BELBaR

EURATOM

Prague, October 30-31, 2014

PROGRESS UPDATE OF CIEMAT'S RESULTS

Tiziana Missana, Úrsula Alonso, Miguel García-Gutiérrez, Trinidad López

(CIEMAT)

OUTLINE

Laboratory tests:

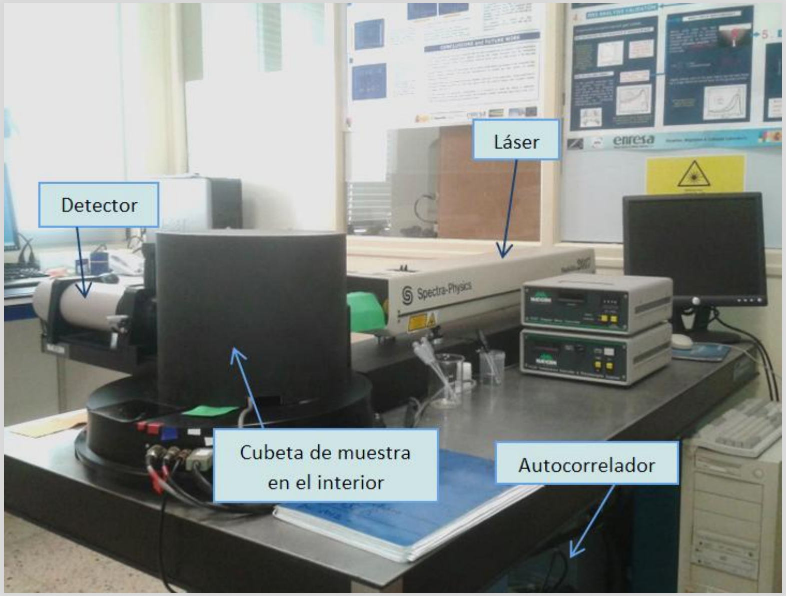
- **Stability of NANOCOR (to be used for the benchmark erosion test);**
- **New generation tests (started): NANOCOR, Saponite and mixed clays;**

In-situ erosion study at GTS (last sampling October 2014). Summary.

Colloid Stability

Zetapotential measurements (surface potential)

PCS measurements (size, aggregation kinetics)

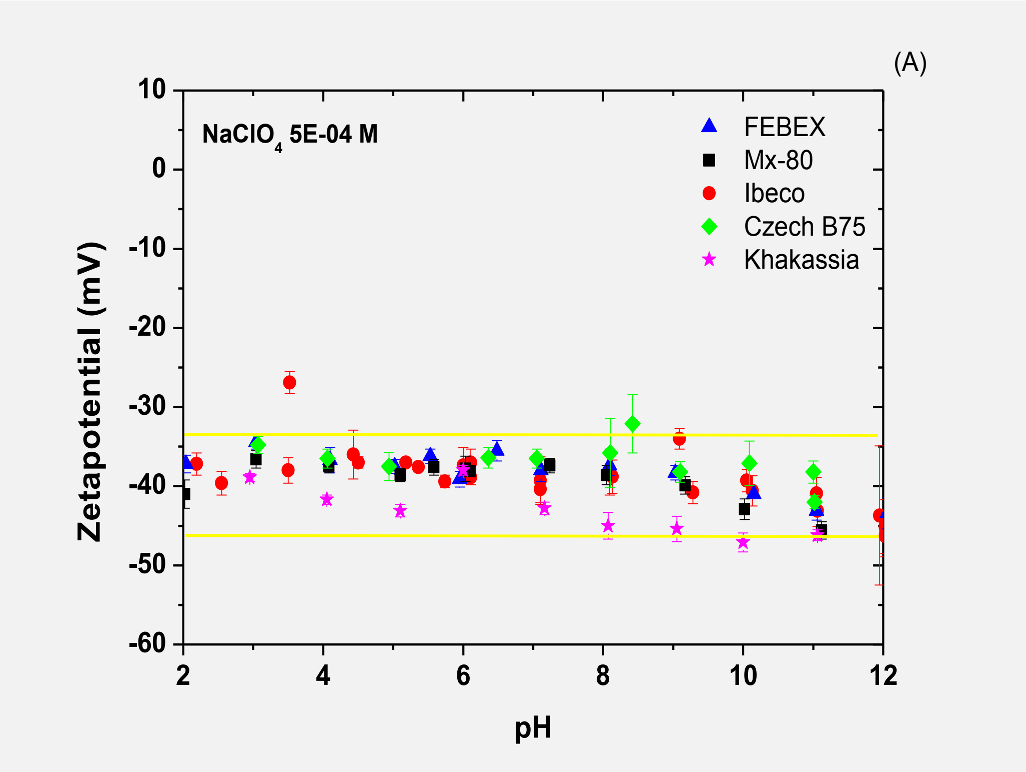


$$U_E = \frac{2\,\varepsilon\,\zeta\,f(\kappa r)}{3\eta}$$

pH and I

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

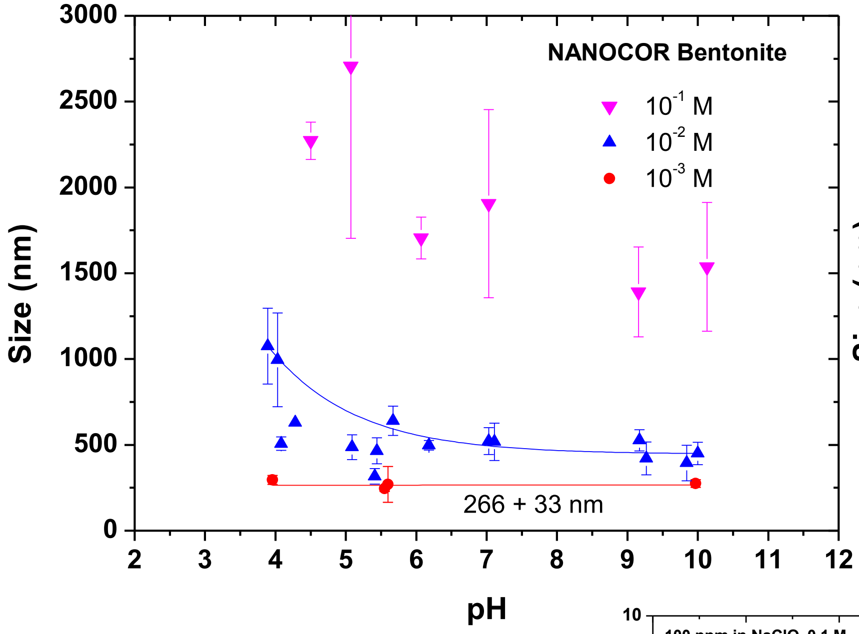
Data Comparison

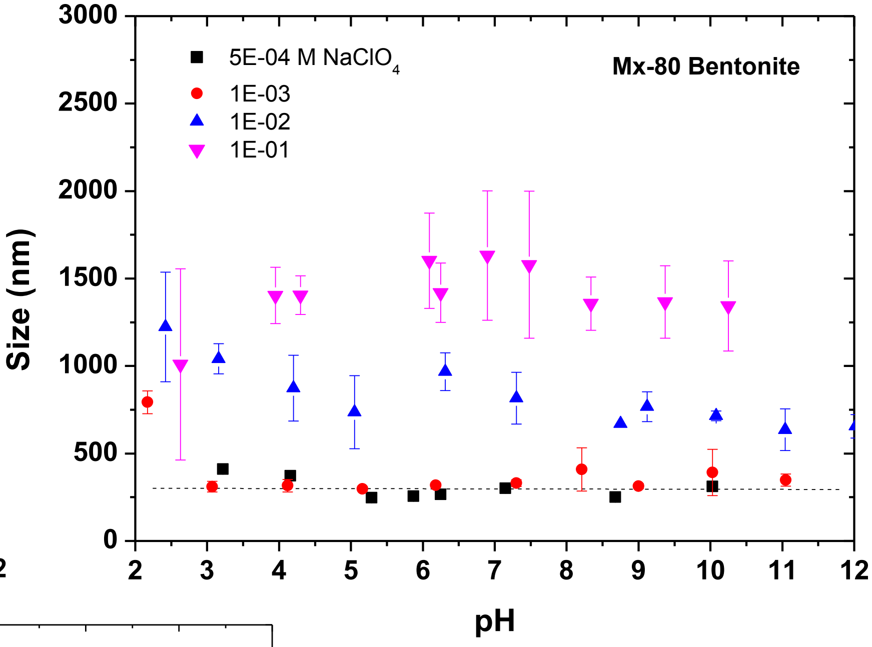


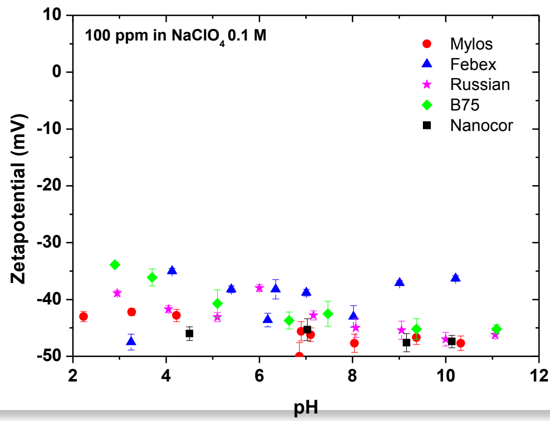
Zetapotential similar in all the cases, even at different ionic strengths. Not particular relevant for the understanding of clay systems stability/erosion.

Coagulation behaviour: size unvaried up to $I=1\cdot10^{-3}$ M with slight increase for pH< 4 (edge-face interactions).
Aggregation observed at 0.01 M in $NaClO_4$, accentuated at acid pH.
At I=0.1 M, colloids are completely destabilized (size outside the colloidal range).

NANOCOR Stability







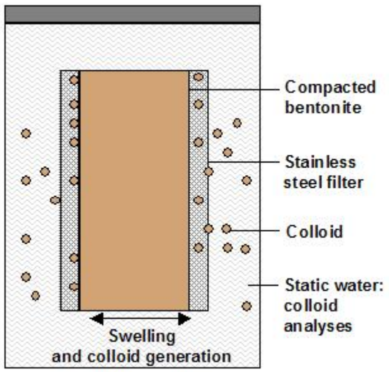
Zeta potential

Erosion tests: static cnd.

