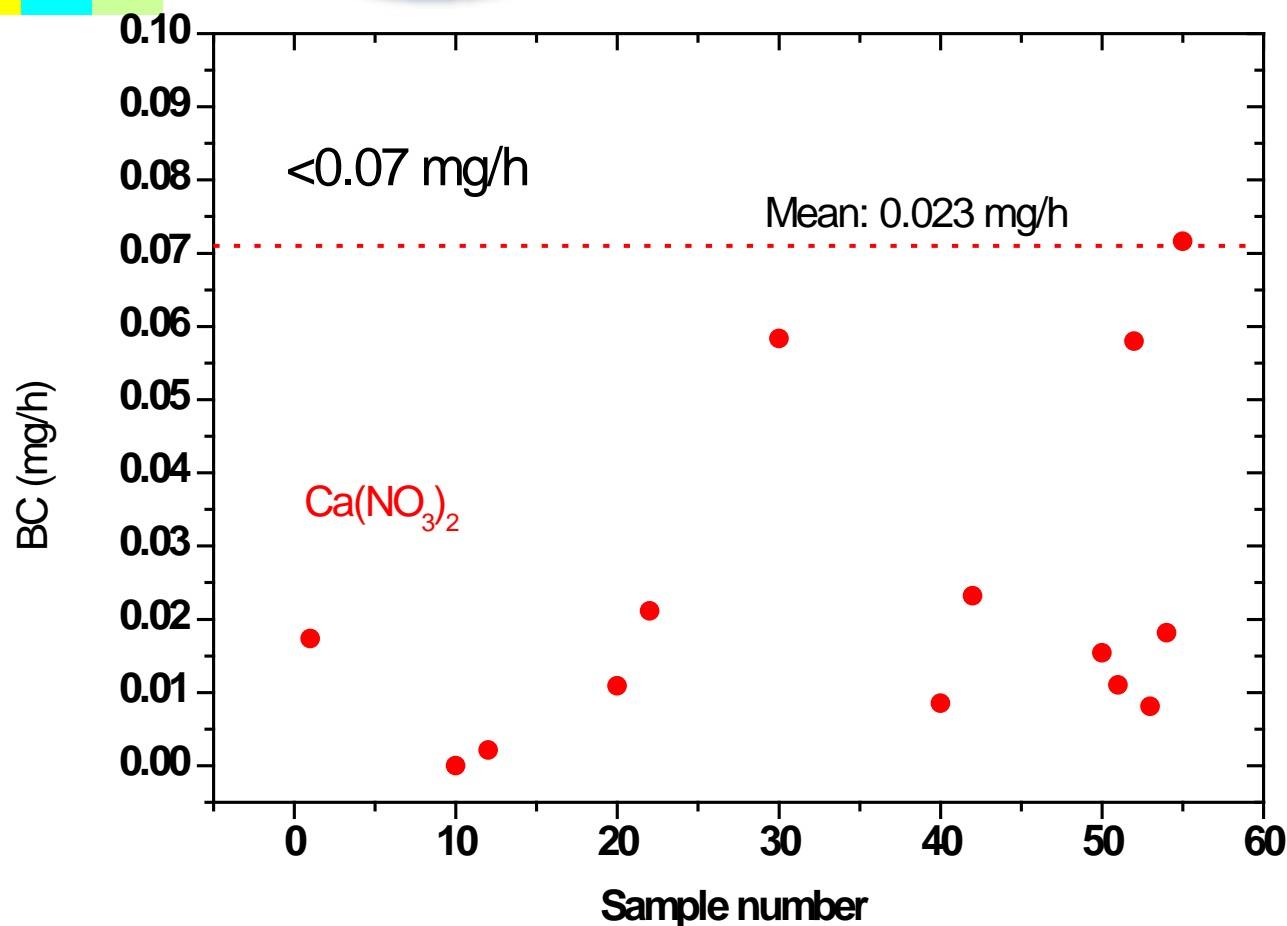
Mean:  $4.8\text{E-}04 \text{ Kg/y}$

$4.4 \text{ mg/(y} \cdot \text{cm}^2) (2.6)$



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FEBEX,  $\text{Ca}(\text{NO}_3)_2$



