BELBaR

EURATOM

Karlsruhe, October, 2015

WP3: COLLOID -RADIONUCLIDE AND -HOST ROCK INTERACTIONS

SUMMARY OF RESULTS CIEMAT

Physico-chemistry of Actinides and Fission Products Unit

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Issue	Safety case position at start of BELBaR	Need for additional studies
Colloid mobility controlling processes	Clay colloids have not been considered radionuclide carriers due to the assumed low contribution. Rather than attempting to develop detailed process models for colloid-facilitated transport, potential mitigating processes are ignored so as to place an upper bound on the possible effect.	Validation or invalidation of this assumption (WP3). Is there an upper bound for colloid mediated transport?
Radionuclide sorption	To assess the possible role of rapid reversible sorption/desorption onto colloids in facilitating transport, the following assumptions have been adopted: 1. equilibrium sorption of radionuclides onto mobile and immobile colloids, 2. equilibrium sorption of colloids onto fracture surfaces, and	Is the assumption of reversible, linear sorption of radionuclides onto colloids justified? (WP3)

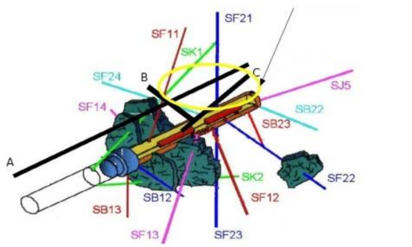
(If generation occurs) COLLOID driven radionuclide migration will be relevant only if colloids are mobile and the contaminant irreversibily sorbed.

COLLOID MOBILITY ⟺

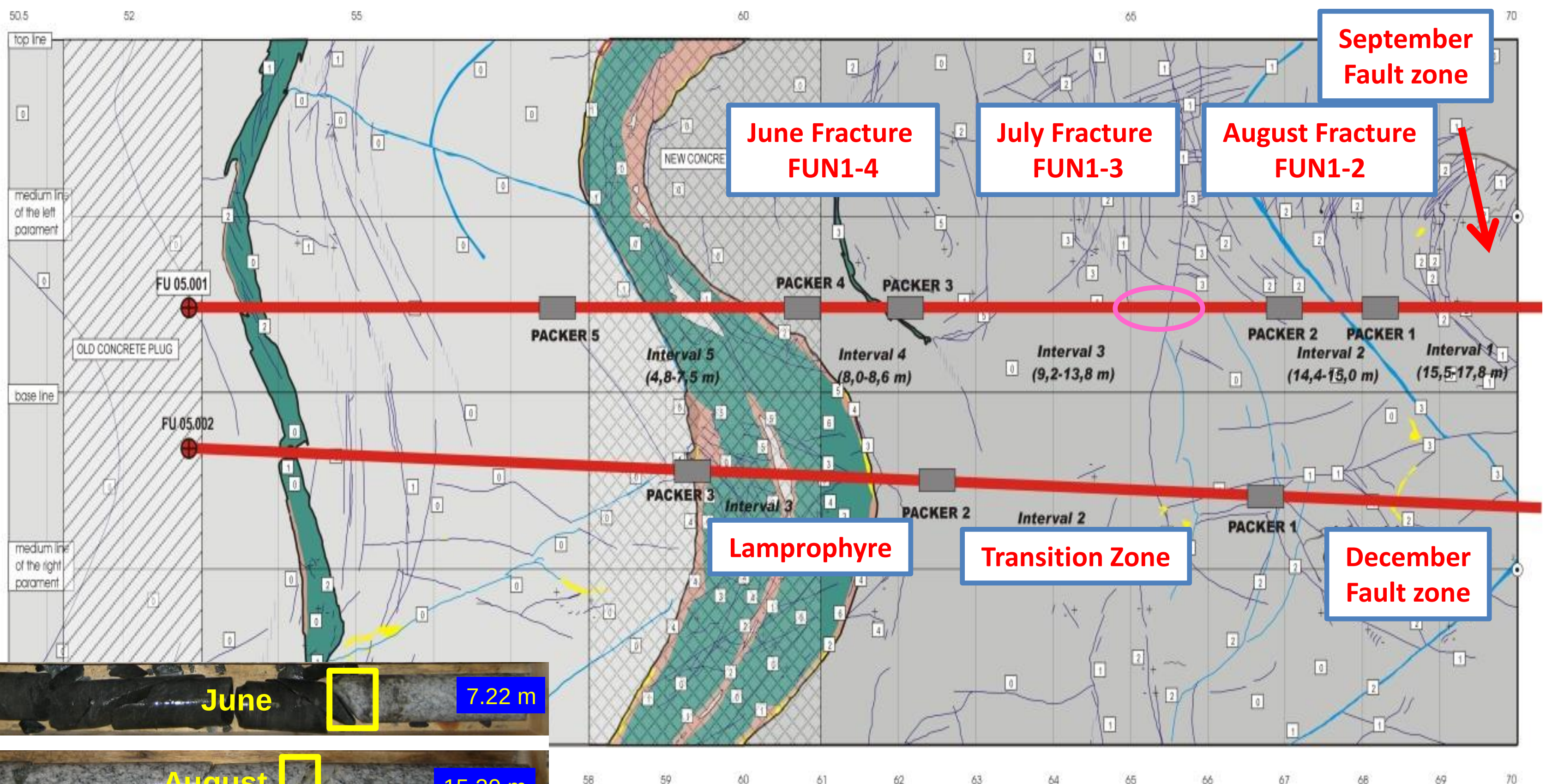
- Colloid size and stability - water chemistry;
- Colloid/rock interactions: very relevant;

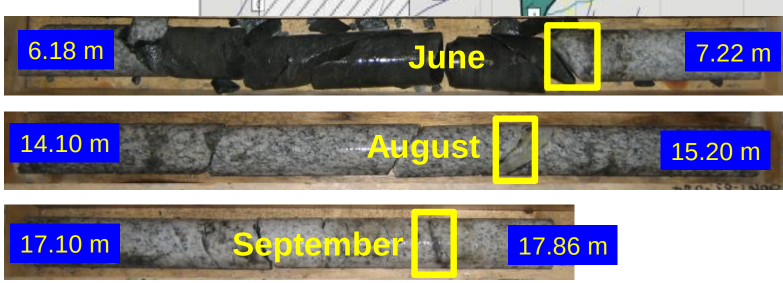
- **Ej: Grimsel Test Site groundwater (low saline and alkaline) presents conditions quite favorable for (bentonite) colloid stability.**
- **Colloid stability in Grimsel water has been largely demonstrated in laboratory (equilibrium size ~ 300 nm). Transport in fractures, in principle, would be a possible transport process.**
- **BUT what we observed in laboratory in transport tests and also *"in-situ"* ?**

In-situ study: the presence of the FEBEX project (1996) at the GTS was an unique opportunity to analyse, the behaviour of BC under realistic conditions for a DGR.