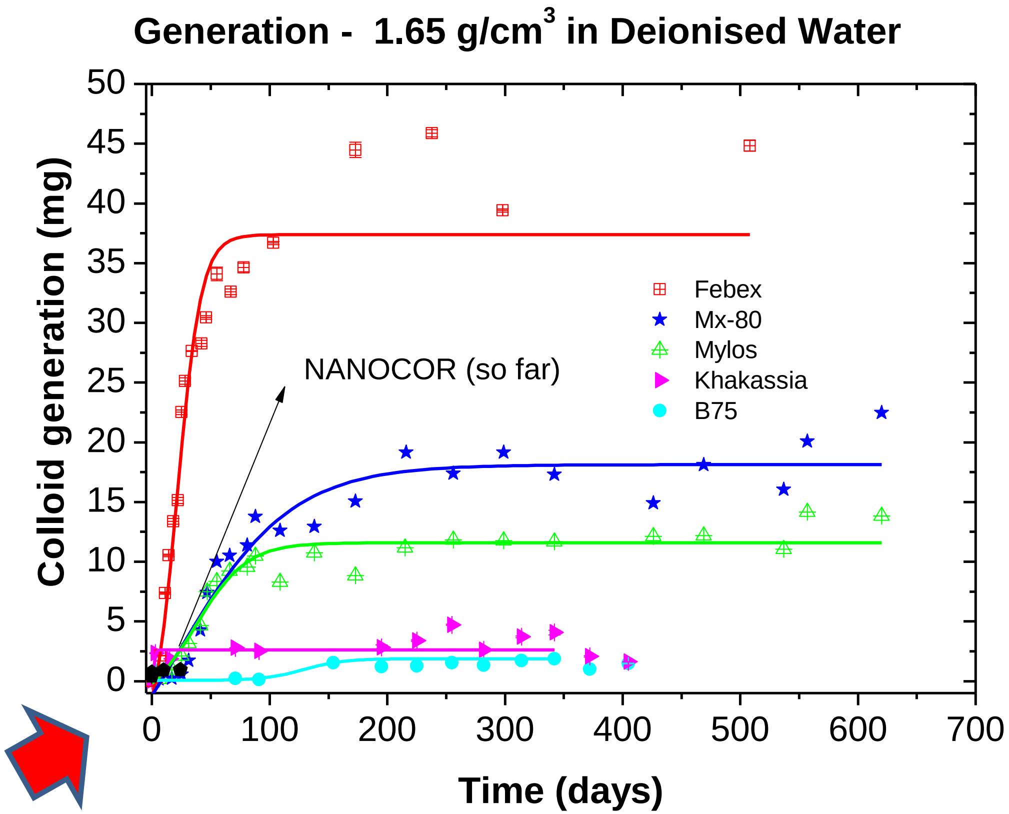
Colloidal masses eroded as a function of time from the five studied bentonite compacted at 1.65 g/cm³ in DW

(a)

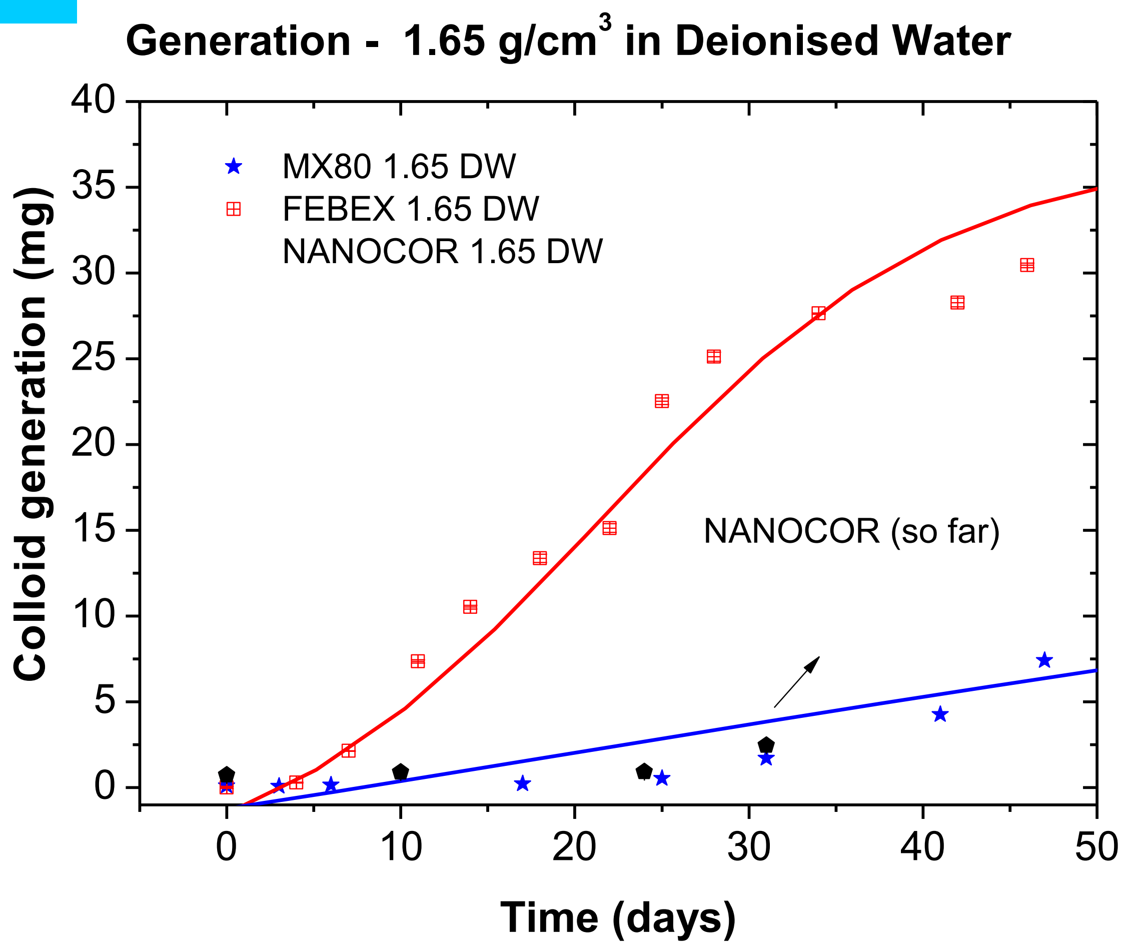
(b)



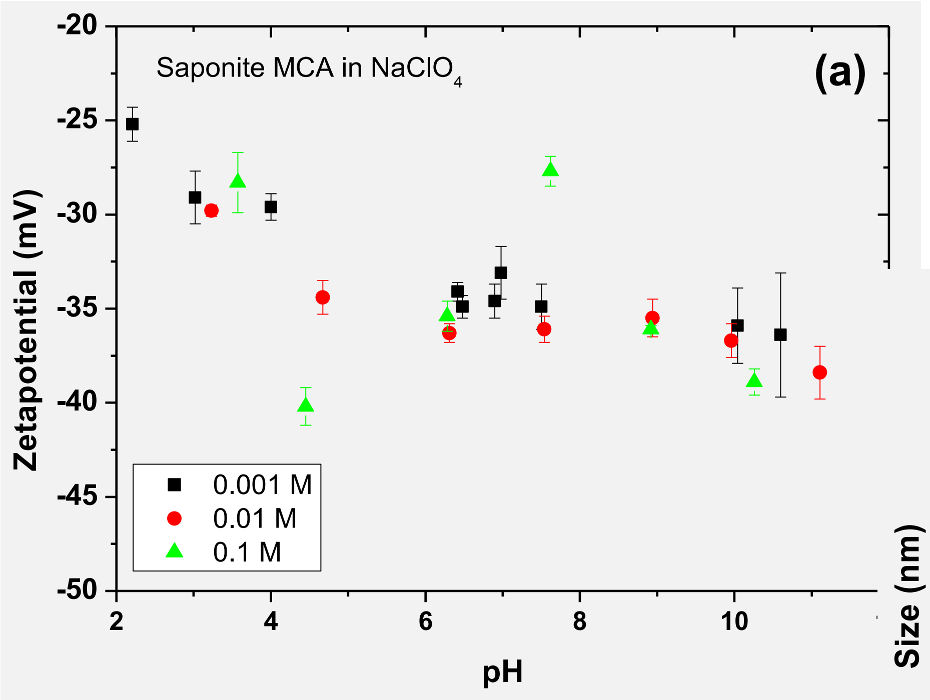
4 g clay, 200 mL
Compacted & Confined
S = 3.5 cm²

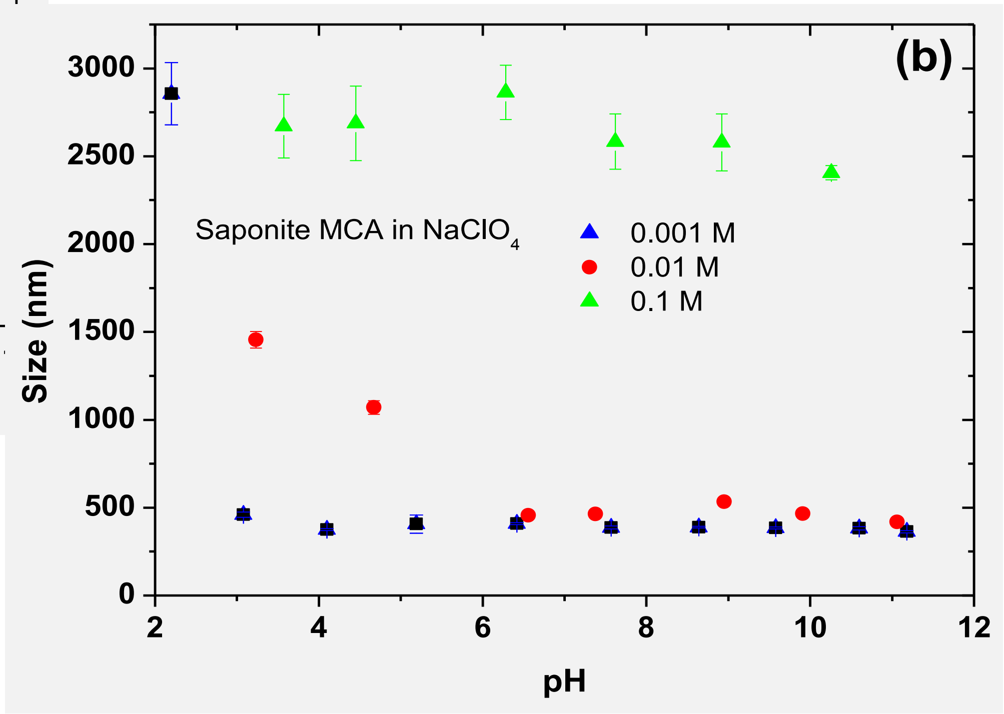


NANOCOR 1.65 g/cm³ in DW

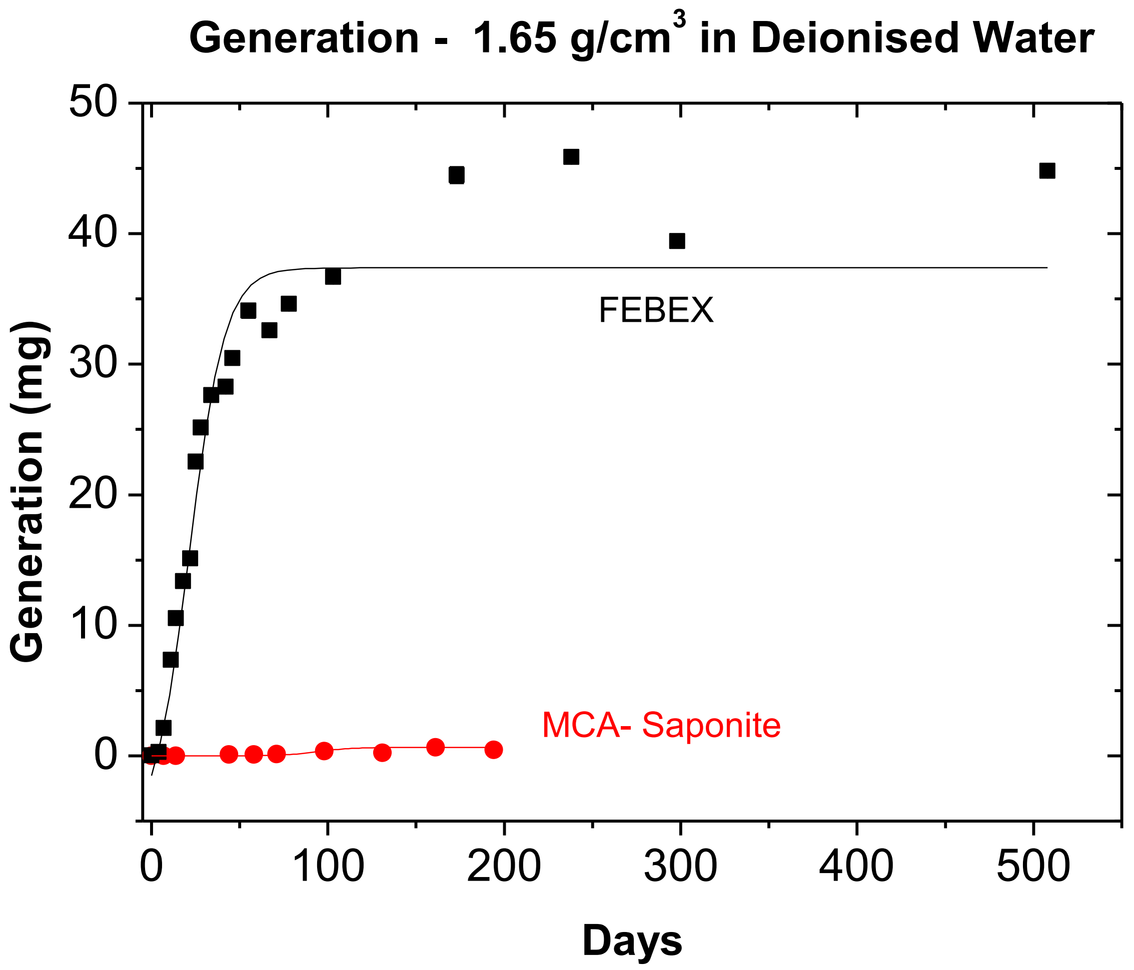


Saponite


Saponite MCA in $NaClO_4$
(a)
Zetapotential (mV)
-20
-25
-30
-35
-40
-45
-50
2
4
6
8
10
pH
0.001 M
0.01 M
0.1 M


(b)
Saponite MCA in $NaClO_4$
0.001 M
0.01 M
0.1 M
Size (nm)
3000
2500
2000
1500
1000
500
0
2
4
6
8
10
12
pH

Erosion tests: static cnd.

