Karlsruhe Institute of Technology

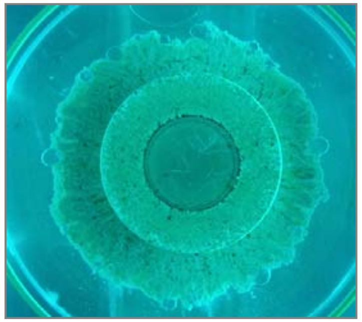
BELBaR

Erosion /destabilisation of compacted FEBEX bentonite with glacial melt type water under quasi-stagnant flow conditions

Muriel Bouby, Stephanie Heck, Florian Huber, Thorsten Schäfer

BELBaR
First Workshop

Helsinki, 5-7 March 2013



Safety Assessments Nuclear Waste Repositories

Colloids formation and stability → **Impact on the overall performance**

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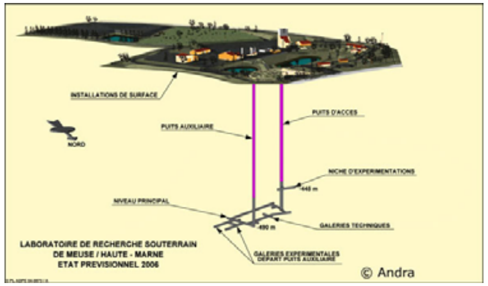
BELBaR: increases the knowledge of the processes that controls clay colloid stability, generation and ability to transport radionuclides (RNs):

- (WP2) erosion of bentonite buffers: main mechanisms, maximum extent, under various physico-chemical conditions
- (WP4) clay colloid stability = f (pH, IS, OM)
- (WP3) interactions (colloids, RNs, host rock): mobility, sorption/desorption



KIT-INE

- WP2
- WP3
- WP4

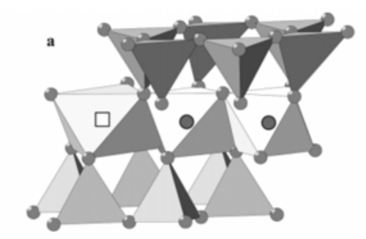
KIT-INE contribution into WP2 : Bentonite erosion

1- *COLLOID GENERATION EXPERIMENTS*

- Compacted bentonite (FEBEX or MX80)
- Raw, different Na/Ca-ratios through cation exchange, contacted or not with RNs
- Erosion under various chemical conditions (pH, IS, cation composition, OM)
- Static or dynamic conditions
- Effect of sand admixture

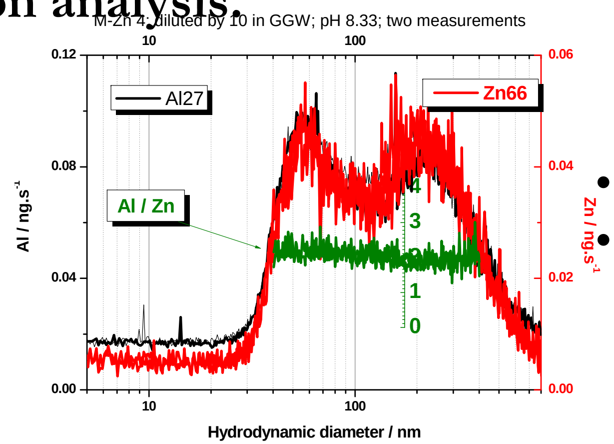
► Detection and characterization/quantification of the colloids: ICP-MS, PCS, SPC, LIBD, SEM/EDX, STEM/HAADF and AsFlFFF/ICP-MS.

► Addition of structural labelled montmorillonite is foreseen to reduce analytical uncertainty on erosion analysis.



- Zn or Ni structural bond (~ 7 mass %)

J.Brendlé, Mulhouse, (F)



- Al/Zn mass ratio ~ 2
- Ca-CCC = 1 mM

KIT-INE contribution into WP2 : Bentonite erosion

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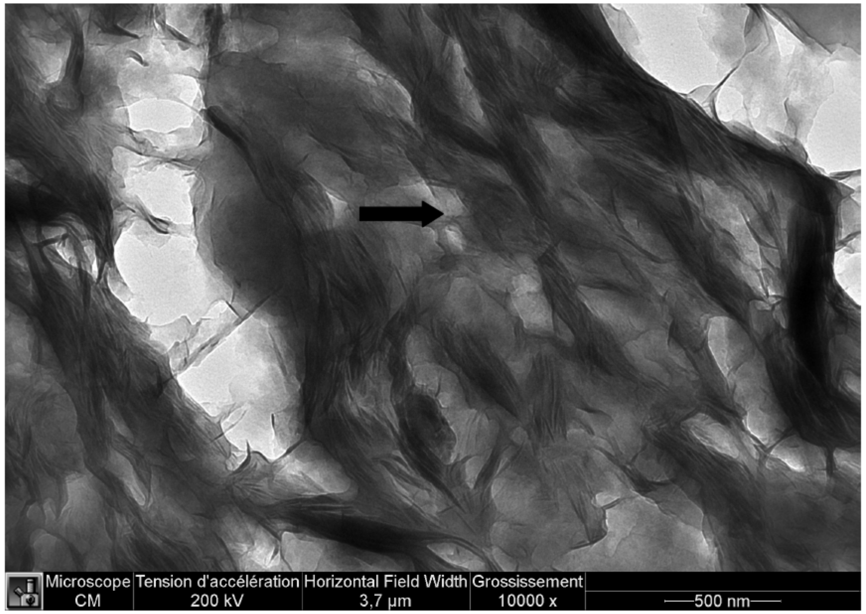
2- *POST-MORTEM ANALYSIS*

(GEL LAYER AND BENTONITE PLUG CHARACTERIZATION)

Water exchange to
1) methanol and 2) to an epoxy resin followed by hardening



• Cutting (FIB, microtome)
• Further characterization
(LA-ICPMS, XRD, STEM-HAADF)

KIT-INE contribution into WP2 : Erosion

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1- *COLLOID GENERATION EXPERIMENTS*