Data analysis not completed

CELL number 1 – 20/2

FEBEX  $1.65 \text{ g/cm}^3$  -  
 $5.31 \text{ g} / 19 \times 10.1 \text{ mm}$

Solution:  $10^{-3} \text{ M}$   
 $\text{Ca}(\text{NO}_3)_2$

Fracture : 0.18 mm

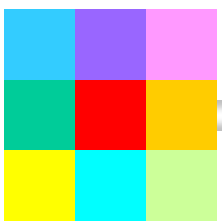
$Q = 8.0 \text{ mL/h}$

<  $6.1\text{E-}04 \text{ Kg/y}$

Mean:  $2.0\text{E-}04 \text{ Kg/y}$

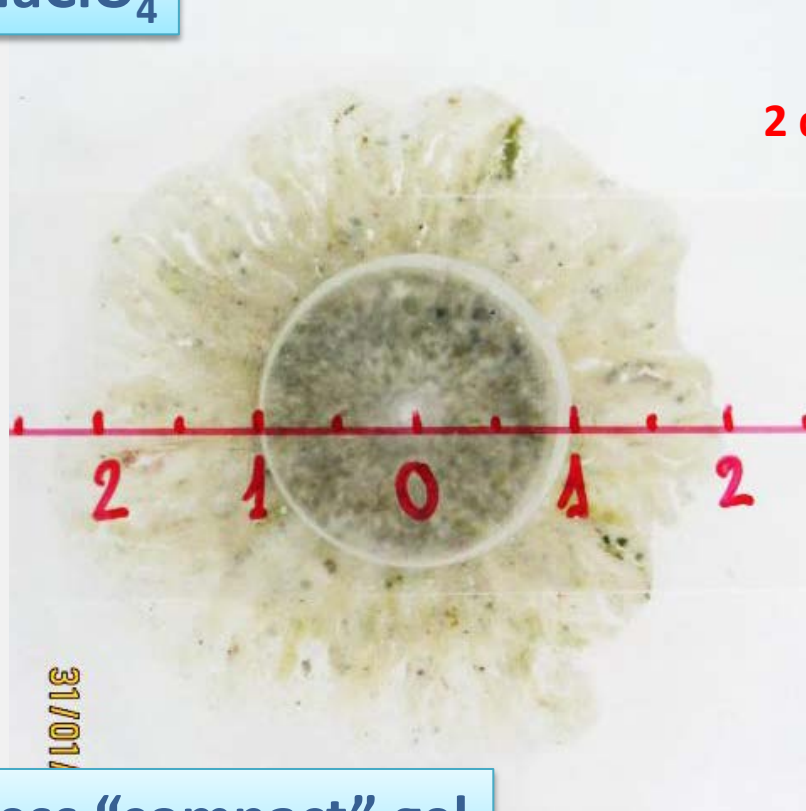
$1.9 \text{ mg}/(\text{y} \cdot \text{cm}^2) (0.5)$





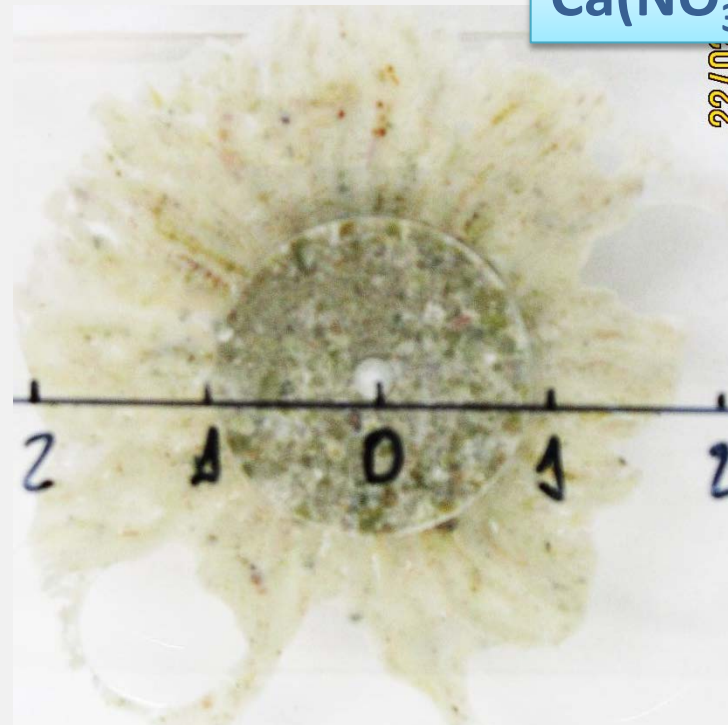
$\text{NaClO}_4$

2 days



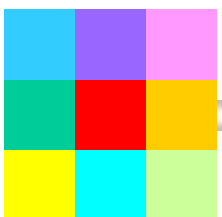
Less "compact" gel

$\text{Ca}(\text{NO}_3)_2$

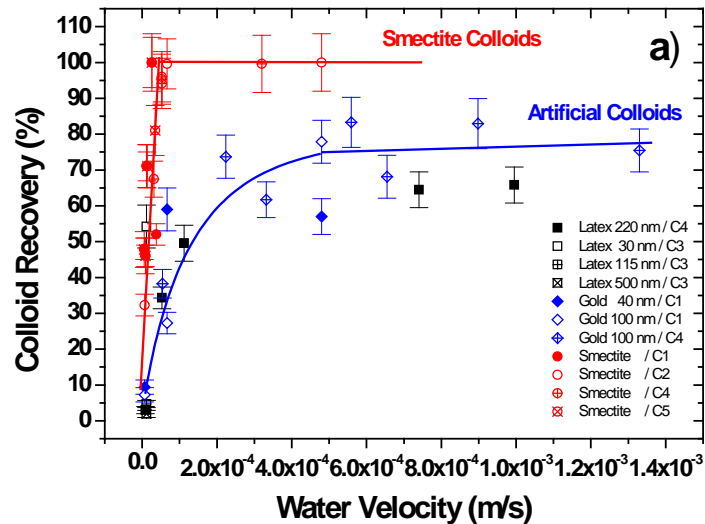
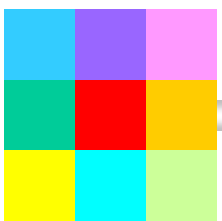