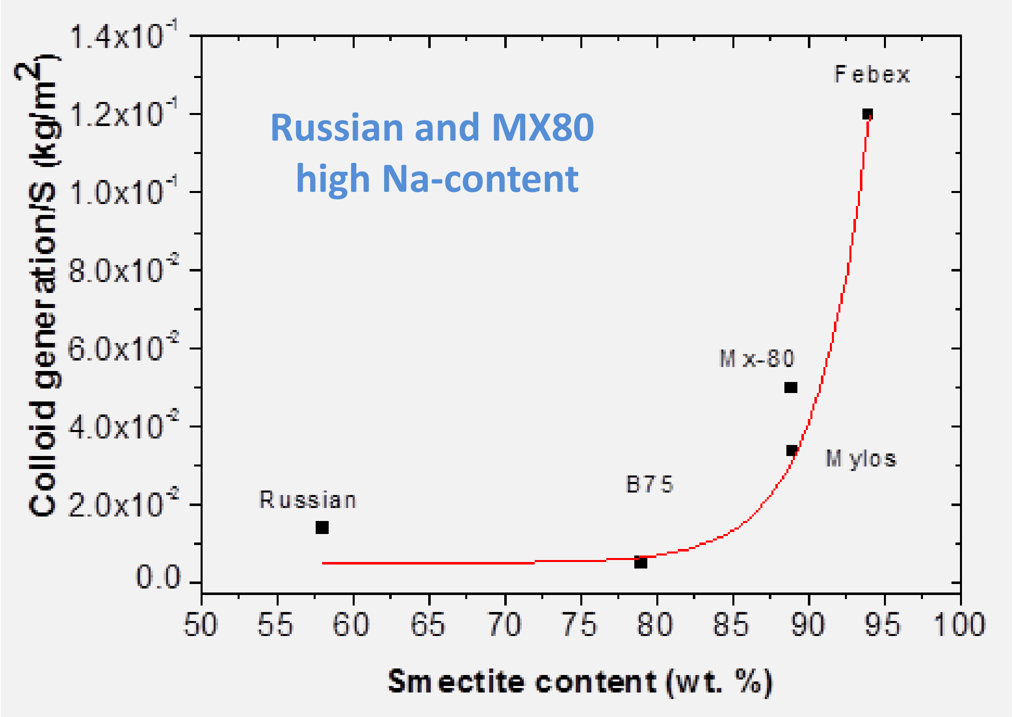


Saponite -MCA

Generation of colloids: very small.

Erosion tests: static cnd.

Bentonite	Colloid/S (Kg/m²)	Mean size (nm)
FEBEX	$(1.2 \pm 0.5)\cdot10^{-1}$	338 ± 24
Mx-80	$(5 \pm 0.5)\cdot10^{-2}$	291 ± 31
Mylos	$(3.4 \pm 0.5)\cdot10^{-2}$	367 ± 46
Russian Khakassia	$(1.1 \pm 0.5)\cdot10^{-2}$	400 ± 150
Czech B75	$(5.3 \pm 0.5)\cdot10^{-3}$	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).

NEW TESTS WITH ILLITE+MONTMRILLONITE & KAOLINITE + MONTMORILLONITE in diff %

Ongoing lab activities

- Complete characterization of all analyzed clays – **Clay structural properties in relation to erosion behavior.**
- Static experiments with FEBEX bentonite mixed with known proportions of other clays in DW - **Verification of colloid erosion relation to smectite content.**
- Continue "long-term" erosion experiments under flow conditions
- Benchmark test (NANOCOR 1.4 g/cm^3)
- Analysis of CIEMAT erosion results form different experimental configurations, including FEBEX experiment – GTS in-situ results.

BELBaR

Bentonite Erosion Processes: the *in –situ* study

EURATOM

Aims

In-situ analyses of the bentonite colloid generation <u>under realistic conditions</u>.

Data from FEBEX tunnel in the Grimsel Test Site, where a real scale experiment simulating a deep geological repository in granite installed 18 years ago.
The study started in 2006 in EC-FUNMIG.

- Processes understanding.
- Comparison with laboratory data.
- Evaluation of colloid formation **in a very favourable** case.

Field work

Water sampling from different boreholes in the FEBEX tunnel for colloid analyses

BELBaR

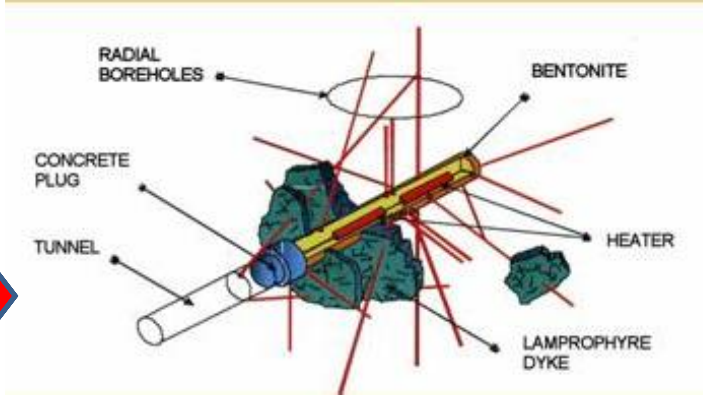
FEBEX

EURATOM

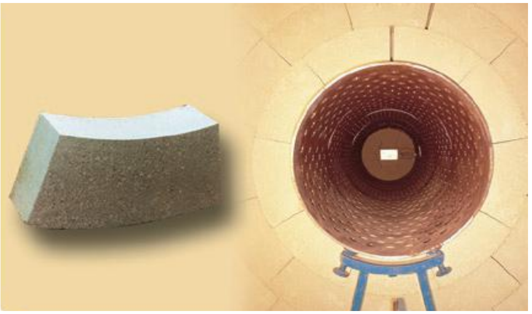
EC-Project: Full-Scale High-Level Waste Engineered Barrier System Experiment.

Real-scale experiment at GTS simulating a repository in granite to study thermo-hydro-mechanical/geochemical (THM/THG) behaviour of the bentonite barrier.

2 Heaters + (Natural) Hidration + Tracers.



1996-1997: mounting and swithing on.

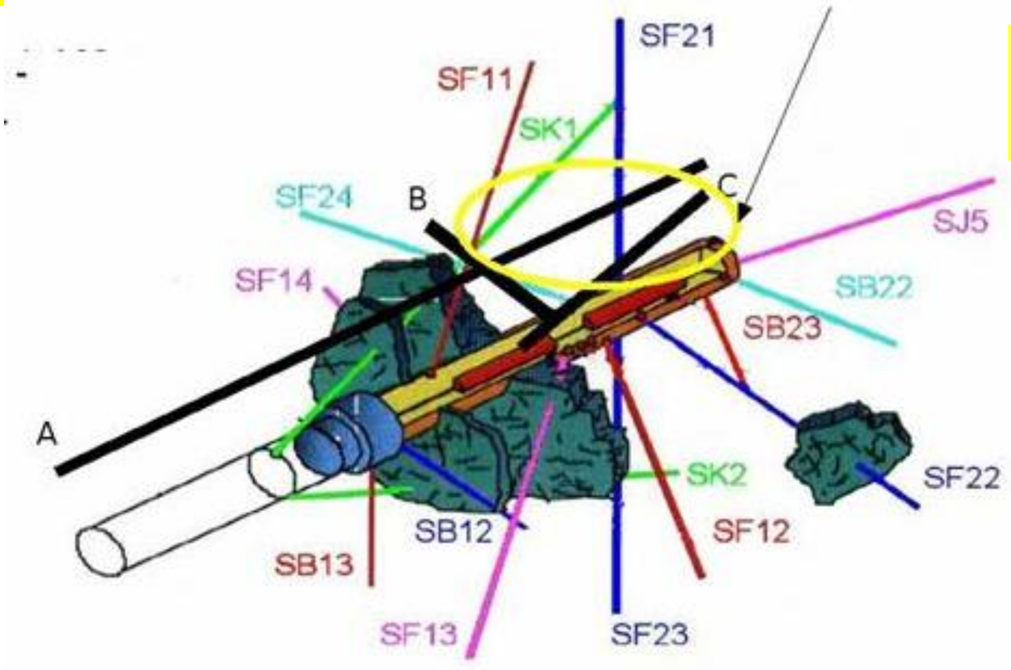


2002: first heater dismantled

2014: 2nd heater and bentonite still emplaced (18 years). Experiment still running. Next year dismantling will start.

- This experiment was an unique opportunity to study colloid erosion under "realistic" conditions. Bentonite was emplaced there in 1996 (18 years now);
- Study on "colloid generation" started in the frame of EC-FUNMIG 2004-2008; Continued by CIEMAT.
- Focusing on the analyses on the effects of the bentonite on GW chemistry; Migration "natural" tracers from bentonite (Na, Ca, Cl) and artificial tracers (Re, I) placed during FEBEX at the bentonite surface.

Chemistry: 19 radial boreholes (41 packed off sections) excavated during the FEBEX experiment installation and 2 new "FUNMIG" boreholes, near to the bentonite, especially to the scope.