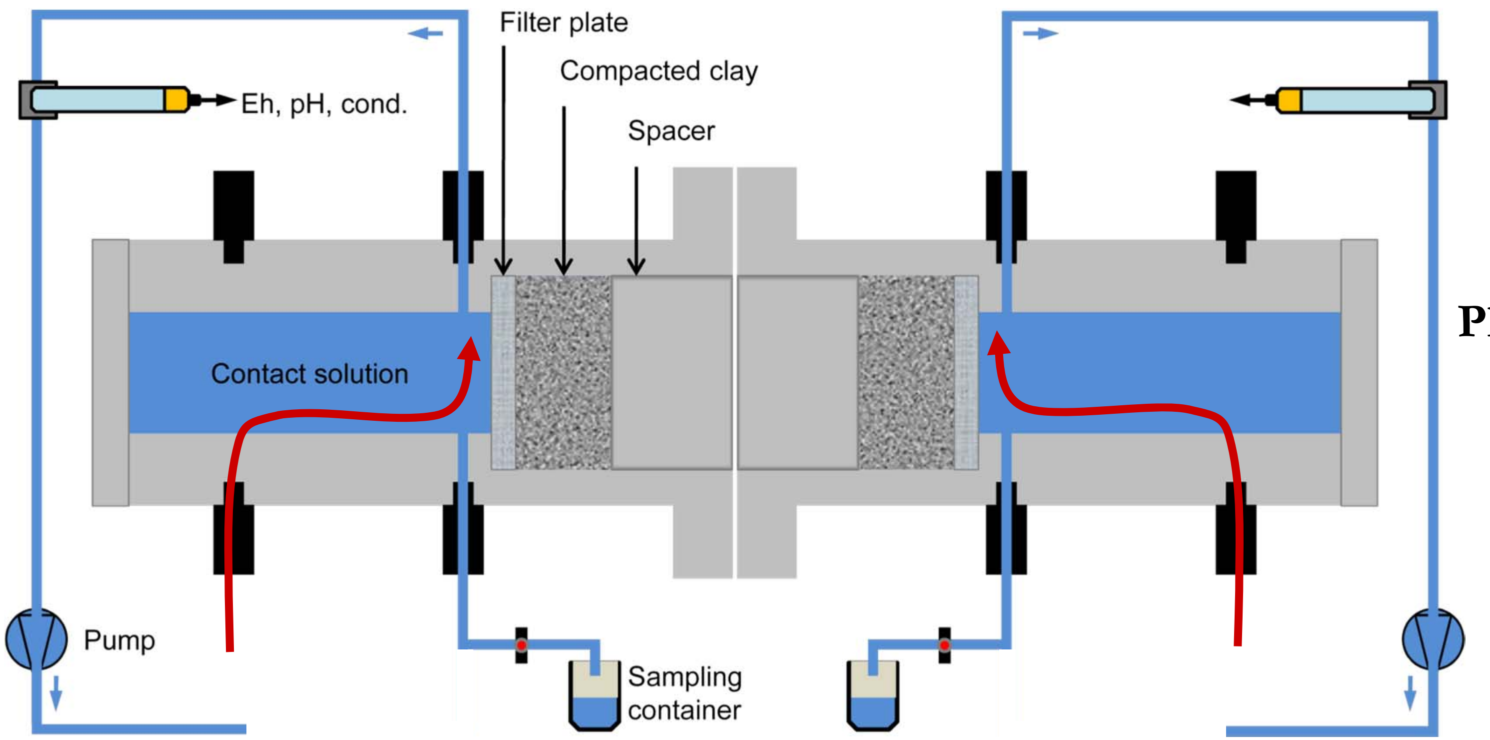
2012/2013

- Compacted bentonite (FEBEX or MX80) → FEBEX, MX80
- Raw, different Na/Ca-ratios through cation exchange, contacted or not with RNs → Raw, various Na/Ca
- Erosion under various chemical conditions (pH, IS, cation composition, OM) → Glacial melt water type
- Static or dynamic conditions → Quasi-stagnant
- Effect of sand admixture

Two different set-ups

- **Erosion of one side of a compacted clay pellet**
- **Radial design with erosion of all the external ring surface**

First design: „Two sided reactor“



Design
PhD H.Seher (2010)

- Test with 1 double reactor
- Compacted clay pellets

  ø: 19 mm, h: 10 mm, dry density 1.6 g.cm^{-3})
- Flow rate: few µL / min (~1-2 L/y)
- Glacial melt water type

First design: „Two sided reactor“

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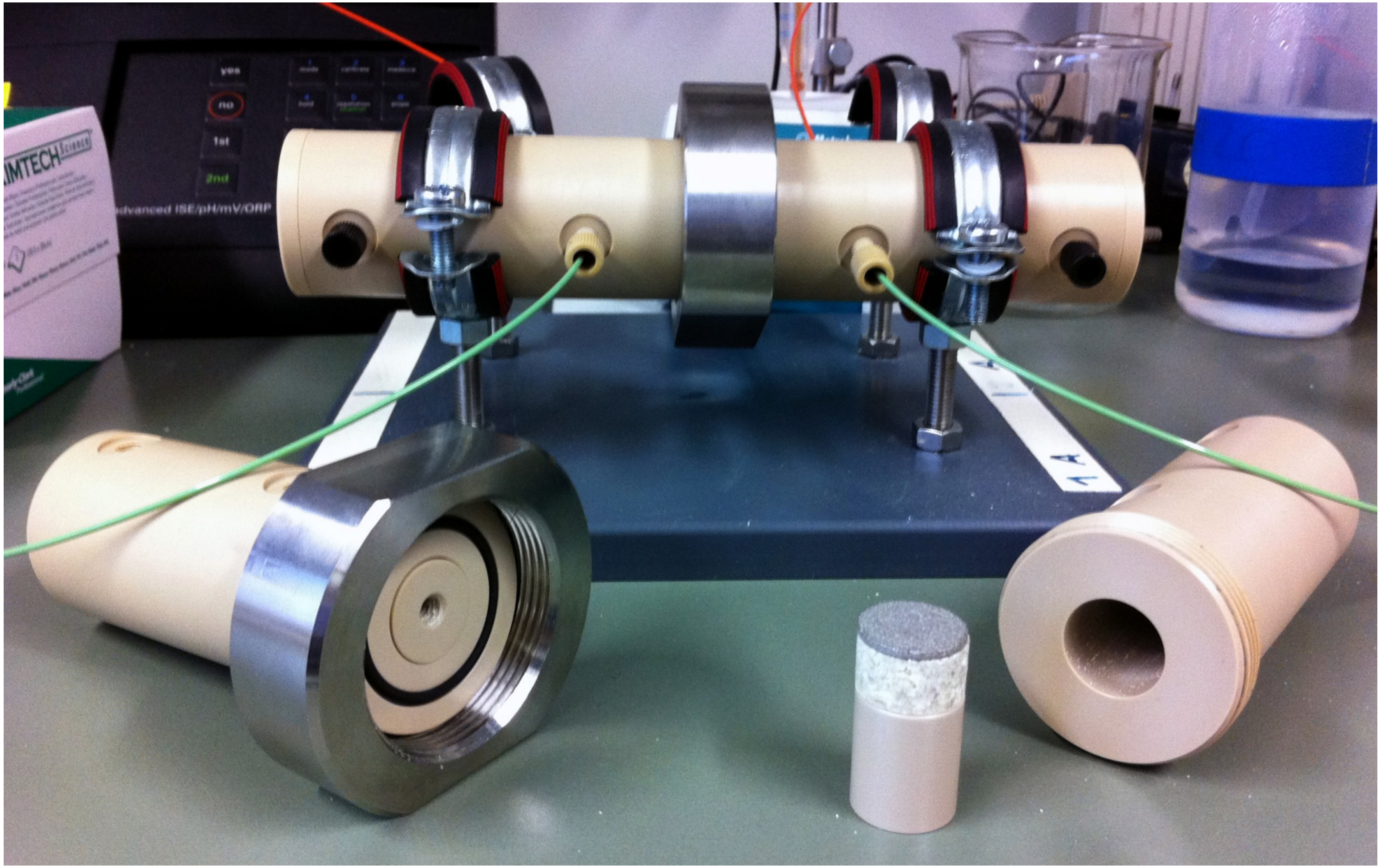