- The study started in 2006 in EC-FUNMIG, the last sampling was carried out in Oct. 2014 (after 18 years of the presence of bentonite in the tunnel).
- Colloid analyses were carried out in the waters from two new boreholes, drilled during the EC-FUNMIG project (FUN 1 and FUN 2), parallel to the bentonite surface and relatively near to it (20-50 centimetres).
- Different fractures cut both boreholes, all with low transmissivity ($1 \cdot 10^{-11}$-$1 \cdot 10^{-12}$ m^2/s) with exception of the interval 1 of FU1 (6-$8 \cdot 10^{-10}$ m^2/s) at the back of the gallery.
- Data from some selected older radial borehole, were also taken as reference.

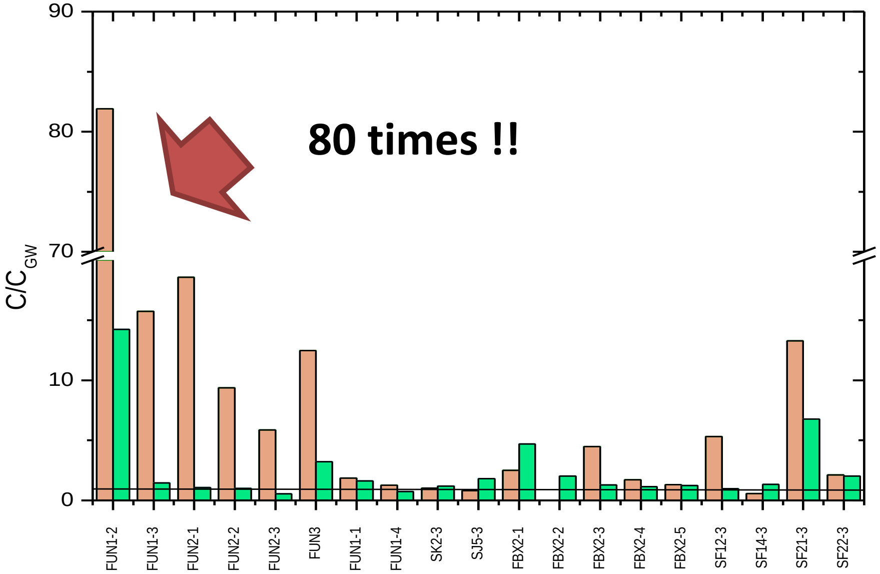




FEBEX TEST: Main experimental boreholes

First phase of the *in-situ* study (2006-2009)

Several samples, above all in the new drilled boreholes, showed surprisingly high colloid concentration (by PCS) even after filtering.
Natural Grimsel background around 0.2 ppm.



- In some interval of new boreholes, clay colloids identified (in very low concentration).

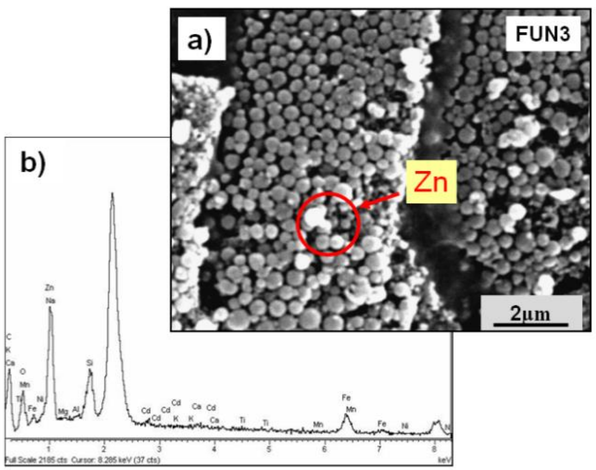
  BUT :

- Lot of possible interferences biasing the identification of “bentonite colloids” were also identified.
- Analysis of these artefacts analysis was absolutely necessary: big particles from drilling, iron oxides from taps, heavy metals and organics (from drilling fluids ?).
- Non reproducible results, not clear trends.

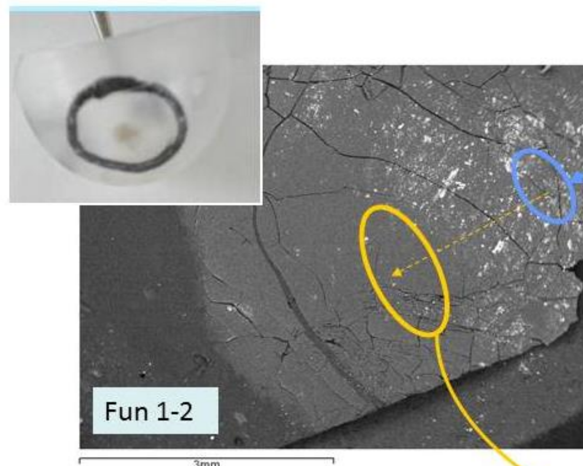
Example of colloid artifacts observed (2006-2009)

- Present in the boreholes, external tubing etc. Stable.
- Unaffected water: zero turbidity, low metal concentration TOC<3 mg/L

Tap corrosion



Heavy metals



Element	Atomic%
O K	58.62
Mg K	0.78
Al K	3.04
Si K	11.67
P K	1.71
S K	3.62
Cl K	0.57
K K	0.75
Ca K	0.86
Ti K	0.01
Mn K	0.01
Fe K	15.38
Ni K	0.00
Cu K	0.90
Zn K	0.81
Sr L	1.27
Totals	100

High TOC values

Sample holder, C, to identify heavy metals.

Decrease Al, Si, Fe
Increase O, P, S

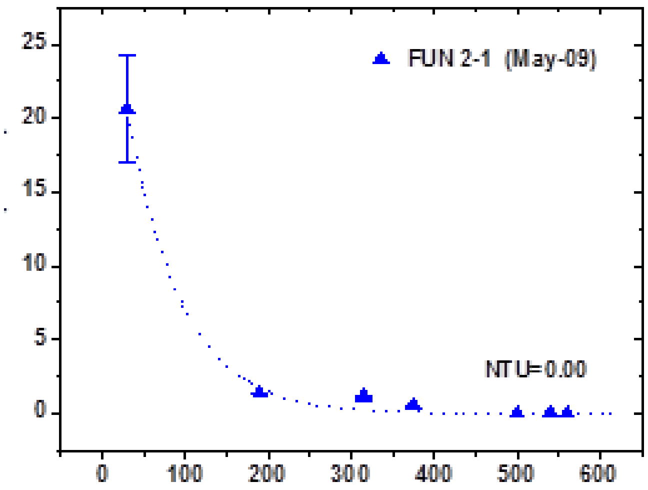
Organics

To "observe" BC it was necessary to minimize these artefacts contribution

"New approach" (kinetic) needed to understand the actual possible contribution of bentonite colloids (BC) and above all to compare adequately results from a sampling to another.