- The quantity of colloids generated from compacted FEBEX bentonite, under similar geometrical and water flow conditions, depends on the contacting electrolyte;
- The quantity of extruded material is similar, but the presence of Ca in the electrolyte decreases the erosion;
- Gel is more easily depleted in absence of Ca;
- Generation rate seems decreasing upon time; gel front velocity decreases.
- The swelling pressure is the first driving force for colloid generation determining the thickness of the gel layer, extruding in fractures and potentially subject to erosion. The presence of colloids in solution will be limited to the surface *available for colloid transport* (fracture) and not to the surface available for clay hydration.
- Results (also quantitatively) are basically in agreement with previous tests. (Missana et al, 2011);

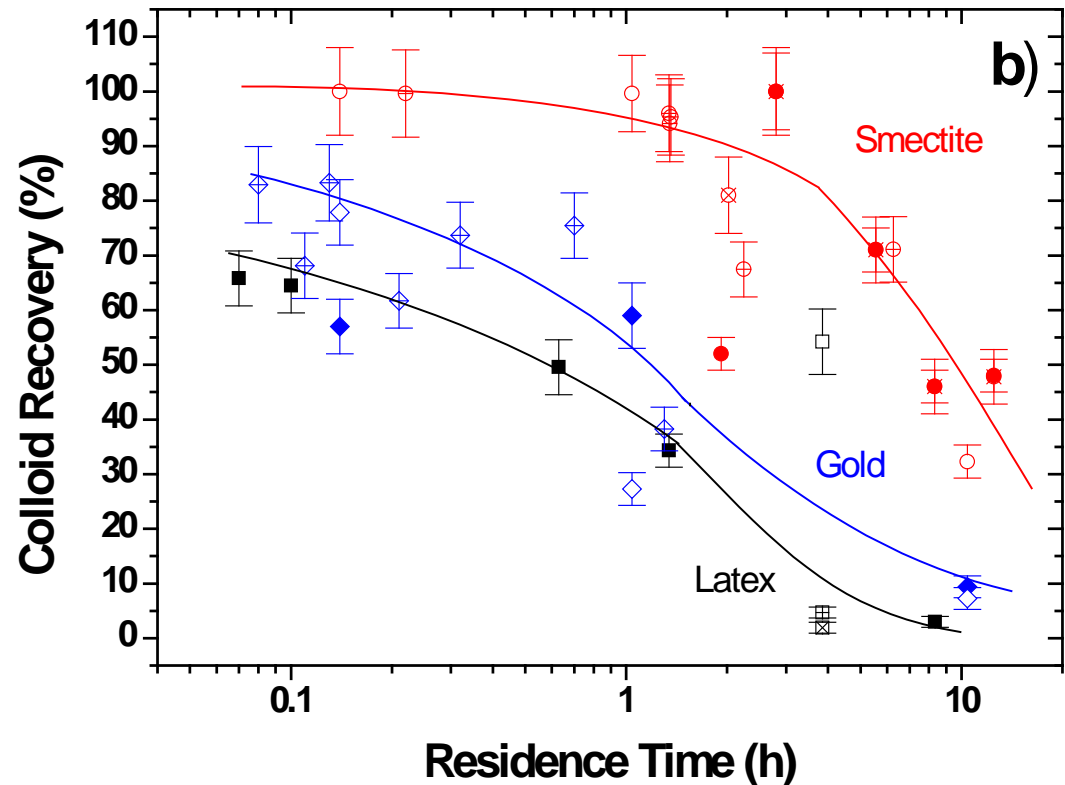




- Understanding of colloid/rock interactions in a crystalline rock. Data on colloid filtration obtained at the macroscopic scale (by performing transport experiments) have to be related with data obtained at the micro-scale, where colloid/rock interactions take place.
- Analyses of RN transport in the presence of bentonite colloids. Overall behaviour.
- Reversibility of adsorption in bentonite colloids;