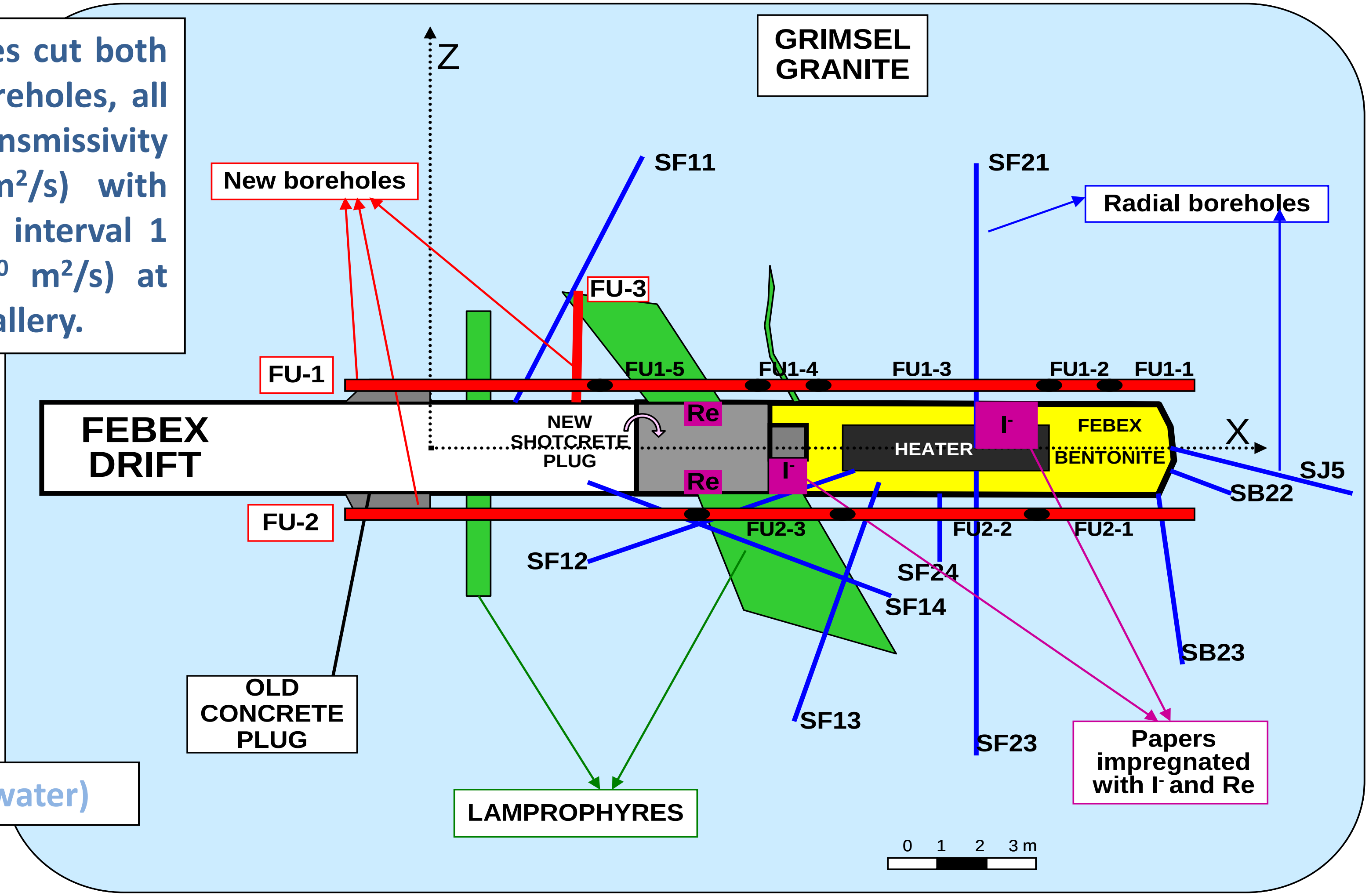


Existing "radial" boreholes (reference)

FU-1: 30 cm from bentonite
FU-2: 60 cm from the bentonite

BELBaR

Different fractures cut both FU1 and FU2 boreholes, all showing low transmissivity ($1\cdot10^{-11}$-$1\cdot10^{-12}$ m^2/s) with exception of the interval 1 of FU1 (6-$8\cdot10^{-10}$ m^2/s) at the back of the gallery.



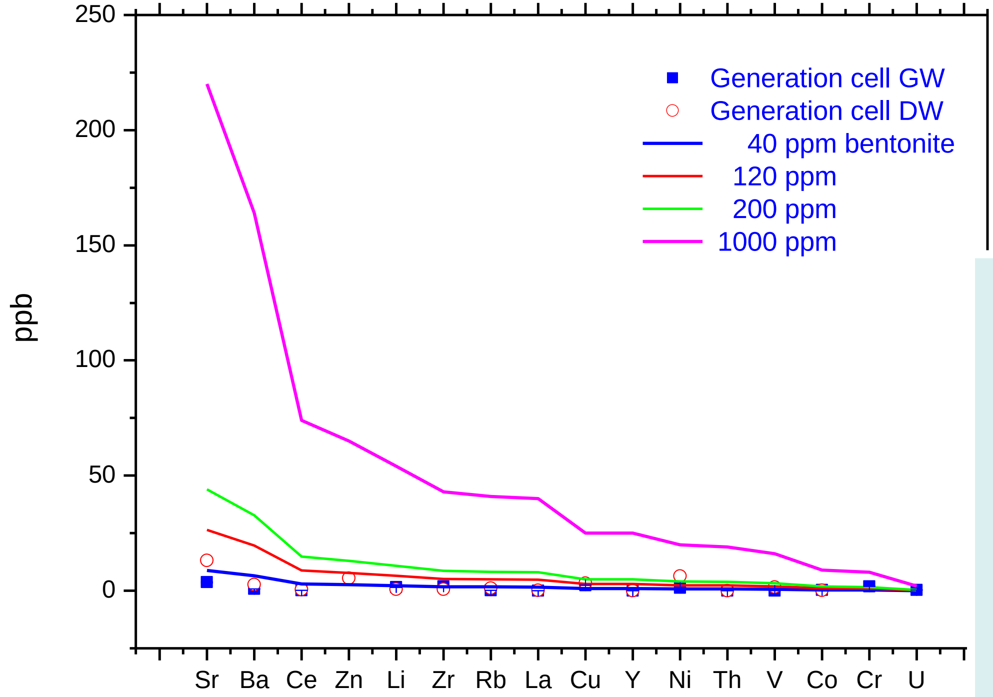
SJ5-3 (Reference water)

Analysis

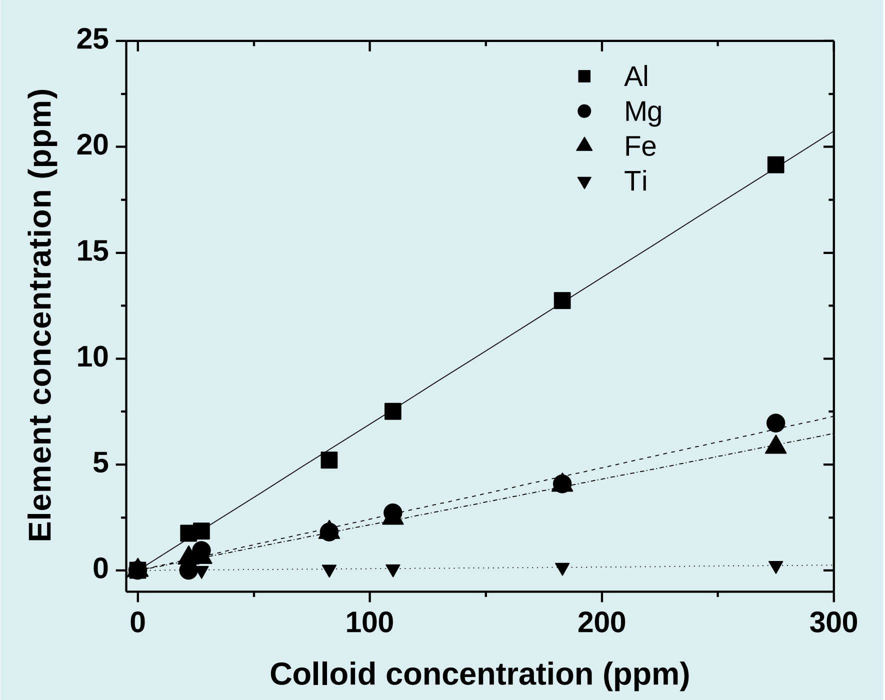
SAMPLING

1. PCS: Photon Light Scattering Spectrometry. Determination of concentration (C/C0) and size, without filtering and filtered by 0.45 um.
2. SEM/EDAX. Morphology and solid composition.
3. FESEM. Morphology
4. Trace analysis (+ Fe, Mn and Al) in filtered (ultracentrifuged) and not filtered samples.
   Solid composition.
5. Other "problems": artefacts.

Comparison with laboratory "erosion" studies



Theorethical curves: elements in bentonite



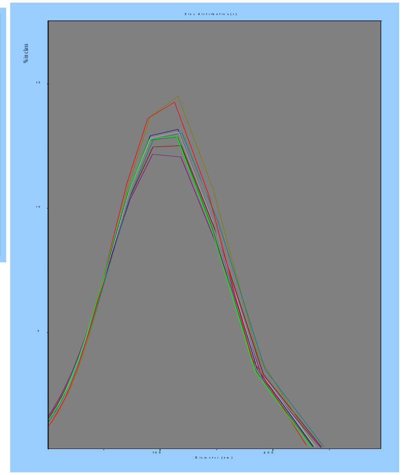
Estimation of BC concentration

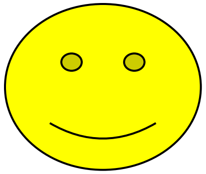
Very first result upon FUN drillings

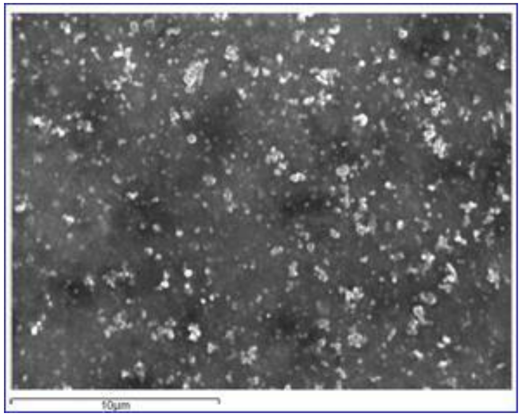
- 4 samplings were carried out between 2006 & 2007.
- Colloid samples were always analysed by PCS to determine the concentration (C/C_0), before and after filtering.
- Several samples, above all in the new drilled boreholes, showed surprisingly high colloid concentration (by PCS) even after filtering.
- In some interval of FU1 (above all FUN1-2) **clay colloids** were identified (concentration estimation <100 ppb) 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 (drilling fluids ?)**

PCS:
Size before filtering: 210 nm
after filtering : 110 nm

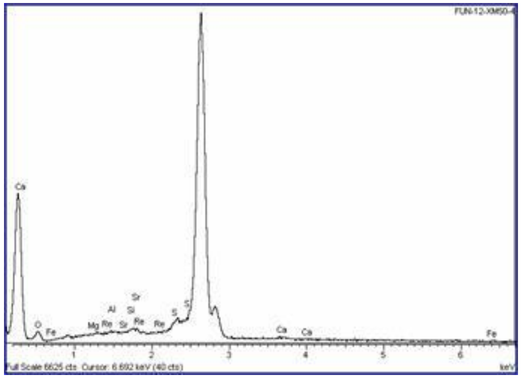
Very good polydispersivity



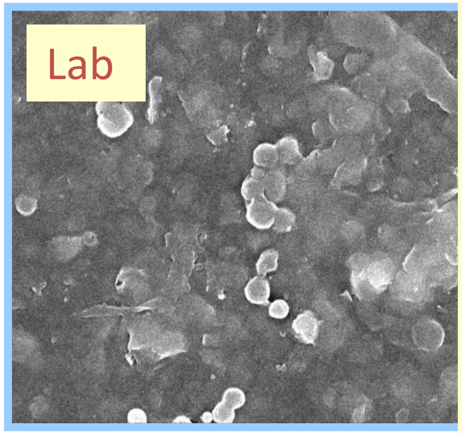


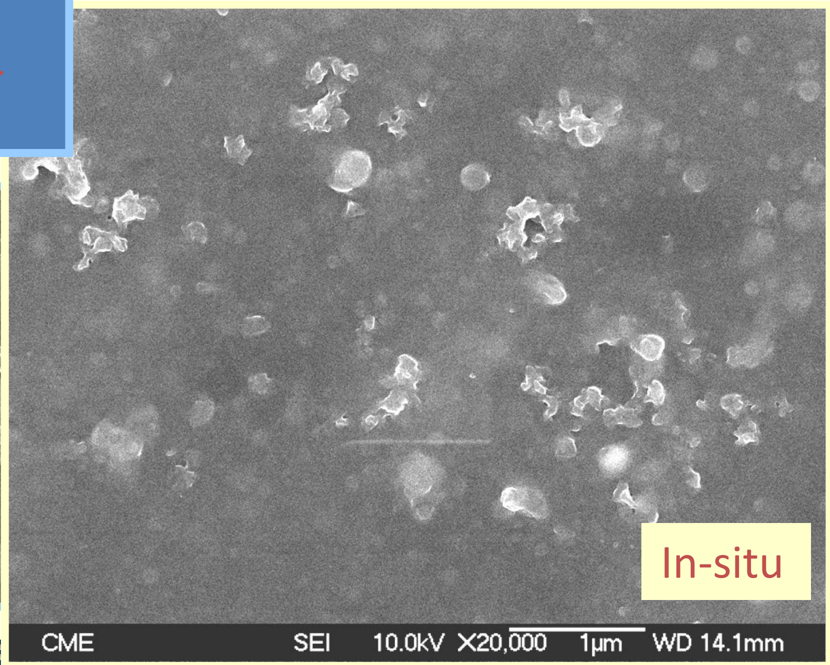


SEM/EDAX:
Ca, Mg, Al, Si, Sr, S



FESEM:
Comparison: lab and in-situ.