- Kinetic behaviour: when the sample is taken is very important for results comparison.
- "Contamination" usually decreases as the volume eluted increases. Other chemical element are stable.
- Very important for BC analyses.
- BC have to be studied at the "steady state"

Ex: Turbidity evolution



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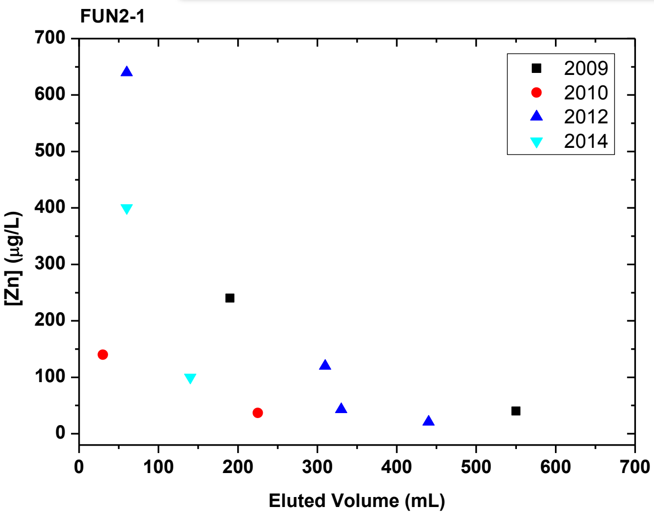
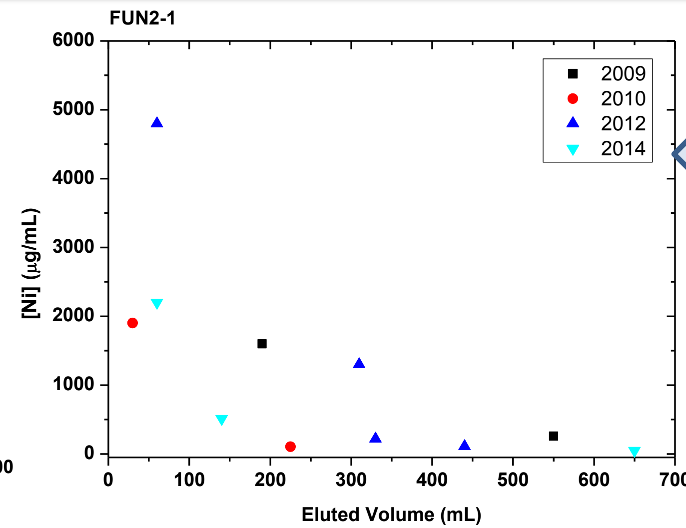
Example of new borehole measurements

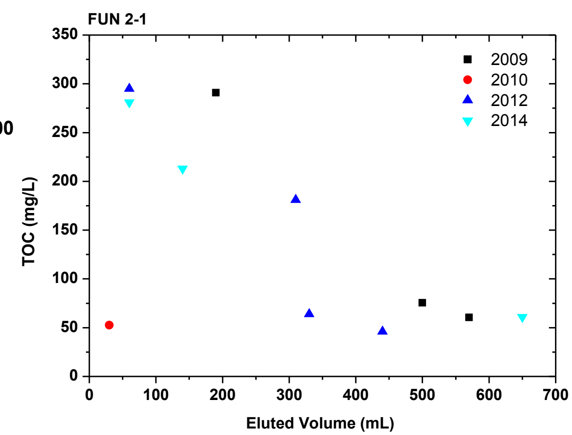
Non zero turbidity, high concentration of anomalous elements, high TOC