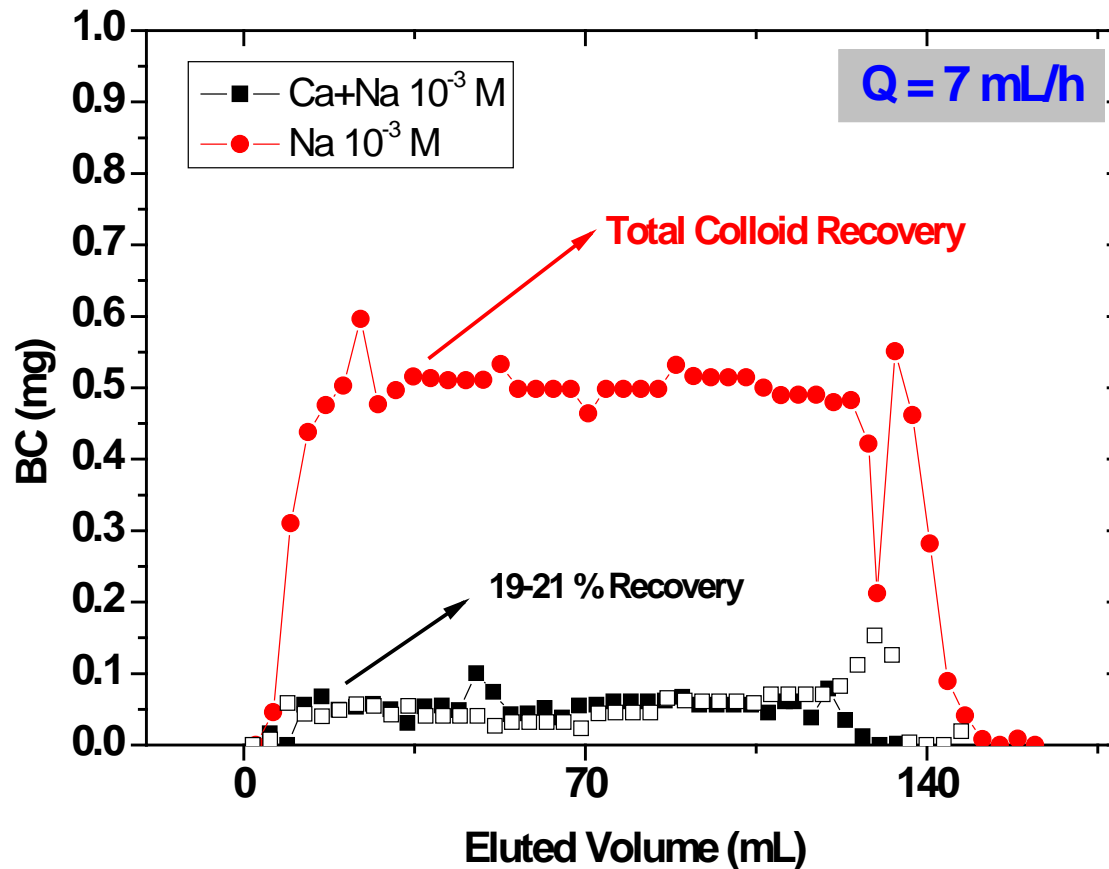


(Albarran et al, Coll Surf A, 2013)



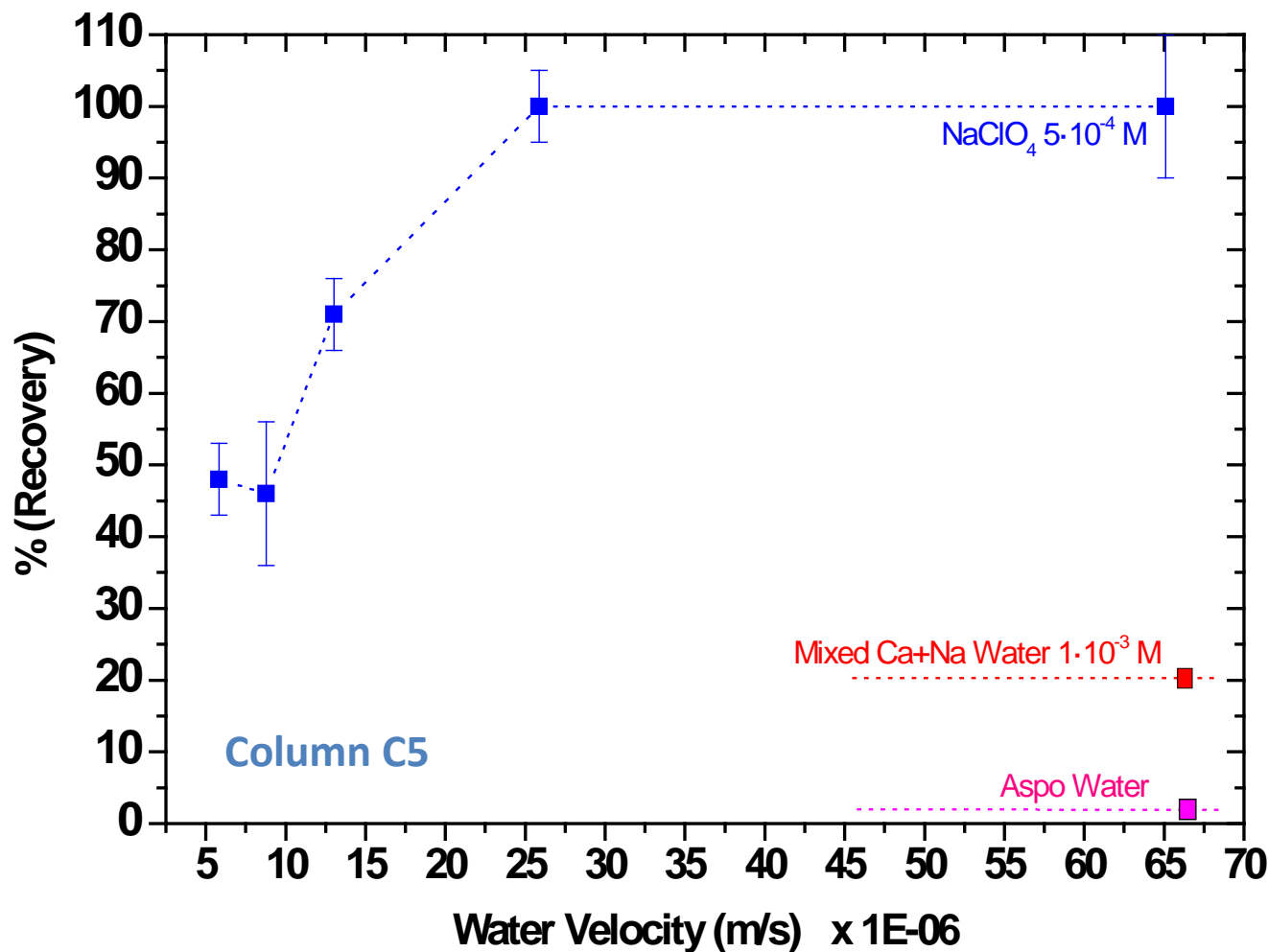
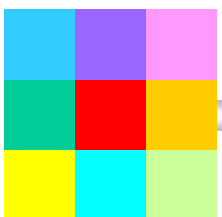
- Filtration under unfavourable conditions;
- Previous results showed the important effect of the residence time on colloid filtration in a fracture; roughness effects;
- BC behaviour different with similar charge ;