Choice of the synthetic water composition from literature

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SKB report TR-06-31

	Forsmark	Laxemar	Äspö	Finnsjön	Gideå	Grimsel: interacted glacial meltwater	"Most saline" groundwater at Laxemar	"Most saline" groundwater at Olkiluoto	Cement pore water	Baltic seawater	Ocean water	Maximum salini from glacial upconing
pH	7.2	7.9	7.7	7.9	9.3	9.6	7.9	7.0	12.5	7.9	8.15	7.9
Na	0.089	0.034	0.091	0.012	0.0046	0.000069	0.349	0.415	[illegible]	[illegible]	[illegible]	[illegible]
Ca	0.023	0.0058	0.047	0.0035	0.00052	0.00014	0.464	0.449	0.018	0.0024	0.0103 .	0.27
Mg	0.0093	0.00044	0.0017	0.0007	0.000045	0.0000006	0.0001	0.0053	< 0.0001	0.010	0.053	0.0001
K	0.0009	0.00014	0.0002	0.00005	0.00005	0.000005	0.0007	0.0007	0.0057	0.002	0.01	0.0005
Fe	33×10^{-6}	8×10^{-6}	4×10^{-6}	32×10^{-6}	0.9×10^{-6}	0.003×10^{-6}	8×10^{-6}	60×10^{-6}	$\leq 10\times10^{-6}$	0.3×10^{-6}	0.04×10^{-6}	2×10^{-6}
HCO_3^-	0.0022	0.0031	0.00016	0.0046	0.00023	0.00045	0.00010	0.00014	≈ 0	0.0016	0.0021	0.00015
Cl^-	0.153	0.039	0.181	0.0157	0.0050	0.00016	1.283	1.275	≈ 0	0.106	0.546	0.82
SO_4^{2-}	0.0052	0.0013	0.0058	0.00051	0.000001	0.00006	0.009	0.00009	≈ 0	0.0051	0.0282	0.01
HS^-	≈ 0	3×10^{-7}	5×10^{-6}	–	$< 3\times10^{-7}$	–	$< 3\times10^{-7}$	$< 1.6\times10^{-7}$	≈ 0	–	–	$< 3\times10^{-7}$
O_2 fugacity (bar)	$<< 10^{-73}$	$<< 10^{-70}$	$<< 10^{-73}$	$<< 10^{-70}$	$<< 10^{-70}$	$< 10^{-0.17(a)}$	$<< 10^{-70}$	$<< 10^{-70}$	$\approx 10^{-70}$	$10^{-0.7}$	$10^{-0.7}$	$<< 10^{-70}$
Ionic strength (mol/L)	0.19	0.053	0.24	0.025	0.006	0.0013	1.75	1.76	0.057	0.13	0.65	1.09
TDS (g/L)	9.32	2.78	11.1	1.33	0.33	0.08	73.7	73.4	1.63	6.81	35.1	47.2
Reference	/1/	/2/	/3/	/3/	/3/	/4/	/5/	/6/	/7/	/2/	/6/	/2/
Notes	Borehole KFM02A, 512 m depth	Borehole KLX03, 380 m depth	Repository depth	Repository depth	Repository depth	Max. O_2 fugacity in glacial meltwaters	Depth ≈ 1,500 m.	See also /Pitkänen et al. 1999/ depth = 863 m, sample 42		Sampled at Simpevarp		Laxemar water at 1,350 m

Na^+, Ca^{2+}, Mg^{2+}, K^+, Fe, Si, Cl^-, SO_4^{2-}, HCO_3^-

SSM Report 2011:22

Table 2. Reference compositions for glacial melt waters.

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
		mg/L						
'Juvenile' glacial melt water	5.8	0.17	0.4	0.18	0.1	0.5	0.5	0.12
'Equilibrated' glacial melt water	9.25	0.17	0.39	3.0	0.1	0.5	0.5	5.43

Table 3. Compositions for glacial melt waters from [19].

Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
		mmol/L						
Robertson Glacier, Canadian Rockies	8.3	0.02	0.01	1.7	0.5	0.01	1.0	2.6
John Evans Glacier, Canadian Arctic	8.3	0.3	0.04	1.3	0.3	0.1	1.5	0.4
Longyearbreen, Svalbard		3.4	0.08	4.5	4.9	0.08	10.0	2.2
Antarctic Ice Sheet, Casey Station	8.4	6.6	0.2	0.5	0.1	2.2	0.3	3.5
Bindschadler Ice Stream, Antarctica	6.5	35.0	0.7	9.0	8.6	2.0	31.0	7.5