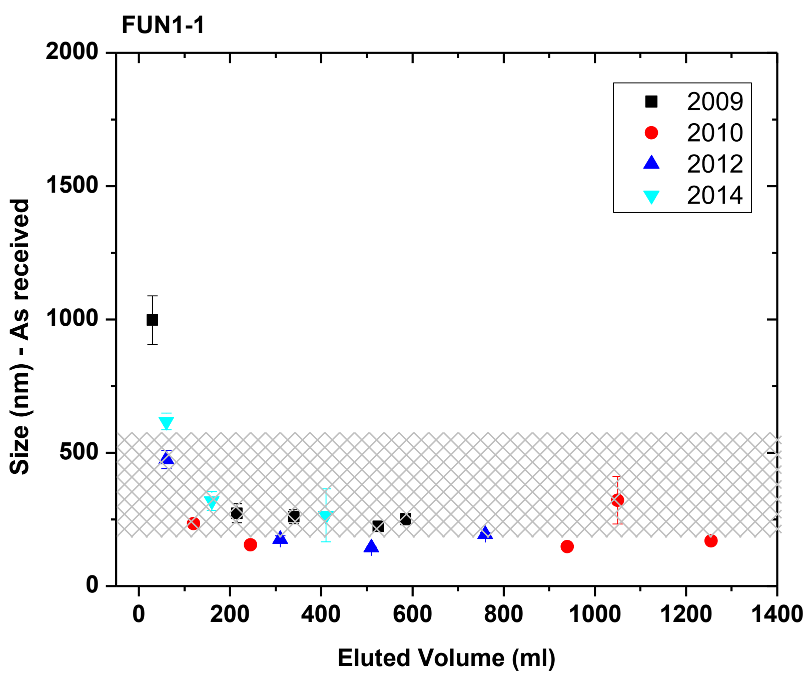
High Zn and Ni

High TOC

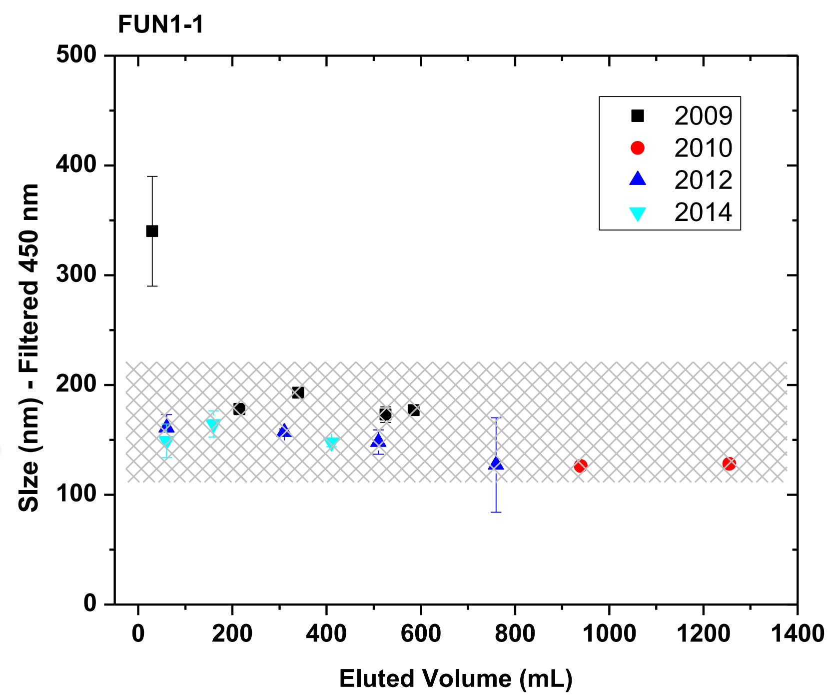


Fun 1-1 borehole: example of size of particles

As-received



Filtered 450 nm



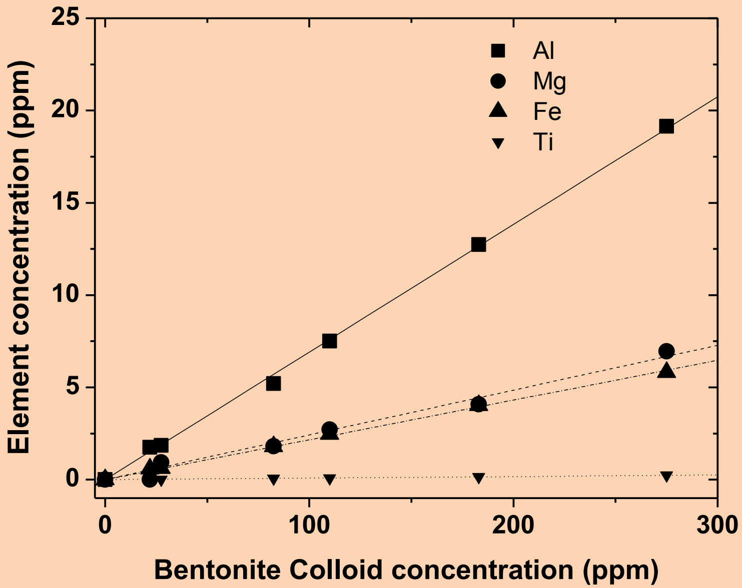
Consistent measurements in different samplings and intervals

Summary of turbidity and concentration ratio data on as-received samples (2009-2014)

Interval	Range of turbidity (general)	Range of turbidity (last 2 samplings)	Range of concentration ratio (general)	Range of ratio of last 2 samplings and colloid concentration estimation
FUN1-1	<10	<5	<40	<5 (0.75-1 ppm)
FUN1-2	<5	<5	<20	<5 (0.75-1 ppm)
FUN1-3	<5	<2	<10	<5 (0.75-1 ppm)
FUN1-4	<10	<5	<25	<10 (1.5-2 ppm)
FUN1-5	<5	<2	<10	<10 (1.5-2 ppm)
FUN2-1	<5	<1	<10	<5 (0.75-1 ppm)
FUN2-2	<2	<1	<10	<3 (0.45-0.6 ppm)
FUN2-3	<1	<1	<5	<2 (0.3-0.4 ppm)

LOW

Supporting chemical analyses: Al, Mg, Fe, Ti



Not detected in significant concentrations

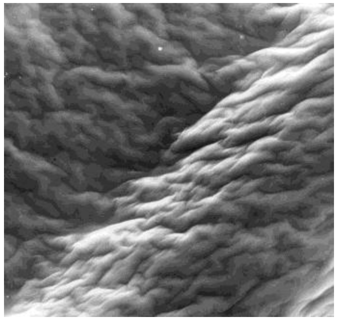
"conditio sine qua non"

No evidence of the presence of BC in the new boreholes in significant quantities
(30 cm from the interface)

Bentonite Gel (& colloids) formed at the site ? YES

For example: Gas sampling tests (AMF)

Finer ⟷ Coarser

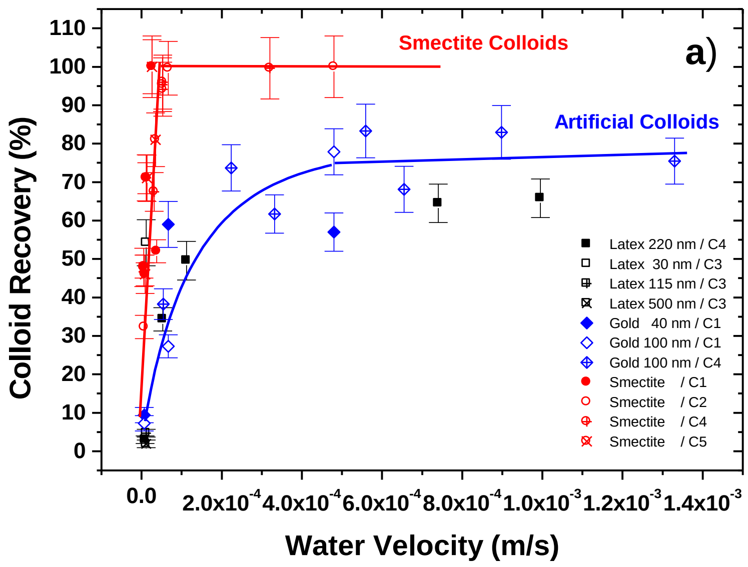


Smectite

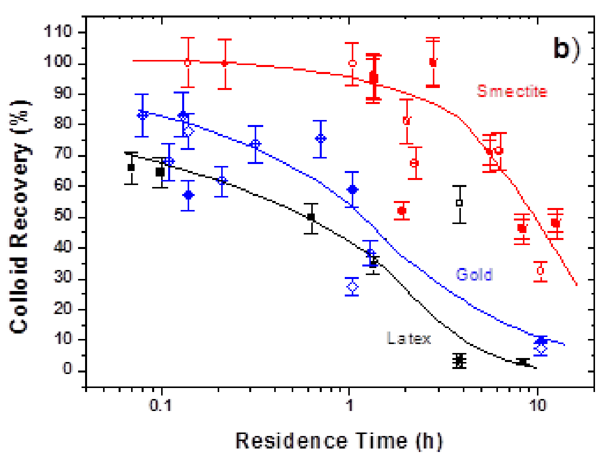
But not evidence of bentonite colloid transport (~30 cm in 18 years). WHY ?