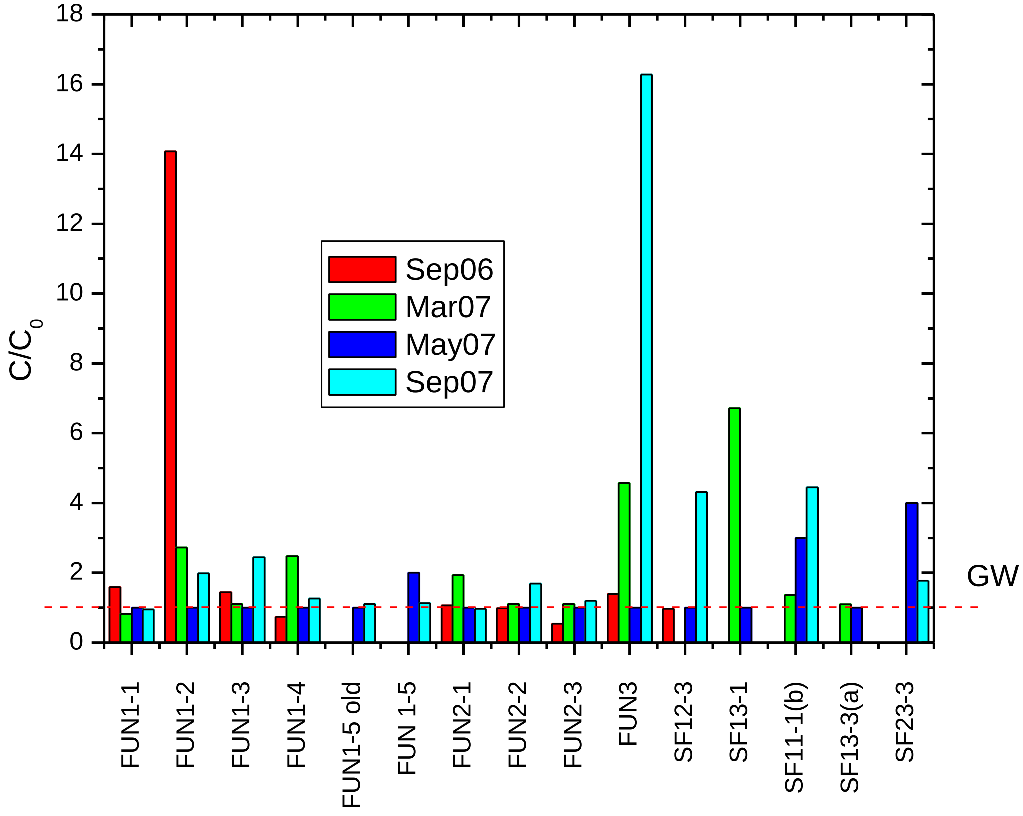
C1

PCS

- Most of "as-received" samples showed non negligible quantity of particles. Poly not good.
- After filtering, most colloids were in the range 100-300 nm.
- Populations with better poly-dispersivities (0.3-0.4) showed a size of 100 nm approximately.
- Different "types" can be identified, as usual considering concentration before and after filtering, size and poly.

SAMPLE	Size	Poli	Size fil	Poli fil
FUN1-1	647.1±45.5	1	204.6±22.8	0.85
FUN1-2	452.7±44.7	1	86.4±3.9	0.33
FUN1-3	256±16.7	0.59	137.0±9.6	0.4
FUN1-4	649±33.7	1	184±68	0.65
FUN1-5 (june)	579.6±49.7	1	208.5±45.7	0.85
FUN1-5	494.8±38.1	1	177.8±89.8	0.73
FUN2-1	382.7±25.4	0.75	135.8±45.6	0.6
FUN2-2	350.4±16.1	0.60	162.4±26.5	0.52
FUN2-3	>1000	1	300	1
FUN3	155.6±1.4	0.2	131.1±29.5	0.3
SK2-1	ND	ND	ND	ND
SF11-1	243.9±34.1	0.85	99.9±1	0.36
SF11-2	405.5±61.1	0.89	161.7±41.0	0.83
SF11-3	253.3±67	0.93	107.8±7.5	0.5
SF12-3	227.3±30.4	0.7	102.0±2	0.44
SF22-1	187.8±32	0.64	135.7±23	0.53
SF22-2	135.7±23.8	0.53	****	1
SF23-3	692.9±112	1	233.2±97.6	0.8
SB22-1	281.8±73	0.85	129.7±23	0.42

Results: PCS. Comparison of all the samplings.



TREND NOT ALWAYS CLEAR

- Colloids in FUN 1 (1-2) decreased.
- FUN 2: values always similar to GW
- FUN 3: Big increase.
- Radials ?

C/C_0 ratio after filtering

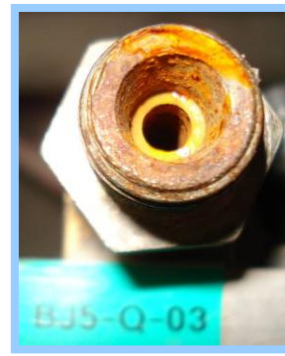
Chemistry

❖ In in-situ samples, Al data, did not always correspond to PCS colloid concentration ! **Other colloids sources must exist !!**

Sample	C/Co	Al (ppm)	Coll conc. (ppm)
FUN3	16.28	0.04	0.58
SF11-1(b)	4.45	0.07	1.01
SF12-3	4.31	<	<
SF11-3	2.75	<	<
FUN1-3	2.44	0.09	1.30
SF22-1	2.43	0.11	1.59
SB22-1	2.07	0.1	1.45
FUN1-2	1.98	0.07	1.01
SF23-3	1.77	<	<
FUN2-2	1.69	0.07	1.01
FUN1-4	1.26	0.07	1.01
FUN2-3	1.2	0.04	0.58
FUN 1-5	1.13	0.03	0.43
SF22-2	0.99	<	<
FUN2-1	0.97	0.03	0.43
FUN1-1	0.95	0.05	0.72
SF11-2	0.79	<	<

❖ High concentration of Zn, Ni, Fe

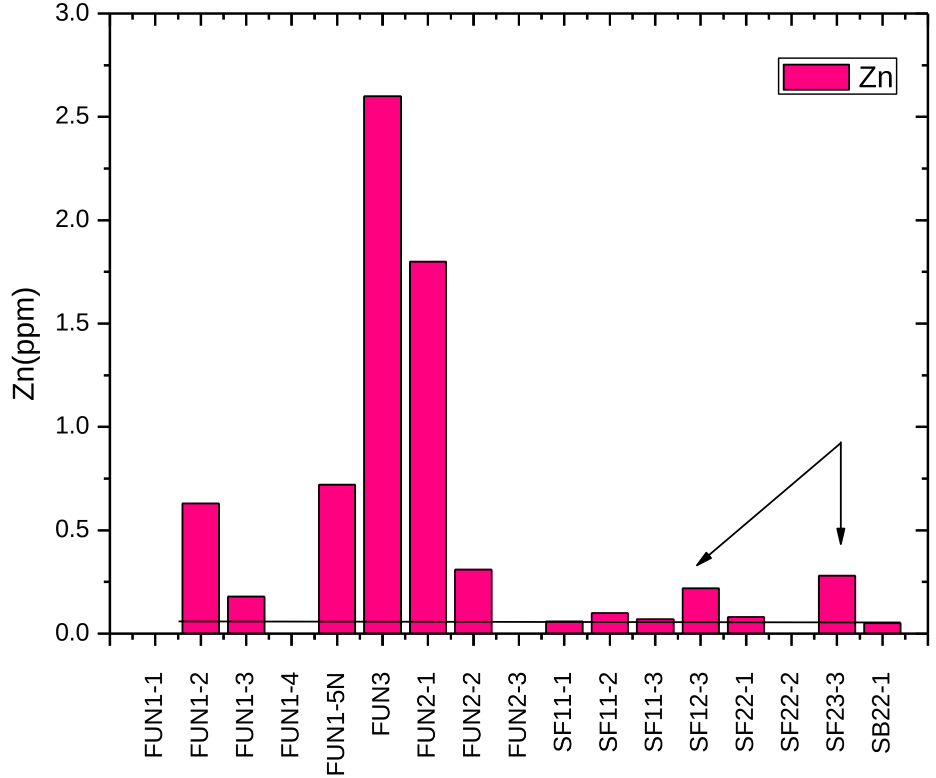
❖ Other anomalous metal concentration (particulate)



BELBaR

EURATOM

- **Other colloids sources must exist !! Analysis of elements with higher concentration : Ni and Zn.**



Interferences SF23-3:
-Drilling FU1 (15 m) FU1-1
-Drilling FU2 (11 m) FU2-2
-Drilling FU3 (lamprophyre)

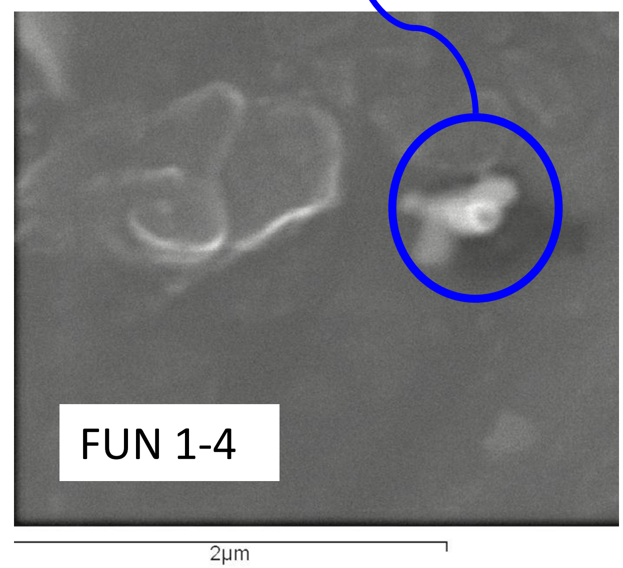
Intereferences SF12-3:
-Drilling FU2 (10.5 m), FU2-2
-Drilling FU3 (lamprophyre).