SKB Report R-06-105

Components	Forsmark groundwater	Initial water in fractures [1)]	Grimsel groundwater [2)]	Equilibrated ice melting water [3)]
pH (–)	7.0	6.95	9.6	6
Eh (mV)	–143	–189	–200	864
$[Na^+]_{tot}$	$8.88\cdot10^{-02}$	$8.88\cdot10^{-02}$	$6.90\cdot10^{-04}$	$6.90\cdot10^{-04}$
$[K^+]_{tot}$	$8.75\cdot10^{-04}$	$8.75\cdot10^{-04}$	$5.00\cdot10^{-06}$	$5.00\cdot10^{-06}$
$[Ca^{2+}]_{tot}$	$2.33\cdot10^{-02}$	$2.33\cdot10^{-02}$	$1.40\cdot10^{-04}$	$1.40\cdot10^{-04}$
$[Mg^{2+}]_{tot}$	$9.30\cdot10^{-03}$	$9.30\cdot10^{-03}$	$6.20\cdot10^{-07}$	$6.20\cdot10^{-07}$
$[HCO_3^-]$	$1.77\cdot10^{-03}$	$2.03\cdot10^{-03}$	$4.50\cdot10^{-04}$	$1.57\cdot10^{-05}$
$[Cl^-]_{tot}$	$1.53\cdot10^{-01}$	$1.53\cdot10^{-01}$	$1.60\cdot10^{-04}$	$4.04\cdot10^{-04}$
$[S]_{tot}$	$6.80\cdot10^{-03}$	$6.80\cdot10^{-03}$	$6.10\cdot10^{-05}$	$6.10\cdot10^{-05}$
$[Br^-]_{tot}$	$2.98\cdot10^{-04}$	$2.98\cdot10^{-04}$	$3.80\cdot10^{-07}$	$3.80\cdot10^{-07}$
$[Si]_{tot}$	$1.85\cdot10^{-04}$	$2.67\cdot10^{-04}$	$2.50\cdot10^{-04}$	$2.50\cdot10^{-04}$
$[Fe]_{tot}$	$3.31\cdot10^{-05}$	$1.00\cdot10^{-06}$	$3.00\cdot10^{-09}$	$3.00\cdot10^{-09}$

1) Groundwater composition obtained in the fracture after the first time step of the simulations, as a result of equilibrating the "Forsmark groundwater" with fracture minerals (calcite, chalcedony, kaolinite and haematite).

2) Grimsel groundwater composition, discharging groundwater from the Migration shear zone [AU 96]. Data compiled from /Bajo et al. 1989, Aksoyoglu et al. 1990/ and /Eikenberg et al. 1991/.

3) Grimsel groundwater equilibrated with atmospheric O_2 and CO_2. $[O_2]=2.74\cdot10^{-4}$M (i.e. 8.76 mg/L).

Synthetic carbonated water (SGW)

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SKB Report TR-99-06

Component	At repository closure	After 1000 years	Glacial period: saline upconing	Glacial period: meltwater
pH	6 to 9	7 to 10	6 to 8	8 to 10
Eh (mV)	0 to –400	–250 ± 100	–200 ± 100	–100 ± 100
Major components (mg/L):				
Na^+	10 to 3000	50 to 2000	4500	4.5
K^+	1 to 20	0 to 10	37	4
Ca^{2+}	1 to 3000	10 to 2000	9900	7
Mg^{2+}	1 to 200	1 to 100	41	1
HCO_3^-	10 to 1000	10 to 40	71	25
Cl^-	20 to 10000	100 to 5000	25000	< 1
SO_4^{2-}	0.1 to 600	0.1 to 400	511	5
HS^-	0.01 to 10	< 1	< 1	< 0.1
TOC	0 to 30	< 2	< 2	< 2

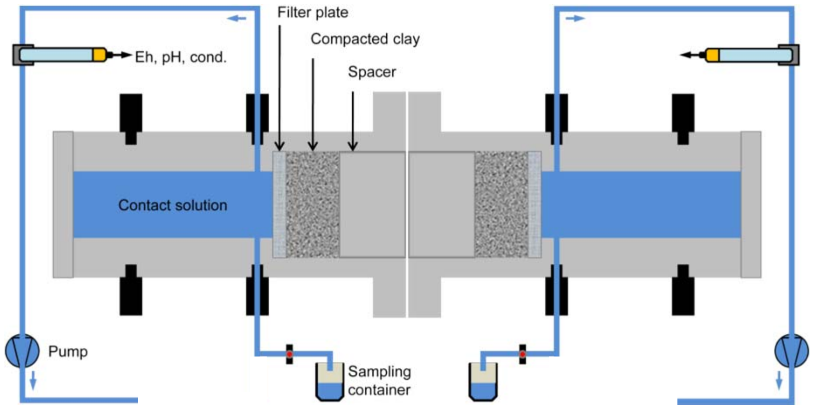
- **Water composition evolution (ICP-OES / MS and IC)**
- **Colloid formation and characterization**
- **AsFlFFF/ICP-MS after spiking with Eu, Th, U**

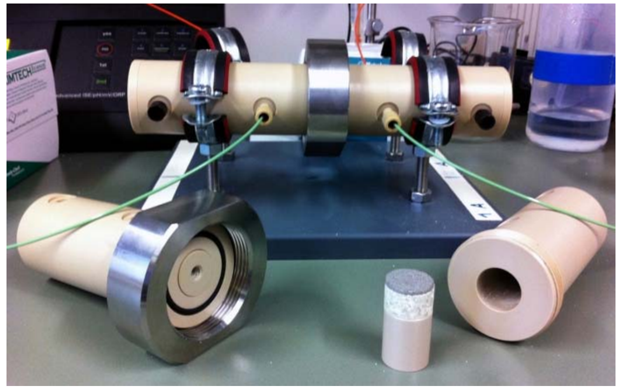
This work (Grimsel type)

- pH = 8.4
- Na^+ 1.2 mM – 28.4 mg/L
- Ca^{2+} 0.05 mM – 1.5 mg/L
- F^- 0.1 mM – 2.8 mg/L
- Cl^- 0.074 mM – 2.64 mg /L
- SO_4^{2-} 0.04 mM – 4.13 mg/L
- Si 0.25 mM – 7 mg/L
- HCO_3^- 1mM – 84 mg/L

- Ionic strength 1.26 10^{-3}M

Results of the preliminary test (1)





- **Bentonite pellets: raw FEBEX, 1.6 g.cm^3**
- **Volumetric Flow rate: (2.8   0.2) µL / min or ~1.5 L/y**
- **Linear Flow rate: 2.3 10^{-4} m/s or 7261 m/y**
- **V_{liquid}: 11.6 mL**
- **pH = 8.4 ± 0.3, constant**
- **Swelling: 30 % solution retained over the three first days**
- **[F^-] ~ constant (fluorite) ; [Cl^-] and [SO_4^{2-}] increase and then decrease (gypsum, celestite, siderite)**