Water Flow

- In the tunnel water flow are quite low, even in the most transmissive zones.
- Transport of BC under GW conditions (different fractures) showed that the recovery decreases with the water flow. Lab tests.



Residence Times (max 10 hours) <<<



Water velocity (min 5E-06 m/s) >>>

But not evidence of bentonite colloid transport (~30 cm in 18 years). WHY ?

Approximation "for diffusion"

$$\frac{C(t)}{C_0} = erfc\frac{x}{2\sqrt{D \cdot t}}$$

Assuming concentration of colloids in the surface of the bentonite constant (C_0)

- D, for colloids of of 300 nm = $1.6 \cdot 10^{-12}$ m^2/s
- C_0= 5 mg/cm^2 (lab experiments): Fracture of 1 cm*1 m: 500 mg/L (20 cm to s.p.)
- C(t) at 20 cm from the source after 18 years = $6.7 \cdot 10^{-4}$ mg/L

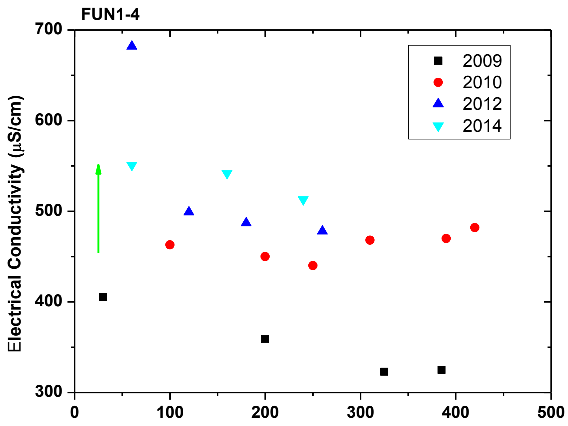
In agreement with experimental observations of in- situ testing. Furthermore these simple calculations do not account for the retention of colloids on granite, largely shown in laboratory experiments which can be further decrease the colloid mobile fraction. See laboratory work.

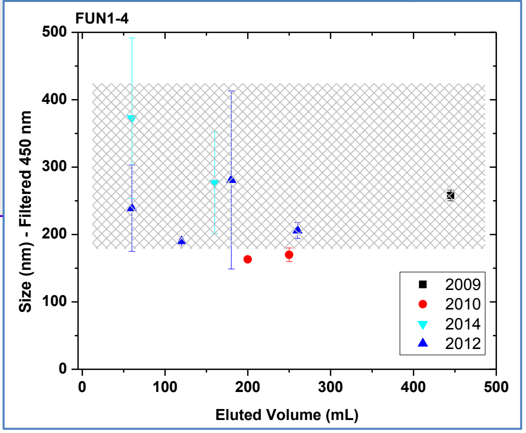
But not evidence of bentonite colloid transport (~30 cm in 18 years). WHY ?

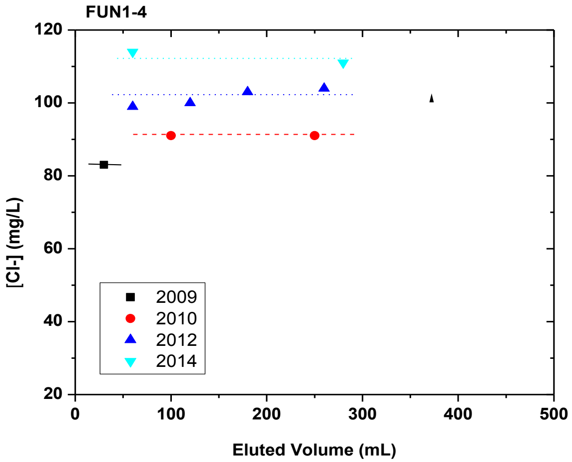
Water Chemistry

- Even when “generated”, for BC colloid to be transported, transport paths must exist. They are the same for colloids and ions.
- The region most chemically affected by bentonite present no negligible increase of salinity due to the NaCl, $CaSO_4$ dissolution;
- Increase in salinity can affect BC stability.

Reference water:
Conductivity < 100 uS/cm
$[Cl^-]$ < 1 ppm



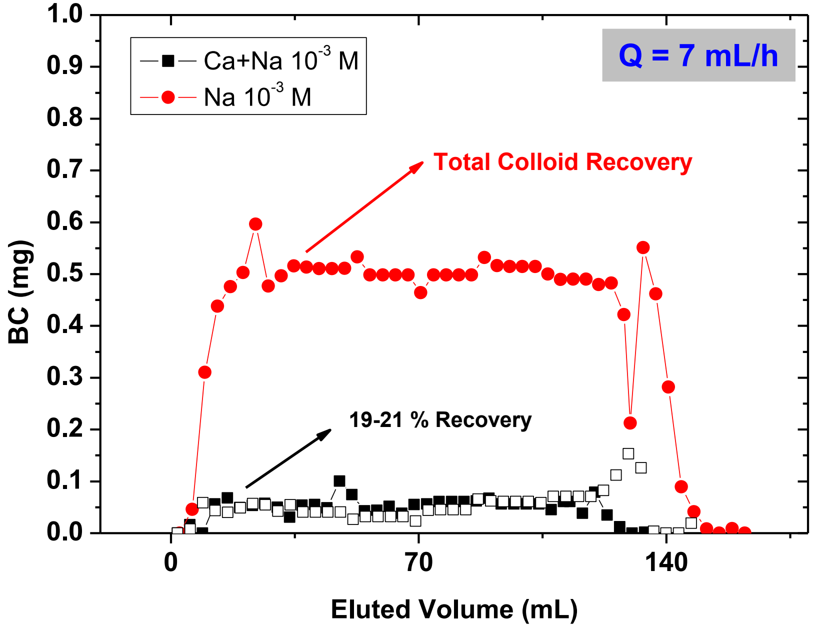


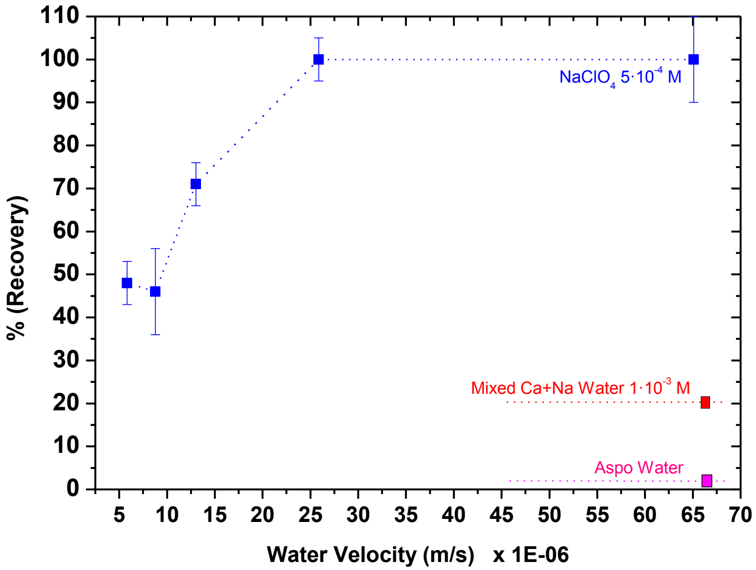


But not evidence of bentonite colloid transport (~30 cm in 18 years). WHY ?