- New: emphasis on water chemistry effects. Flow selected to maximize BC recovery



Calcium promotes  
Colloid aggregation and  
filtration

Significantly less colloid elution  
observed in the presence of  
small ( $2.00 \cdot 10^{-4}$  M) Ca.



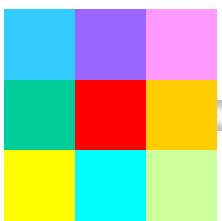
1. Water Flow Rate

2. Chemistry (colloid size & stability)

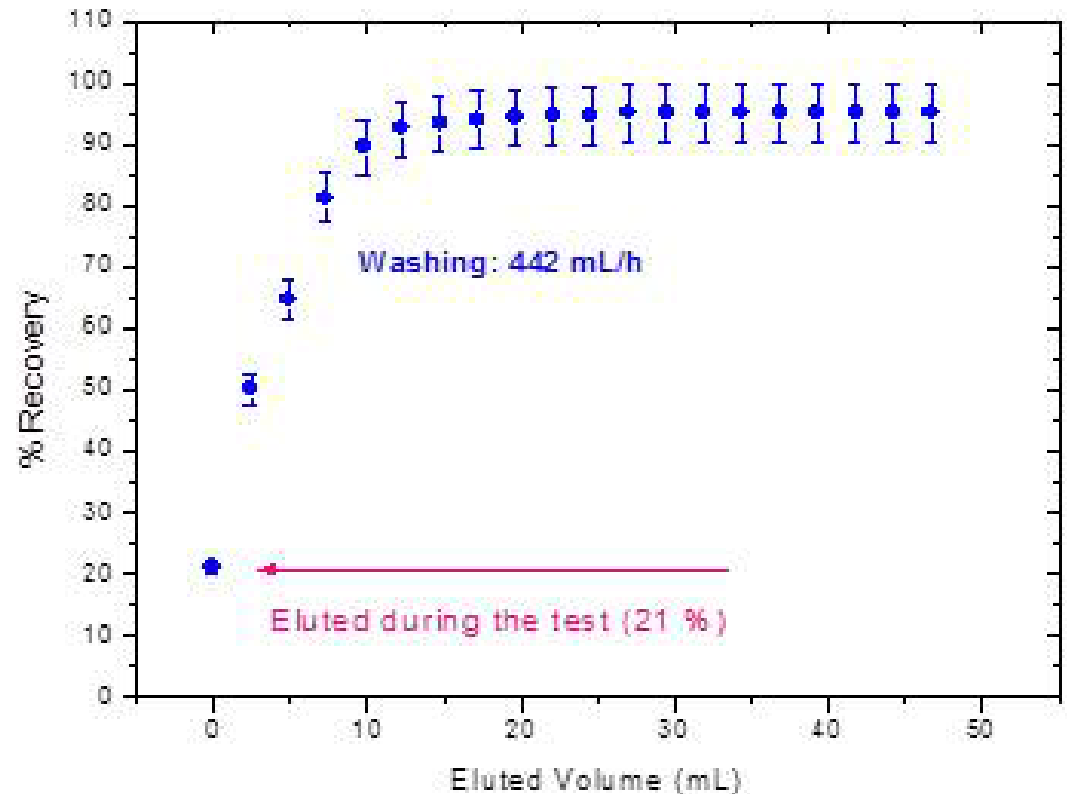
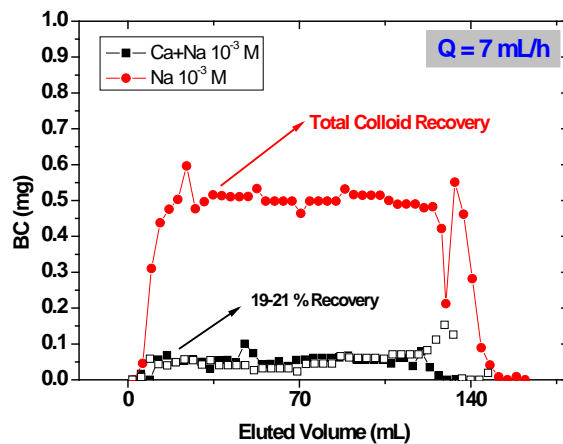
ACT jointly on BC retention

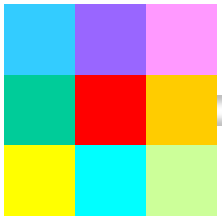
Attachment  
Reversibility

- By flow
- By chemistry ?



## Reversibility ?





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WP 3: ROCK & RN interact.