Results of the preliminary test (2)

✓ Colloids are produced :

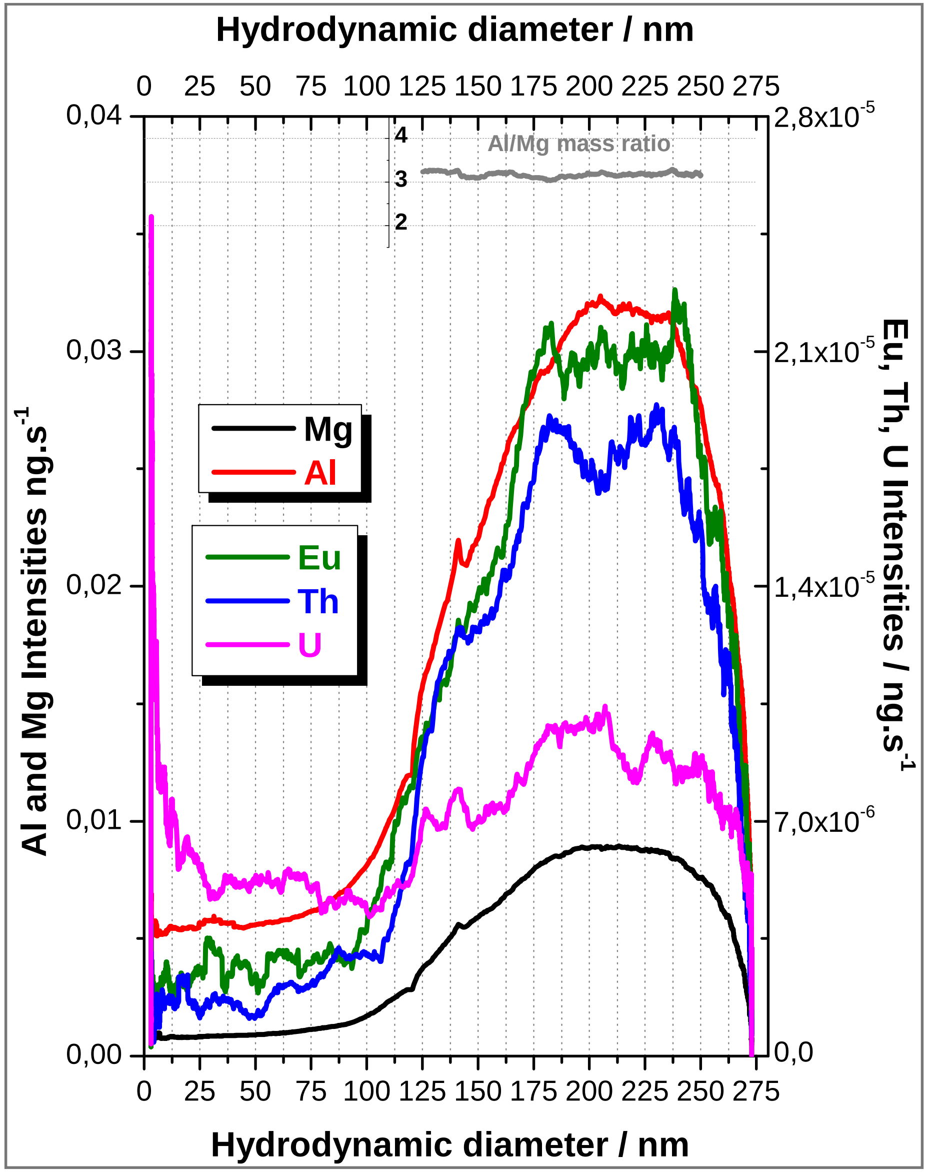
* 0.2 g/L SGW after 1 month

* 193 g/L/m² in agreement with PhD work H. Seher ☺

* but reproducibility ?

✓RNs (Eu,Th, U) spiking to test the sorption behaviour of the eroded colloids (AsFlFFF/ICP-MS : size fractionation method)

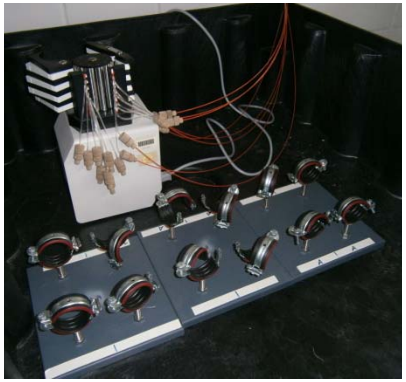
- Peak max. (210 ± 10) nm, broad size distribution
- Colloidal recovery: (61 ± 5) %
- Al/Mg mass ratio (3.17 ± 0.05)
- Al/Mg mol ratio (2.85 ± 0.05)
- Eu, Th, U: very low sorption (4,16, 1%)



Results of the preliminary test (3)

✓Huge deformation observed „post-mortem“

NEXT STEPS…starting in 1 week for…



- FEBEX pellets ready for use: raw, Na-, Ca- and Na/Ca- exchanged
- Post-mortem analysis in…
- New reactors ordered: MX80, Grimsel ground water, OM, Sand admixture, RNs-sorbed, Ni/Zn montmorillonite included