Presence of Ca in water

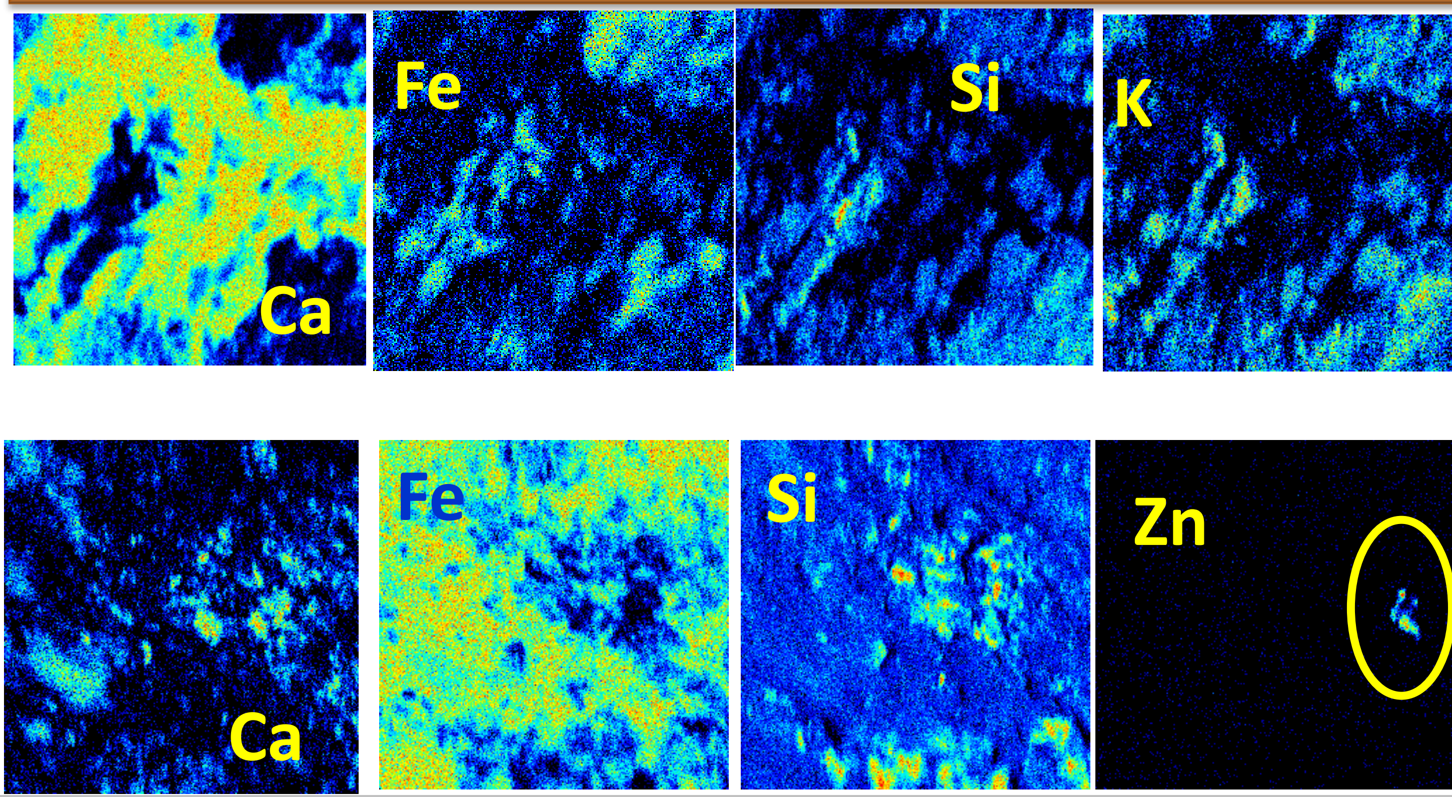
- Even when the flow conditions are favourable to colloid transport, small quantity of Ca (1E-04 M) inhibits it. Filtration occurs.





But not evidence of bentonite colloid transport (~30 cm in 18 years). WHY ?

Presence of Ca (and/or Fe) in fracture surface
(fracture fillings important for coloid stability)



June Fracture

August Fracture

CONCLUSIONS

- Under favorable chemical conditions as those present in Grimsel, colloids can be formed and be stable.
- However, bentonite colloids have not been clearly detected in any of the sampling points after 18 years of experiment.
- Transport of these colloid in the natural system is limited by the low water flow rates and the retention/filtration of particles on the fracture surface.
- Even after the strong perturbation of the system, produced by the drilling of the new boreholes with introduction and mobilization of colloids (artifacts), the quantity of these particles is slowly decreasing with time (equilibrium).
- The actual concentration is still higher (but not than one order of magnitude) than the natural background.

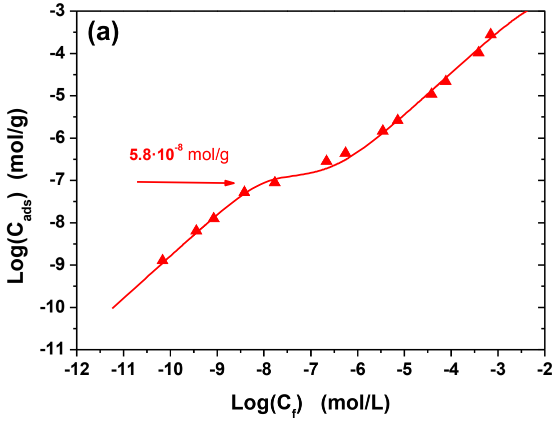
(If generation occurs) COLLOID driven radionuclide migration will be relevant only if colloids are mobile and the contaminant irreversibily sorbed.