Artifacts

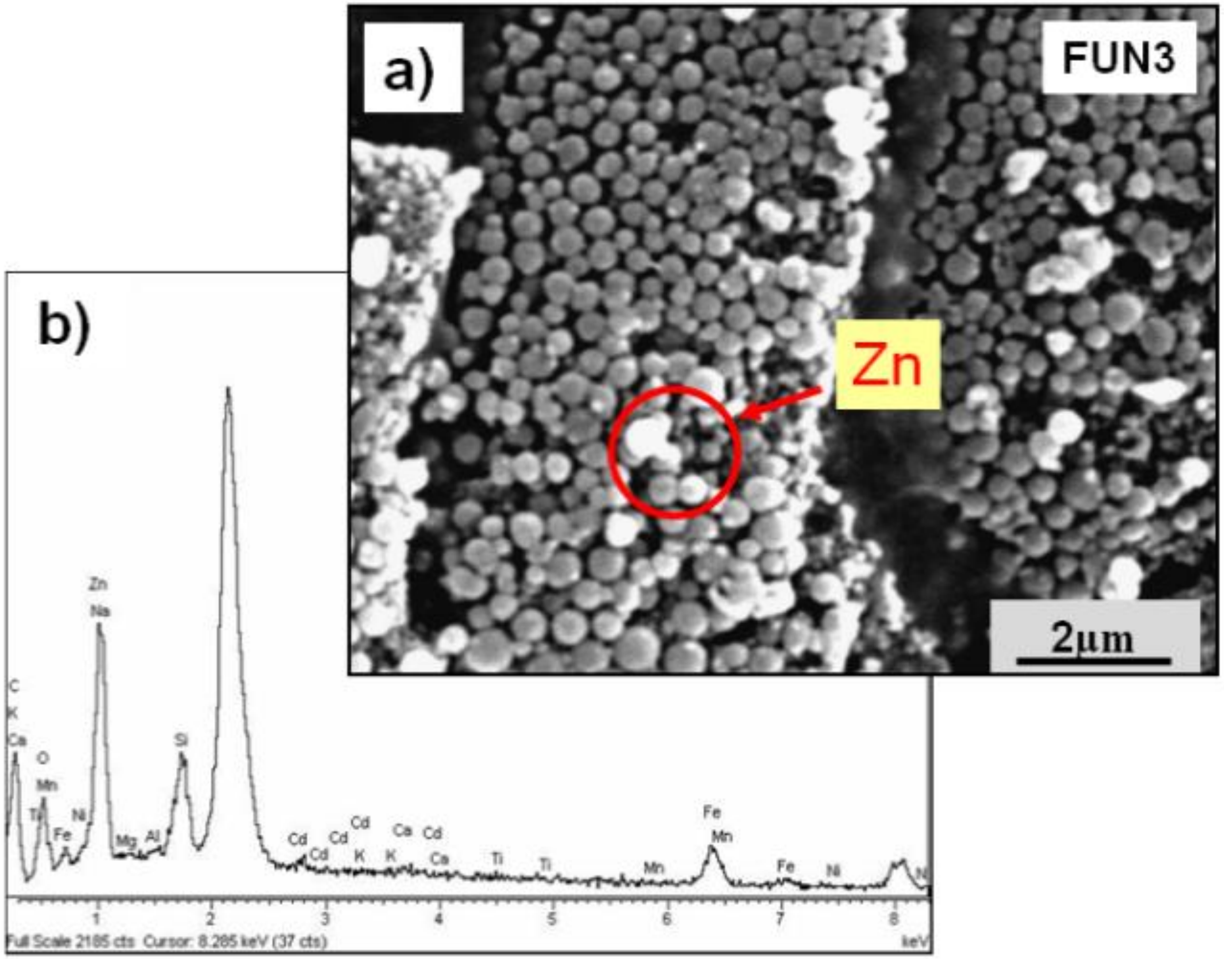
(Zn ?)

Element	Atomic%
C K	0.00
O K	42.41
Na K	13.11
Mg K	0.00
Al K	0.00
Si K	15.42
K K	0.00
Ca K	0.67
Ti K	0.00
Mn K	0.00
Fe K	7.95
Ni K	0.00
Zn K	20.17
Cd L	0.27
Total	100

Element	Atomic%
O K	61.33
Zn K	38.67
Totals	



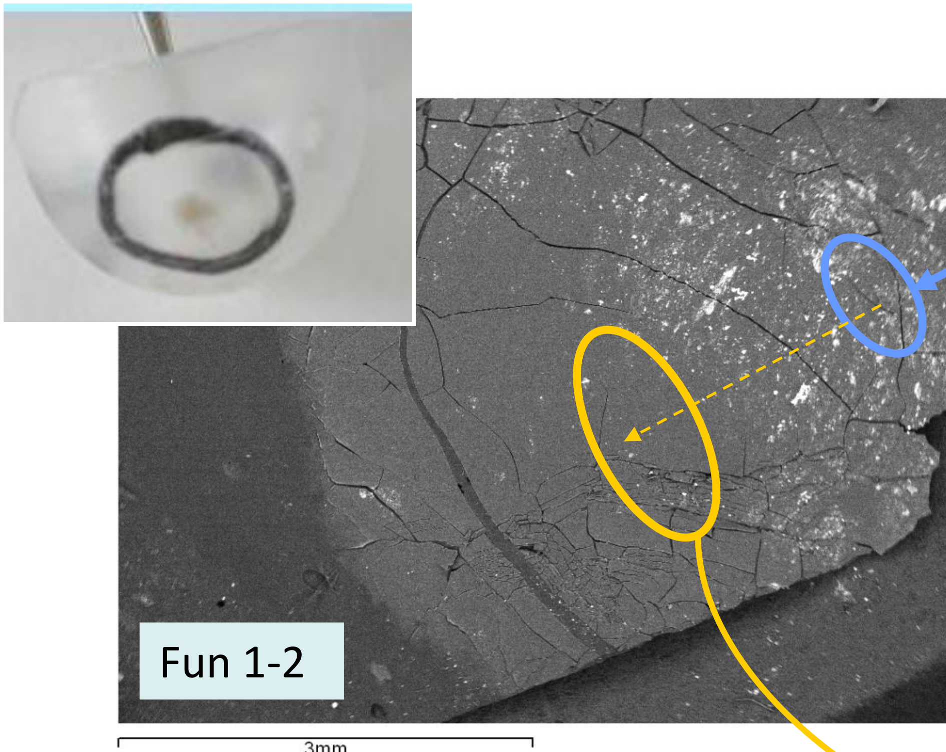
Artifacts



(Sampling : 2009)

Artifacts

(other problems….. ?)



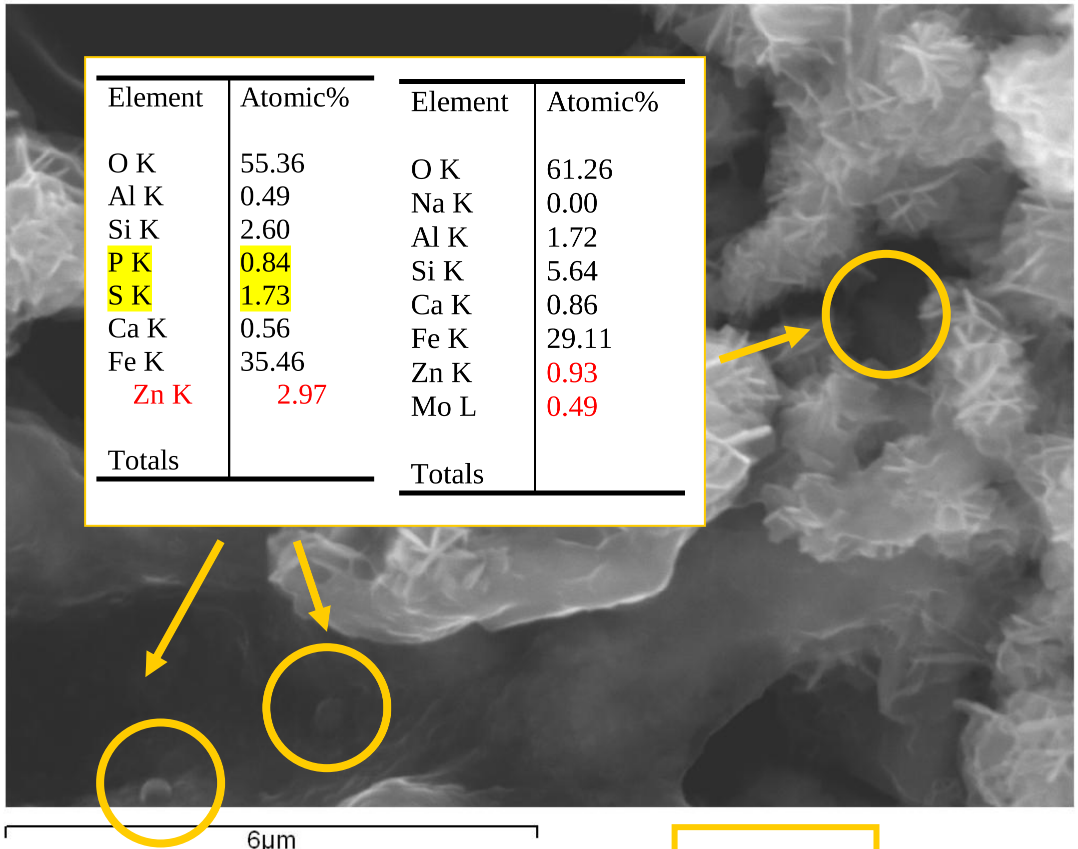
Element	Atomic%
O K	58.62
Mg K	0.78
Al K	3.04
Si K	11.67
P K	1.71
S K	3.62
Cl K	0.57
K K	0.75
Ca K	0.86
Ti K	0.01
Mn K	0.01
Fe K	15.38
Ni K	0.00
Cu K	0.90
Zn K	0.81
Sr L	1.27
Totals	100

High TOC values

Sample holder, C, to identify heavy metals.

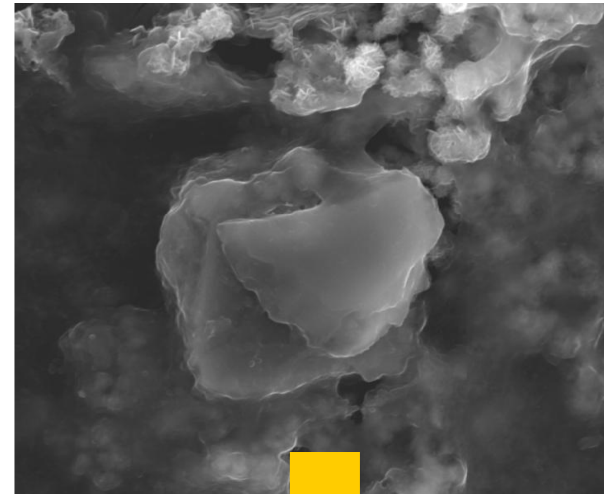
Decrease Al, Si, Fe
Increase O, P, S

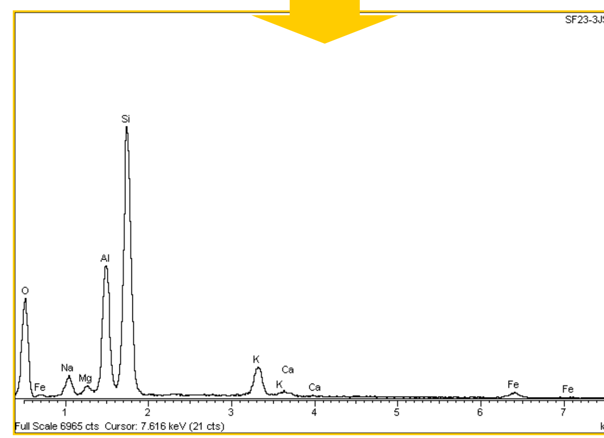
(natural colloids ?)



Element	Atomic%
O K	55.36
Al K	0.49
Si K	2.60
P K	0.84
S K	1.73
Ca K	0.56
Fe K	35.46
Zn K	2.97
Totals	

Element	Atomic%
O K	61.26
Na K	0.00
Al K	1.72
Si K	5.64
Ca K	0.86
Fe K	29.11
Zn K	0.93
Mo L	0.49
Totals	



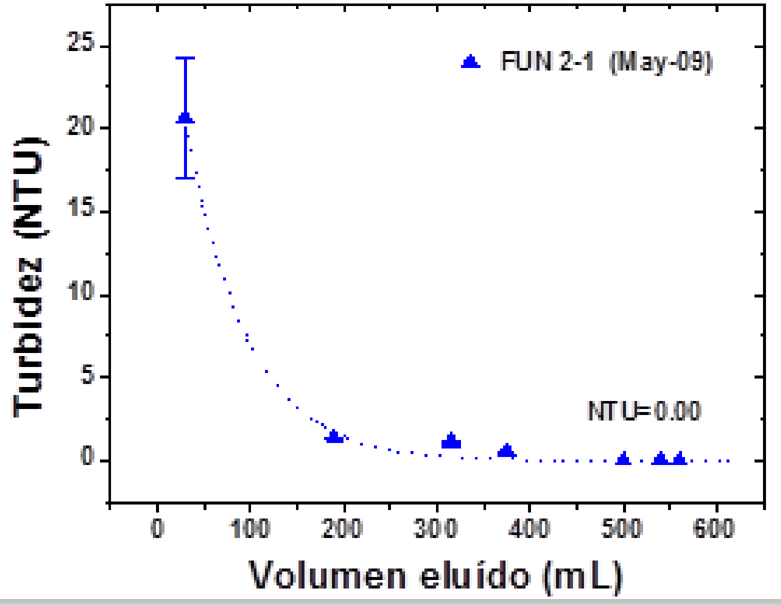


SF23-3

"New methodology" needed to clarify what happens and to quantify the actual contribution of BC. Last sampling Oct.2014.