## WP 3: RN +bentonite colloids.



Comparison of cesium transport behaviour in two very different chemical environments:

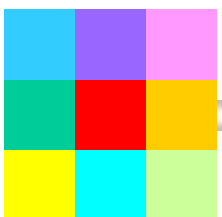
Grimsel

Äspö

“stable BC”

“unstable BC”





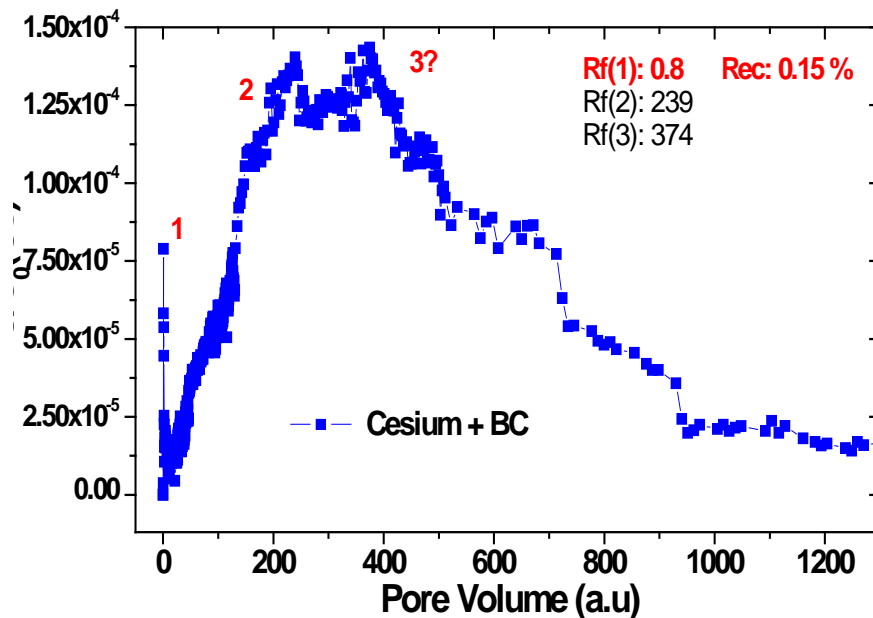
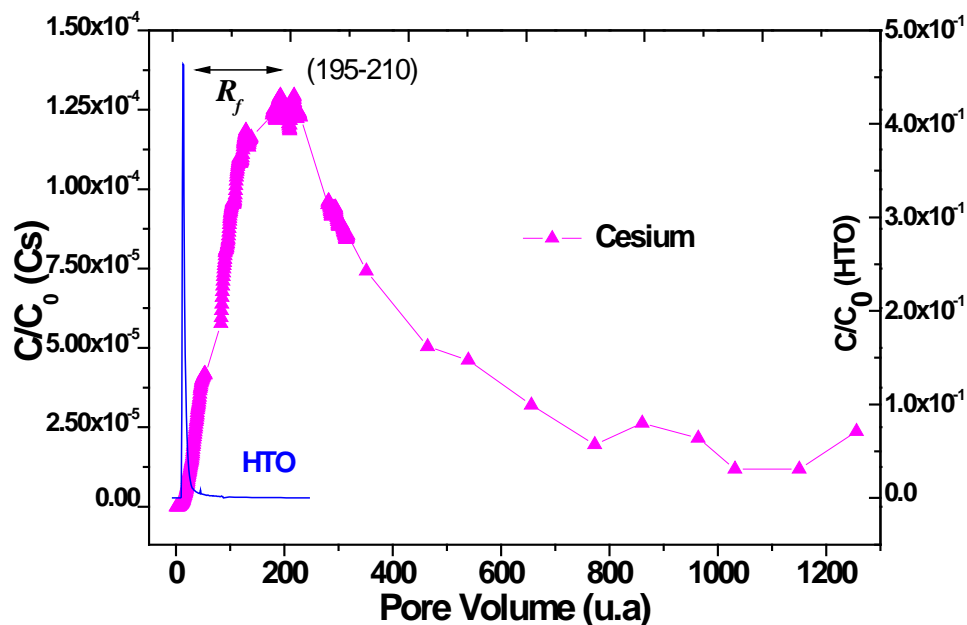
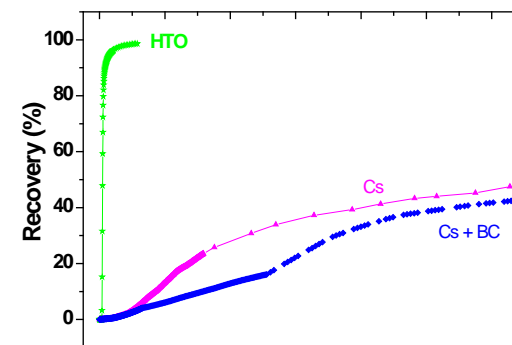
COLUMN: C6 Grimsel --- Solution:  $5 \cdot 10^{-4}$  M  $\text{NaClO}_4$

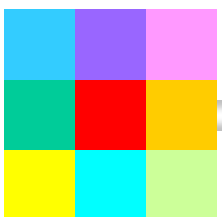
Colloids: FEBEX, 100 ppm

Cs:  $Q = 4.5$  mL/h ;  $v = 3.8 \cdot 10^{-5}$  m/s;  $rt \sim 2$  h

Cs+BC:  $Q = 4.4$  mL/h ;  $v = 3.5 \cdot 10^{-5}$  m/s;  $rt \sim 2$  h

Cesium recovery similar in both cases 48 % (Cs), 43% (Cs+BC) .