Second design: radial set-up, mock-up test, Grimsel GW

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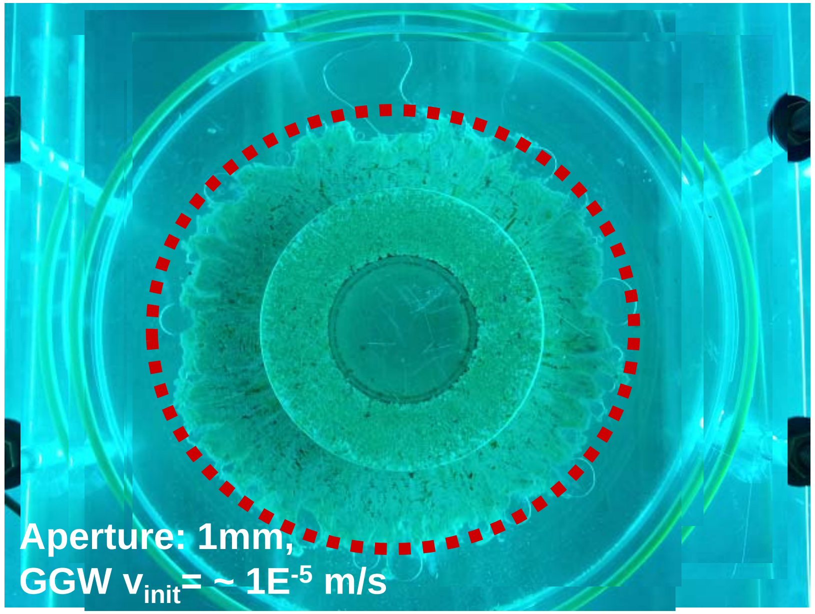
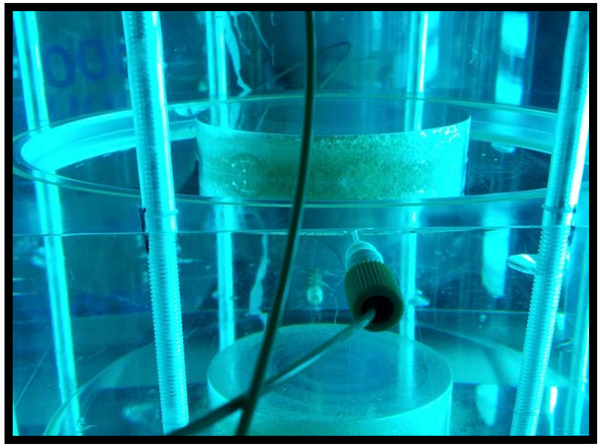
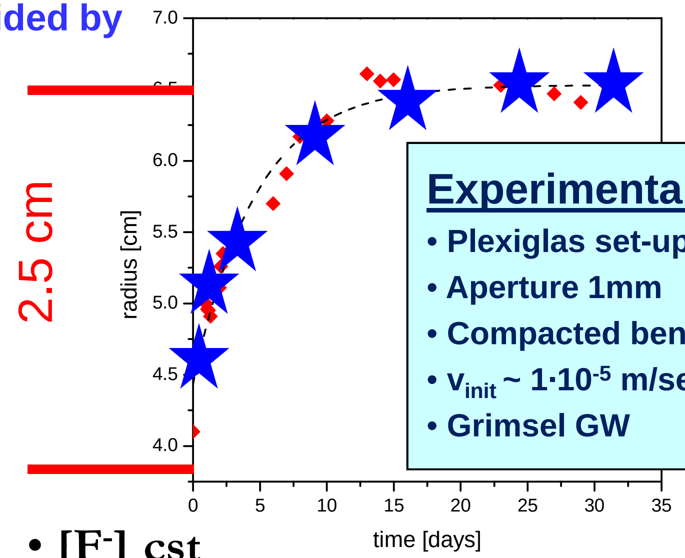
Compacted Febex bentonite ring (2.5 cm) provided by CIEMAT



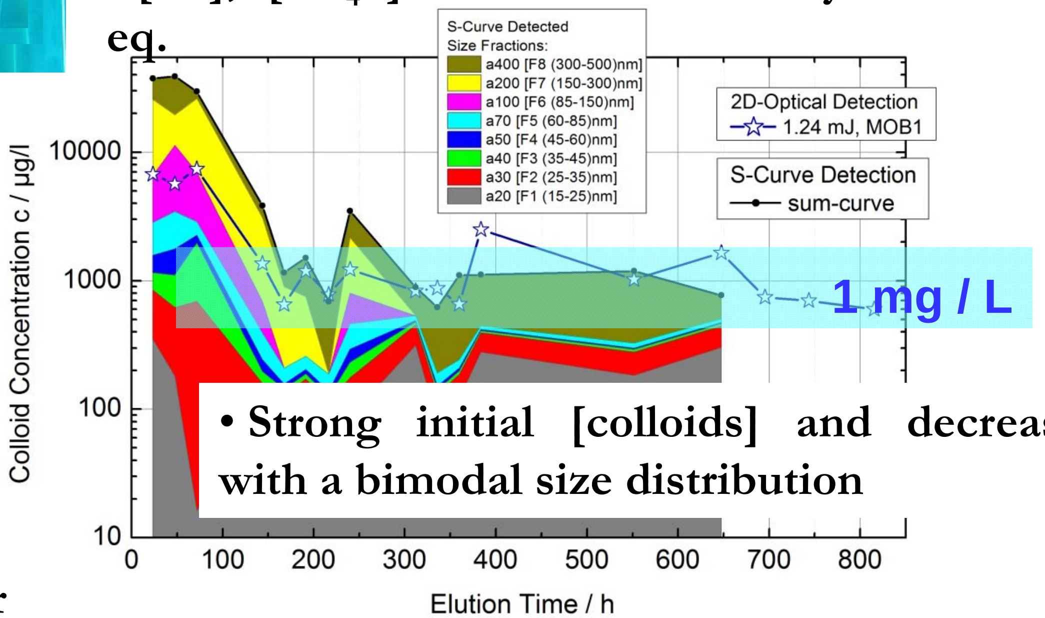




Experimental details:

- Plexiglas set-up
- Aperture 1mm
- Compacted bentonite 1650 kg/m^3
- v_{init} ~ 1·10^{-5} m/sec
- Grimsel GW

- [F$^-$] cst
- [Cl$^-$], [SO$_4^{2-}$] increase and in dynamic eq.