- Chemical affects of bentonite on GW.
- Sample selection, to minimise existence of artefacts as e.g. iron oxides. Successive sampling with the same methodology (2009-2014).

- When the sample is taken is very important for results comparison.
- "Contamination" usually decreases as the volume eluted increases. Not important for other elements. Very important for BC analyses
- BC have to be studied at the "steady state"

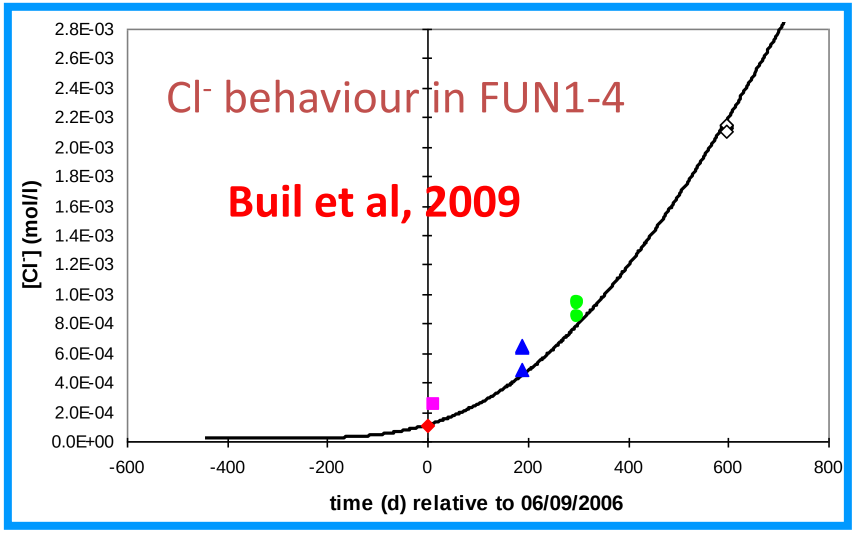


Chemical effects ?

Bentonite in contact with GW:

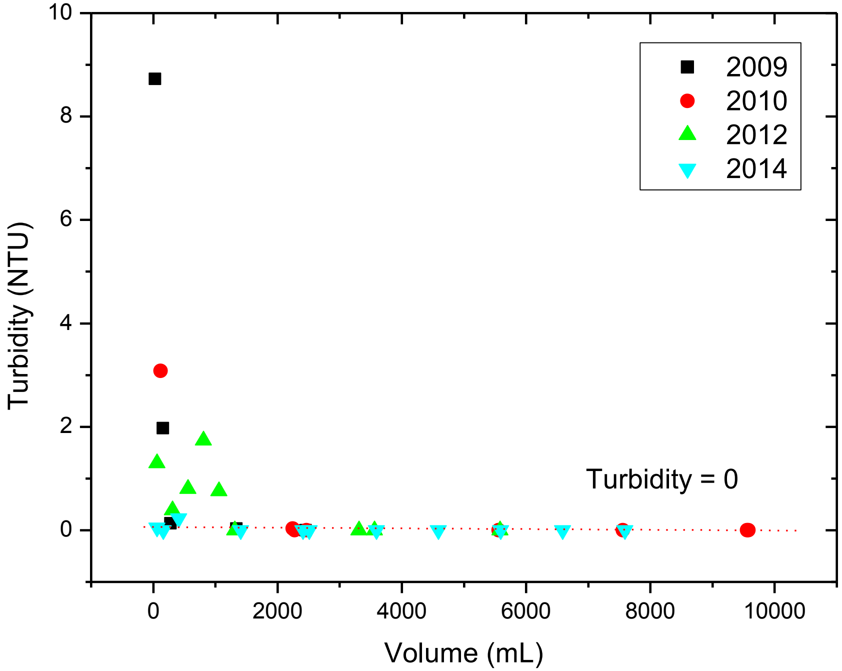
- Dissolution of main soluble salts (in FEBEX: halite and gypsum)
  Cl, Na, Ca, SO_4^{2-} (variation), conductivity
- Cl is conservative
- Na and Ca: ionic exchange
- SO_4^{2-} : other "problems"

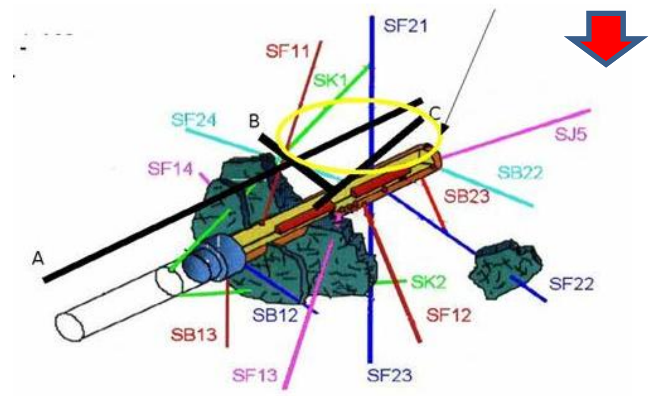
If we do not observe these effects, we do not expect the presence of bentonite colloids

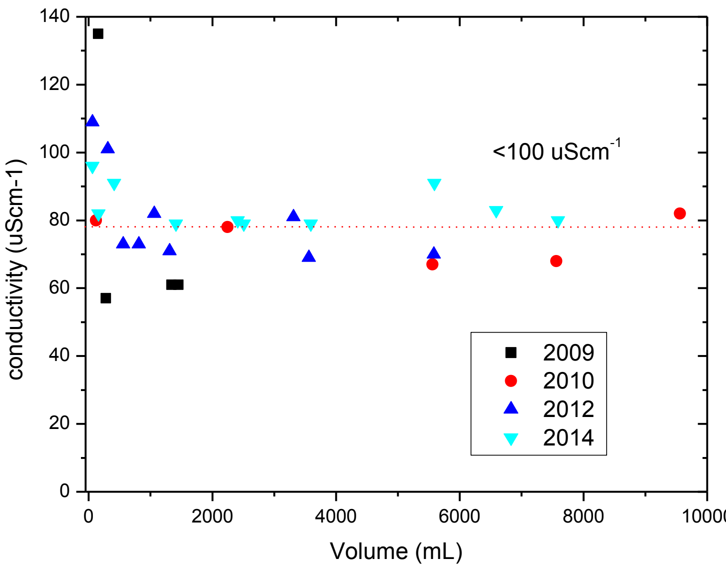


❖Simple 1D diffusion model: De (Cl^-) = 5,0E-11 m^2/s.