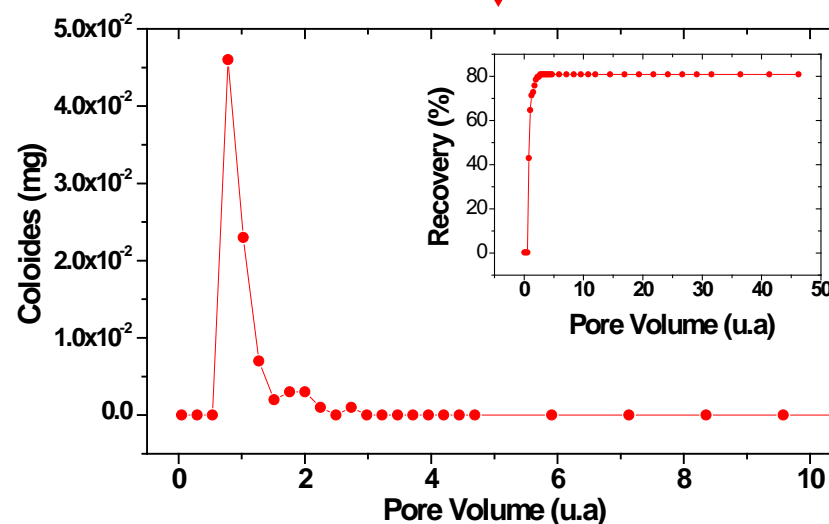
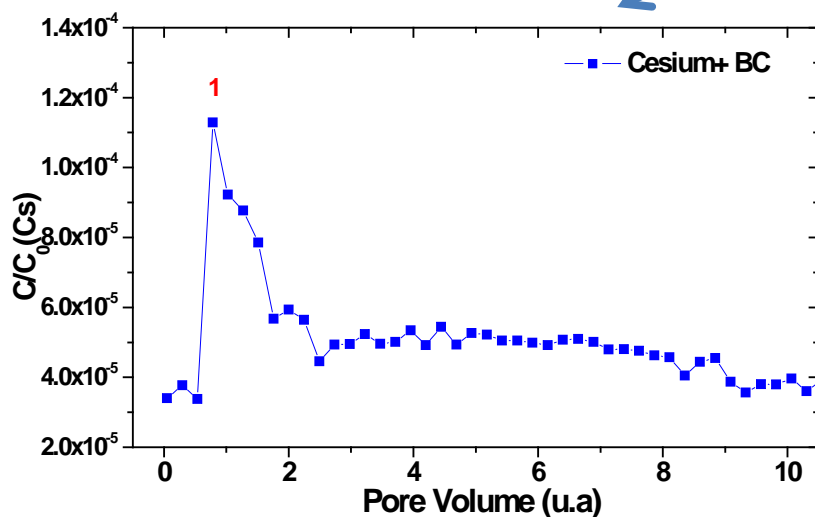
COLLOID RECOVERY: 81 %

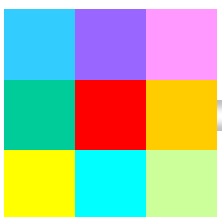
Unretarded cesium perfectly visible but only **0.15 %** of the injected is recovered.