RADIONUCLIDE SORPTION ⟷

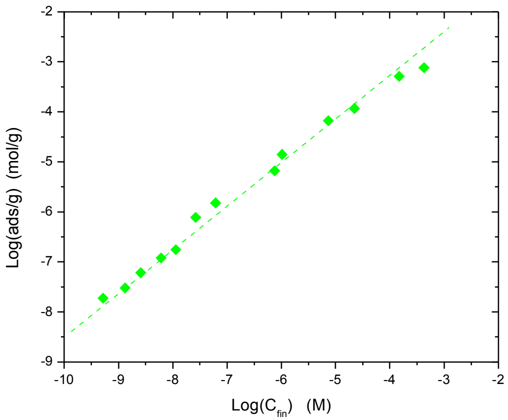
- Sorption of different radionuclides on FEBEX clay colloids (especially Na-clay, size lower than 500 nm) analyzed at CIEMAT during the last years: Cs, Sr, Ca, Co, U, Cd, Se, Eu,…

- Sorption mechanisms depend on the radionuclide and chemical conditions.
- Linearity and irreversibility ?.
- Ion exchange; outer or inner sphere complexes; Sorption modelling of test under a wide range of experimental conditions.

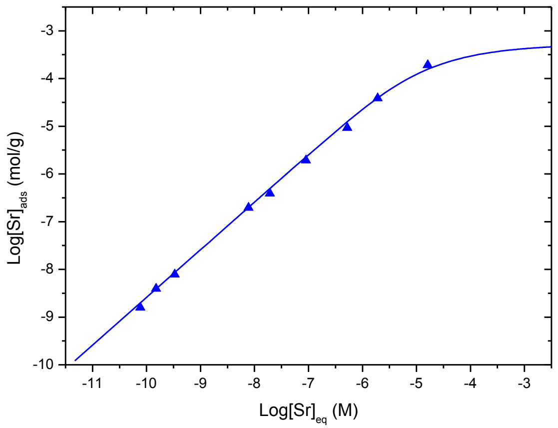
RADIONUCLIDE SORPTIONN BC: EXAMPLES



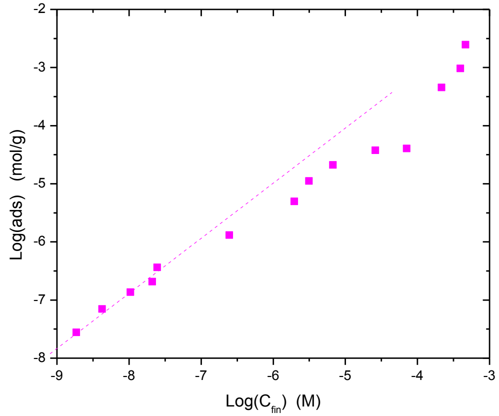
Cs
- Cation exchange
- **Non-linear**



Eu /U
- Cation exchange
  & I.S. surface complex
- Linear (**)



Sr
- Cation exchange
  (& I.S. surface complex)
- **Linear**



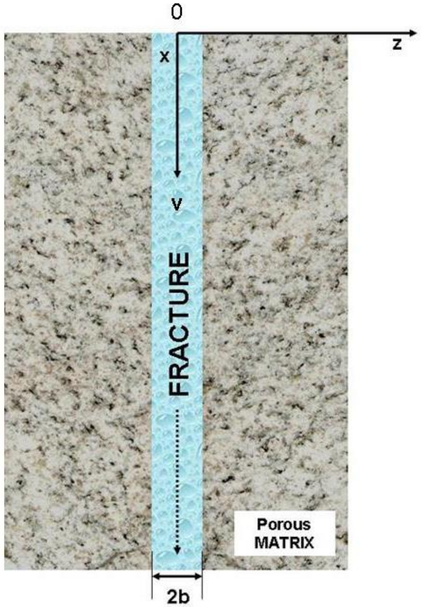
Cd
- Cation exchange
- I.S surface complex)
- O.S. surface complexation

Sorption reversibility ?

$$K_d(sor) = \frac{(C_{in} - C_{fin})}{C_{fin}} \frac{V}{m} \quad \Longleftrightarrow \quad K_d(des) = \frac{C_{ads,s} - C_{fin,des}}{C_{fin,des}} \cdot \frac{V}{m}$$

- In most of the cases and depending on the main mechanism (pH and I) Kd(sor) similar to Kd(des);
- Cs sorption: partial irreversible (incorporation in illite/smectite interstratified present in FEBEX) (< 1%CEC)

BUT when colloids are transported in a fracture sorption equilibrium includes also the rock solid phases. The distribution of the radionuclide at the equilibrium change (rock fractures and ffm).



Sorption reversibility: observations in colloid transport tests

Element	Initially adsorbed on BC	Transported "unretarded" with BC	Recovered BC
Sr	>80 %	<2 %	VV
Eu	>80 %	<7 %	VV
U	~30 %	<1 %	VV
Cs	>80 %	0.15 %	~ 80 %

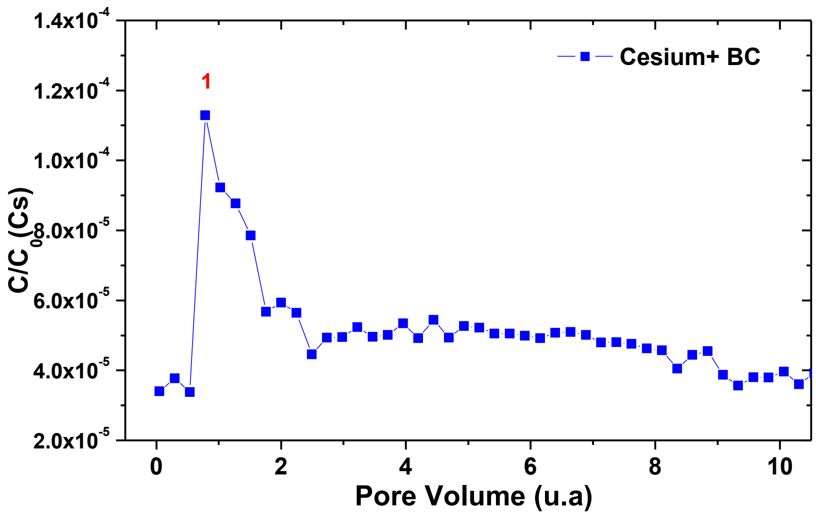
Colloid Residence Times
(max 10 hours)