- Strong initial [colloids] and decrease with a bimodal size distribution

S. Heck, W. Hauser, R. Götz, J. Laber

Second design: radial set-up, mock-up test, Grimsel GW

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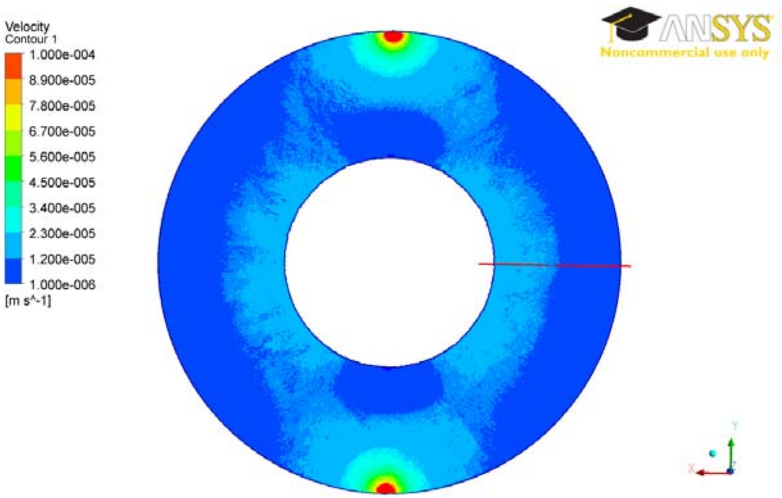
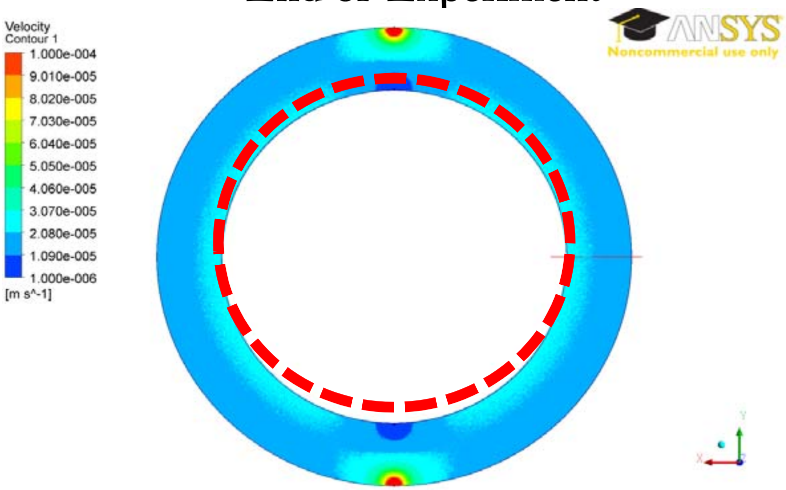
Start of Experiment



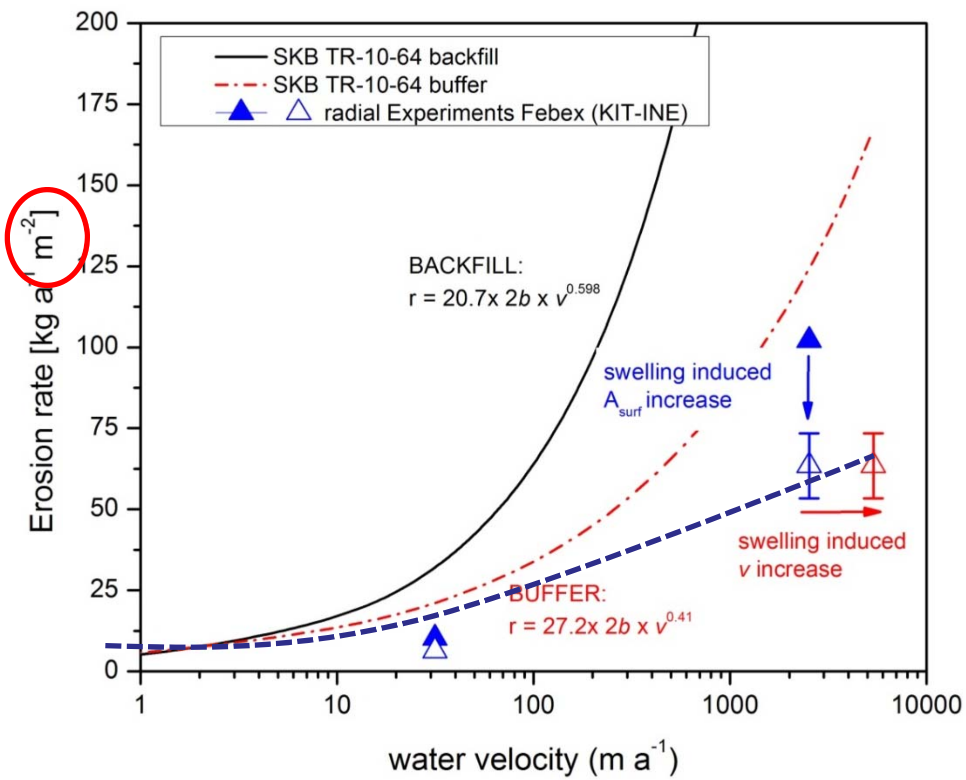
End of Experiment



3D Fluent model

SKB TR-10-64 (Bentonite erosion model)

- Fracture aperture (*2b*) 1mm
- Water velocity (*v*) varied
- Cylindrical deposition borehole (Ø 1.75m)



First conclusions

Erosion rates determined from the lab. expts are below the model predictions for a bentonite buffer material

Next step

- **More precise characterization of the eroded material (amount, mineralogy)**
- **Determination of the gel layer surface area (digital imaging)**
- **Variation of the fracture aperture**
- **Variation of the water flow velocity**
- **Control of the swelling pressure: comparison with a real situation, swelling depth into fracture = f(pressure)?**
- **Water composition evolution (pH, ions…)**
- **Raw, Na-, Ca-, Na/Ca-exchanged, Sand admixture, Ni/Zn Mont. added**
- **In-Situ integral experiment (CFM, GTS, Switzerland)…**

KIT-INE Contribution into WP3: Colloid radionuclide & host rock interaction

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1. Colloid attachment probability α (G. Darbha/F. Huber)

a) from the nanoscale to real systems

- **effect of divalent cations concentration (Ca) and NOM (FA) by AFM,**
- **force distance maps on granite components and synthetic material (Si- wafer),**
- **batch type studies on Fracture Filling Material,**
- **colloid migration studies in natural over-cored fractures from e.g. the Äspö system.** ***Idea: use of synthetic structural labeled montmorillonite colloids to reduce the uncertainty in attachment factor quantification and test the attachment reversibility (K_D approach)***

b) from CT data of a replica in PE of a natural core fracture

- **direct differentiation between charge heterogeneity and surface roughness effects contributing to colloid retention**

KIT-INE Contribution into WP3: Colloid radionuclide & host rock interaction

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2. **Clay colloid size heterogeneity effects on their stability and interation with RNs (PhD work K.K. Norrfors)**

   - **Applicability of the BET surface area scaling ?**

3. **Radionuclide bentonite sorption reversibility/ irreversibility**

   - **Mechanistical understanding for An(IV) clay colloid interaction as ≠ An(III) : eigencolloid formation or surface precipitation on clay surface?**