Reference: SJ5-3

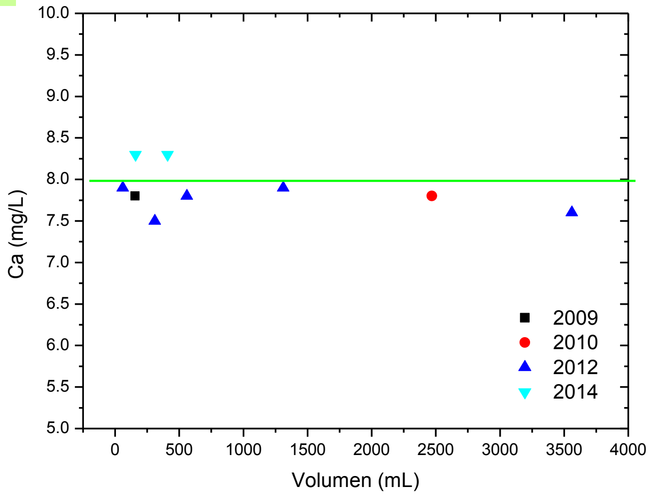


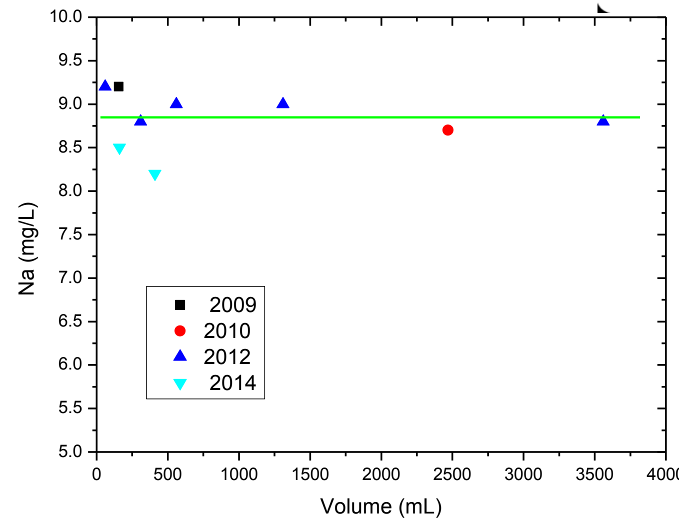


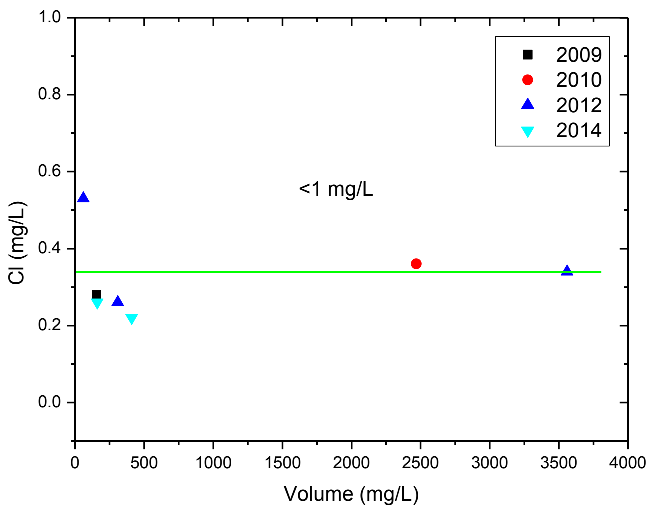


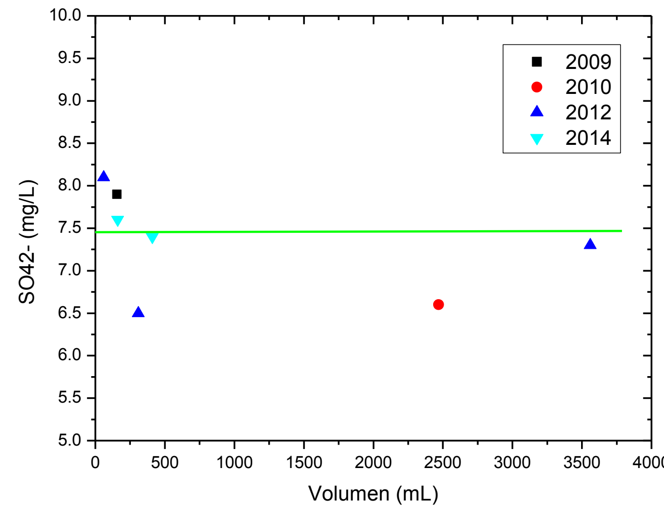
Stable

Reference: SJ5-3



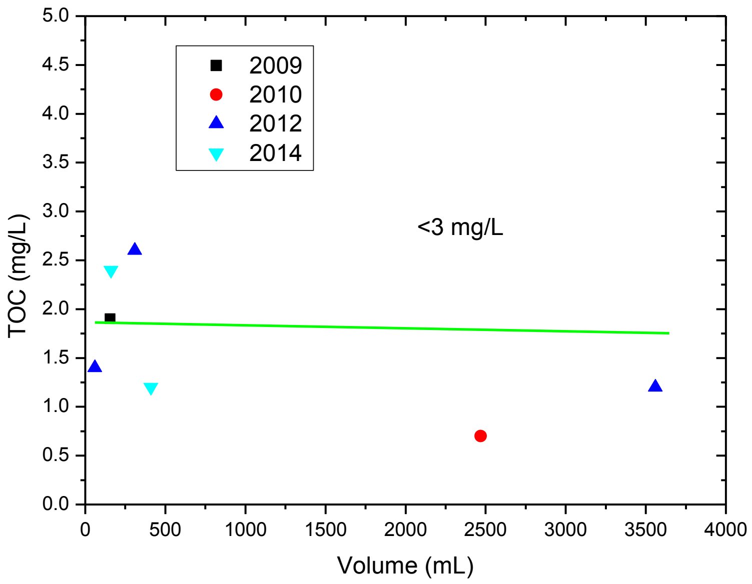




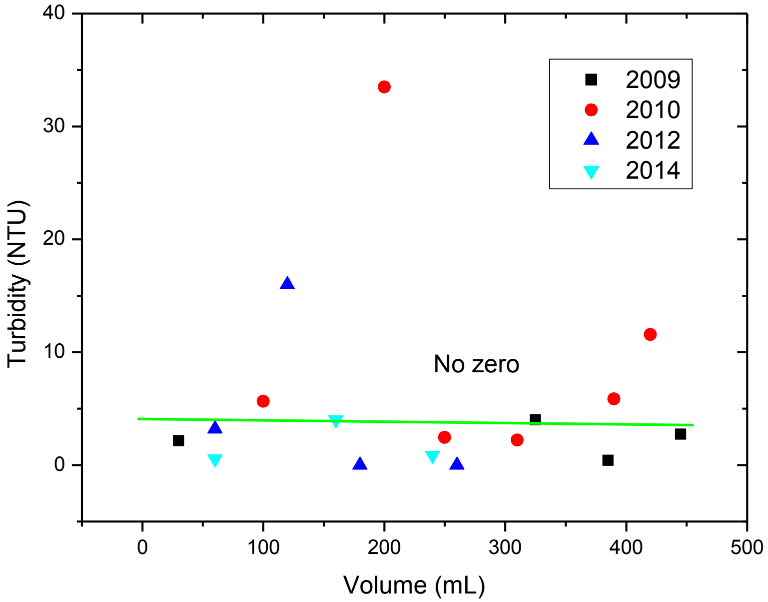


Physico-chemistry of Actinides and Fission Products Unit

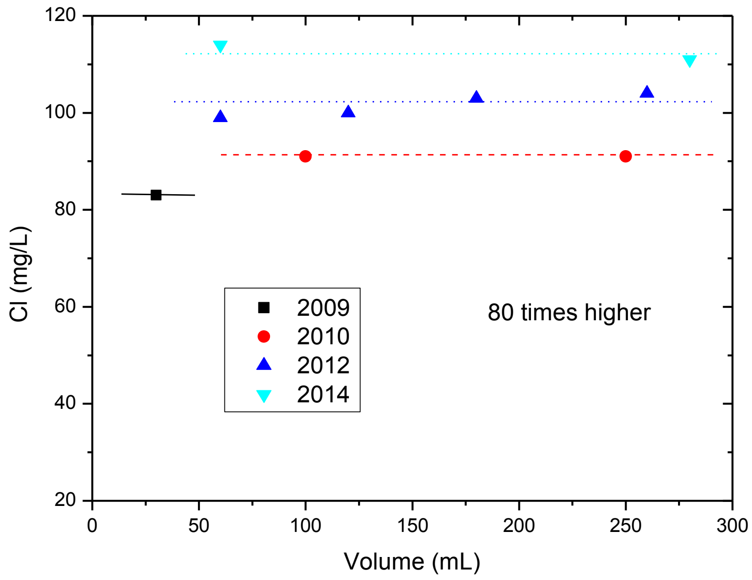
Reference: SJ5-3



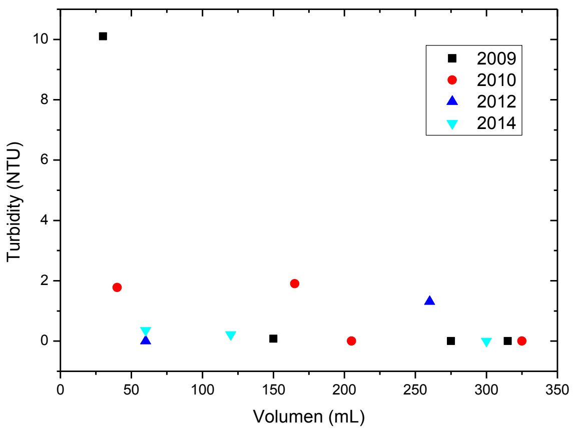
FUN1 and FUN2

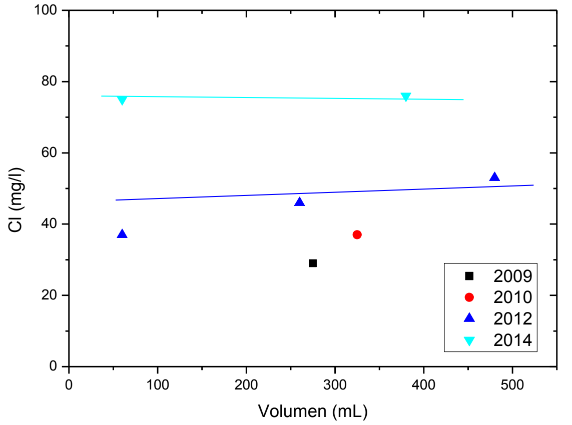


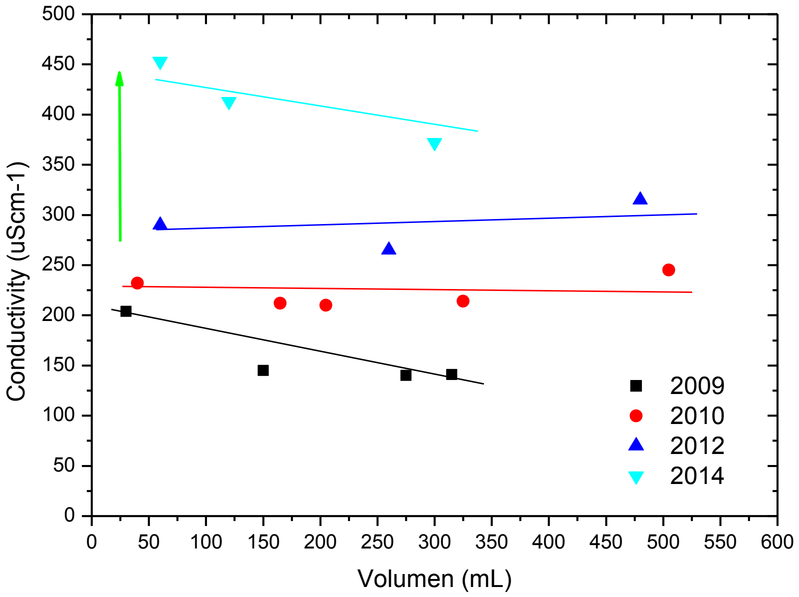
FUN 1-4 (30 cm)



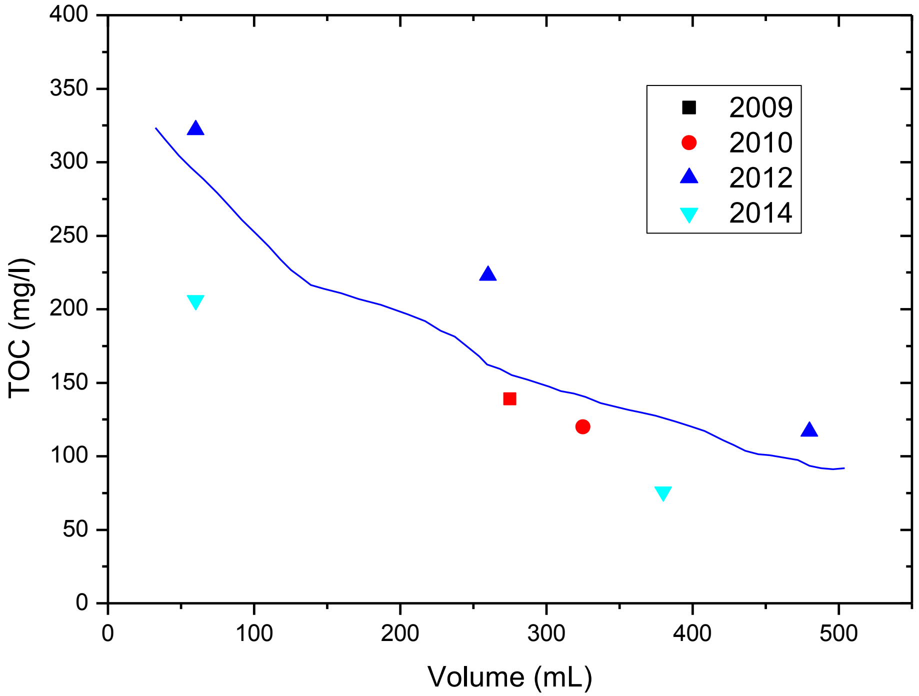
FUN 2-2 (30 cm)


Turbidity (NTU)
Volumen (mL)
2009
2010
2012
2014


Cl (mg/l)
Volumen (mL)
2009
2010
2012
2014


Conductivity (uScm-1)
Volumen (mL)
2009
2010
2012
2014

FUN 2-2 (30 cm)



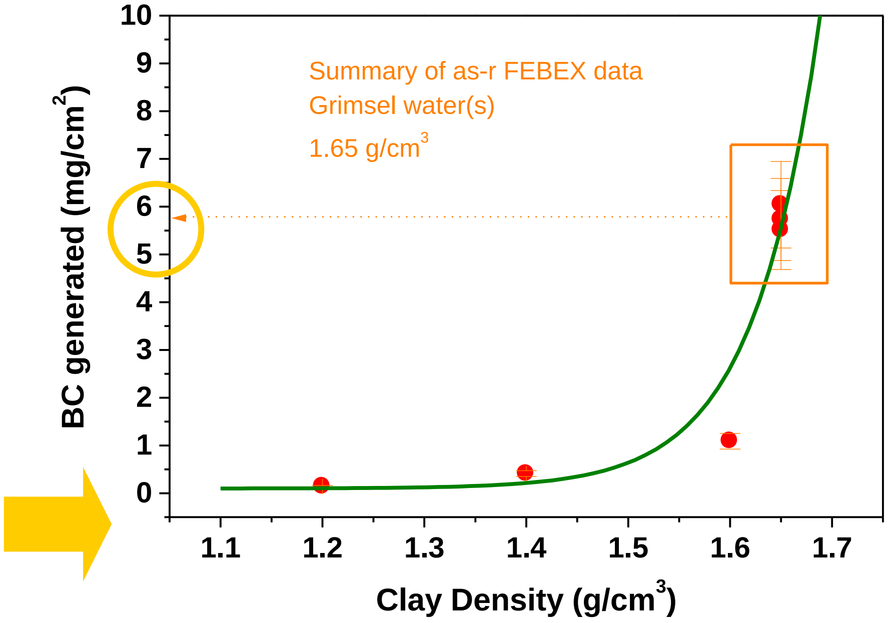
Not related to the bentonite

Colloidal material still coming from the excavation disturbance still exist: it decrease very slowly with time.

The highest Al concentration (main BC indicator) found in the "bentonite disturbed" water.

Still very low (max around 0.5-0.8 ppm, equivalent BC)

- FEBEX tunnel area: "quasi-diffusive regime" low transmissivity regions: (data from static experiments).
- Total surface: 124,57 m^2; max at equilibrium: 6850 g. Size paths and "mobilisation by diffusion".



For 100-300 nm colloids, *D*, is $4.9 \cdot 10^{-12}$ / $1.6 \cdot 10^{-12}$ m^2/s, thus the relation $C(t)/C_0$, at 20 cm from the bentonite (mínimum to FUN 1) after 13 years (Missana *et al.*, 2011) : $1.6 \cdot 10^{-3}$ / $3.4 \cdot 10^{-8}$, significantly lower than than 100 ppb estimation. Deposition due to chemistry of roughness effects not included. FEBEX tunnel, Ca in fillings materials.

NEXT BELBAR ANNUAL MEETING: IN MADRID

26-27 February or

05-06 March

Doodle (?)

- Full first day with evening poster presentation + half a day;
- Submission of extended abstract for presentation/posters: a CIEMAT report can be published;
- People of BELBAR (other institutions to be invited ?);
- Topical meeting (on clay properties?).