WP3 CIEMAT

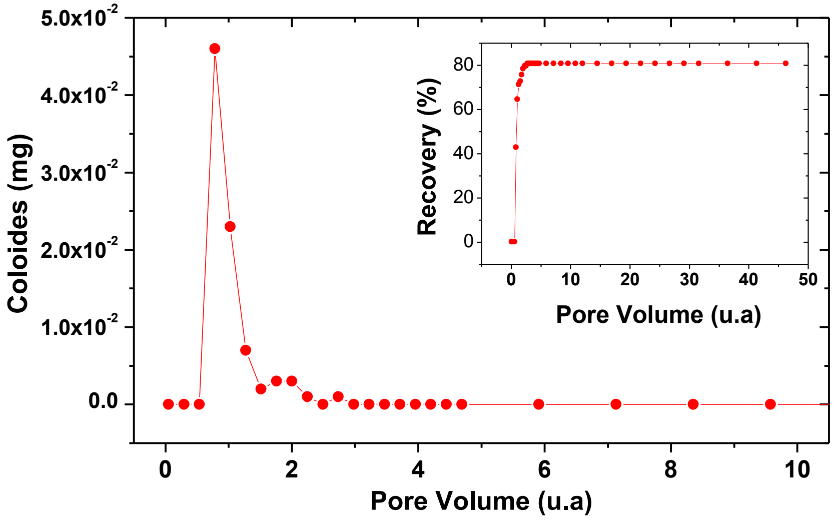
COLLOID CONCENTRATION AND ACTIVITY MEASURED IN THE SAME SAMPLES

Cs perfectly visible eluting with colloids (only 0.15 % of the initial activity)

Cs Elution (with colloid)

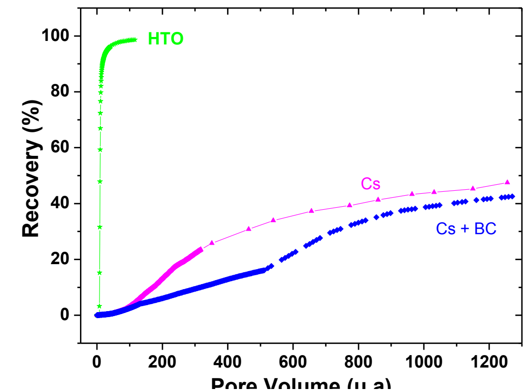


Colloid Elution

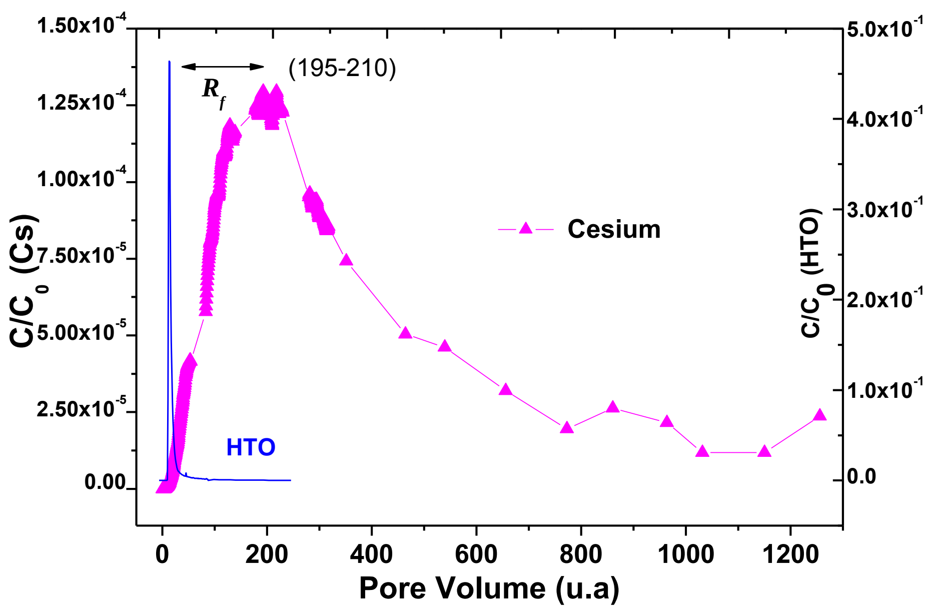


BC, 100 ppm in 5·10^{-4} M $NaClO_4$
Cs: v = 3.8·10^{-5} m/s; rt ~ 2 h
Cs+BC: v = 3.5·10^{-5} m/s; rt ~ 2 h

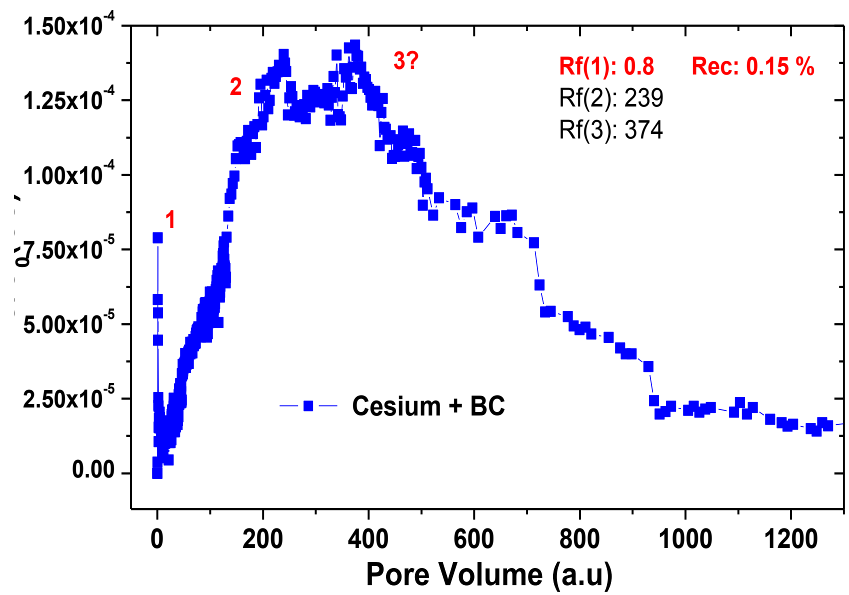
Cesium recovery similar in both cases 48 % (Cs), 43% (Cs+BC)



ONLY CS (and HTO)



CS and BC



CONCLUSIONS

- Sorption linearity depends on the radionuclide.
- In bentonite colloids, batch experiments indicated "sorption reversibility" for most of the radionuclides analyzed.
- Reversibility is strictly dependent on adsorption mechanisms involved in retention.
- Irreversibility of Cs was related to *fixation* in FES site of illite/smectite mixed layers of FEBEX. (Co)precipitation can be also of importance.
- However, in all the cases, the presence of the rock surfaces implies the establishment of new conditions for sorption equilibrium (rapid).
- The quantity of radionuclide measured with the mobile BC was always lower than the expected considering the initial adsorption on BC.

Thanks for your attention