Initial sorbed cesium = 80 %

**Cs is desorbing**

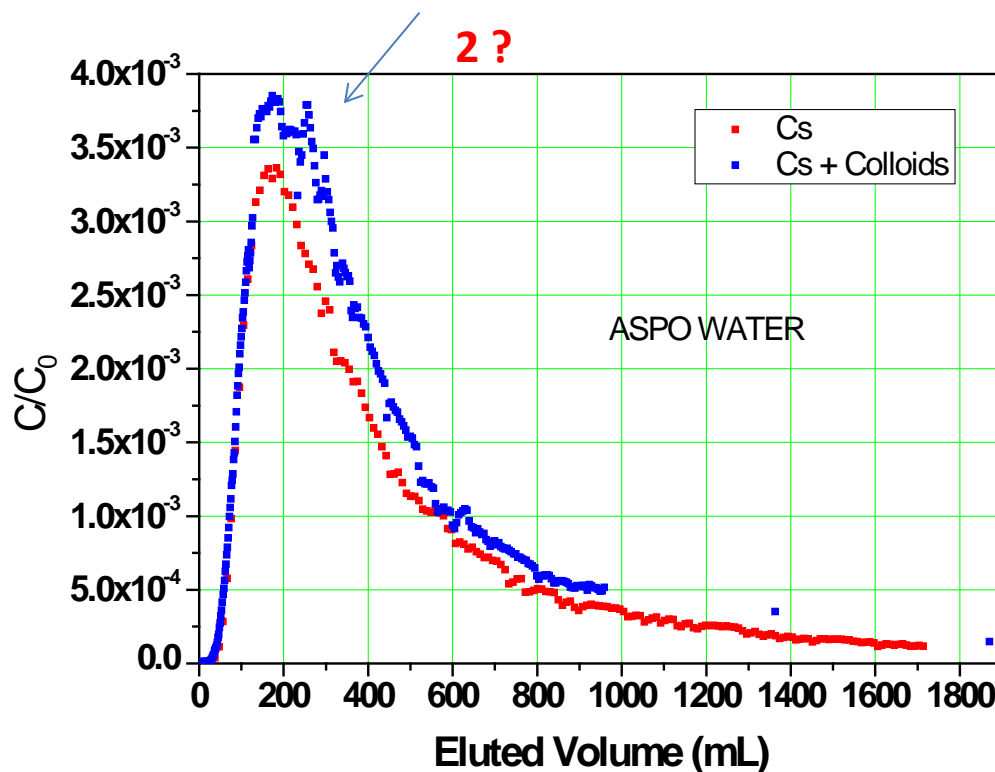
Cesium activity  
**PCS analyses**



**COLUMN 1: ASPO: Aspo Synthetic Water****Colloids: FEBEX, 100 ppm****Cs: Q = 1.71 mL/h ; Cs+BC: Q = 1.66 mL/h ;**HTO peak  
~ 1 mL

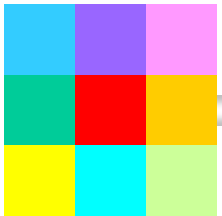
Rf=174

Rf=270 ?



No colloid elution  
observed !!  
No unretarded Cs  
peak !

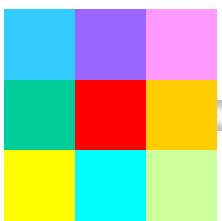
Initial absorbed Cs  
20 %



### COMMENTS on RN transport in granite fracture:

The existence of additional peaks in the presence of bentonite colloids ( $R_f > 1$ ) was already observed: f.e. transport of Sr (Albarran et al, JCH, 2010);

RN desorption during transport in column (favourable case): Cs (here); Sr and U (Albarran, Ph.D Thesis, 2010); Eu not for Pu (Missana et al App. Geo, 2008).



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WP 3: ROCK & RN interact.



**Combining generation and filtration effects  
is important for RN transport evaluation.**



**Future tests:**

**Granite Base**

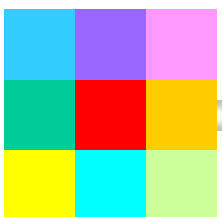


Sorption, Migration and Colloid Lab



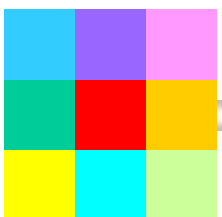
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- Under similar geometrical and water flow conditions, the recovery of colloids strongly depends on the water chemistry;
- Retention of colloids can be reversible (flow and chemistry changes);
- The effect of the presence of bentonite colloids is always clearly visible in the “Grimsel case” (favorable for colloid stability);
- However, the presence of colloids is not very significant for cesium transport because cesium is desorbing from colloids;
- In the “Äspö” case, the presence of colloids is almost insignificant on the overall transport;
- But... in all the cases, retained colloids possibly contribute to RN retardation.

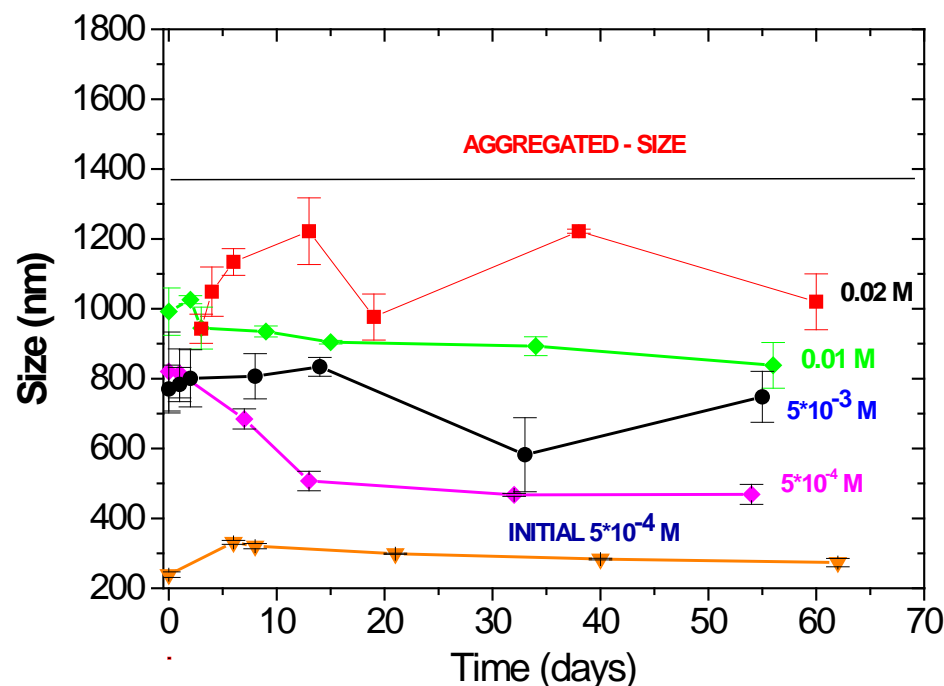




## WP 4

1. Coagulation / peptization kinetics of clays. Reversibility;
2. Comparison of surface properties and stability of different clays:

## (2) Des-aggregation (dialysis)



First year results' already presented in the Montpellier meeting

Thanks for your attention !!