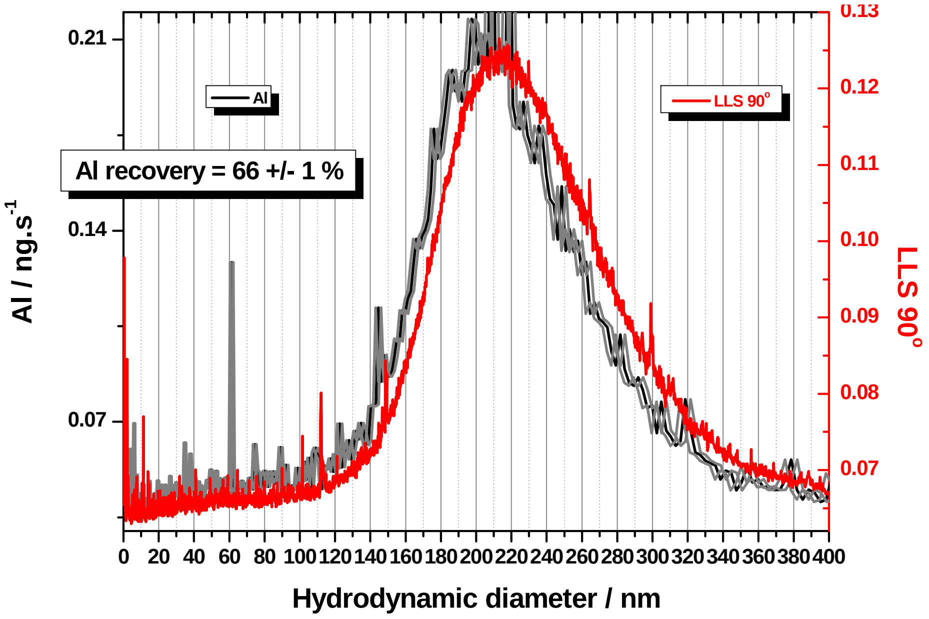
     - **AsFlFFF/ICP-MS, CE/ICP-Ms**
     - **Isotope Exchange**
     - **STEM-HAADF**

KIT-INE Contribution into WP4: Colloid stability

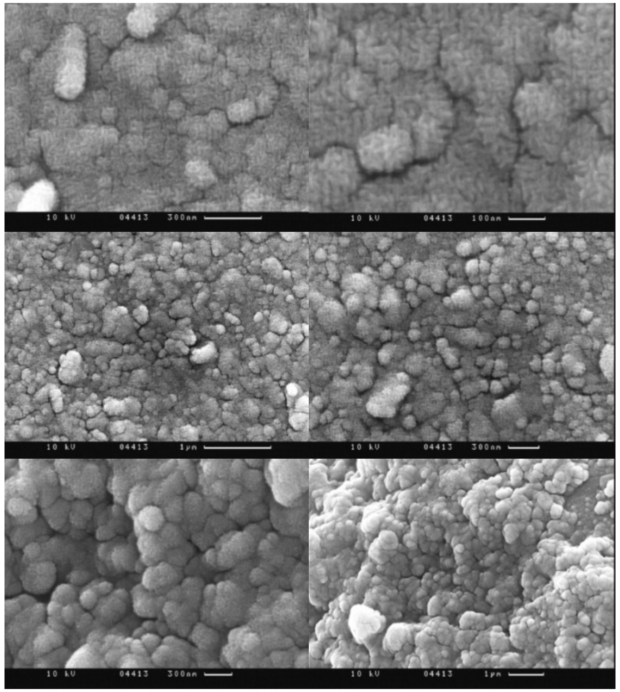
Systematic colloid stability studies: pH, low IS, OM

Why ? Contradicting results showing that the low IS and high pH conditions of the Grimsel GW were not sufficient to fully stabilize clay colloids: Long-term agglomeration demonstrated

EXAMPLE 1



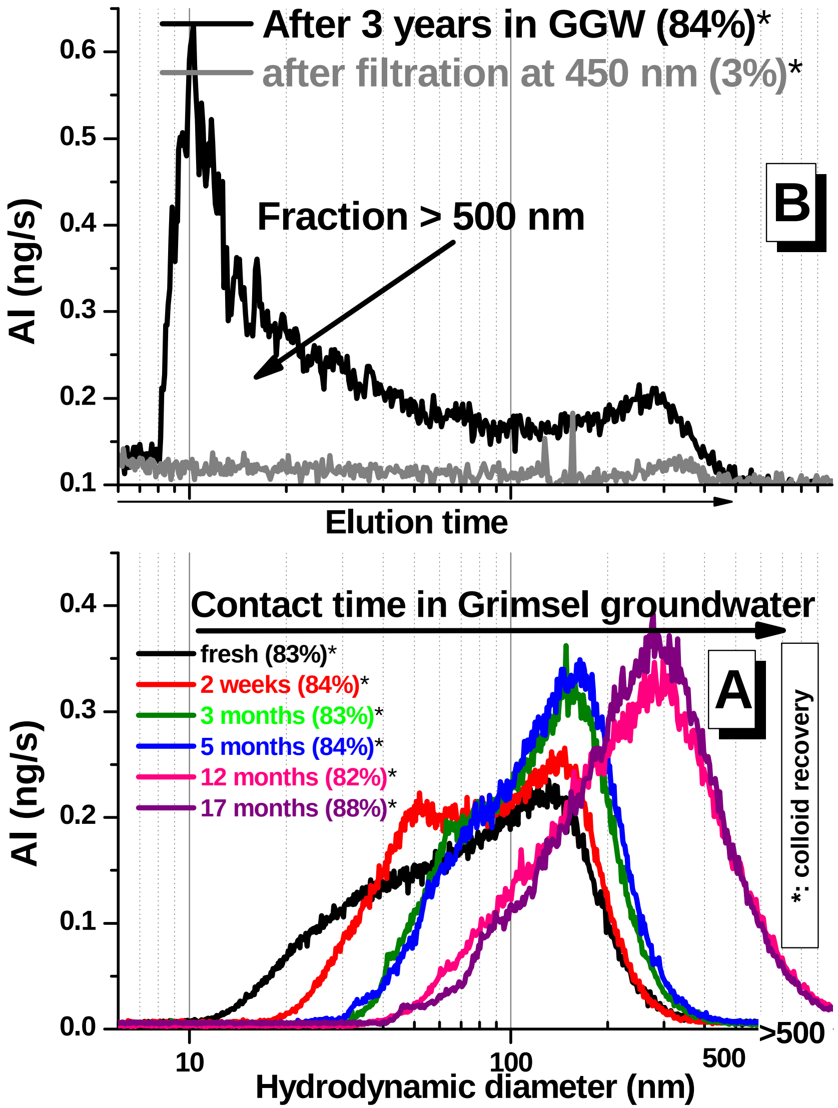
Colloidal fraction + huge aggregates found in a 10 y old FEBEX bentonite colloid solution stored in a brown PET, pH_f 8.0



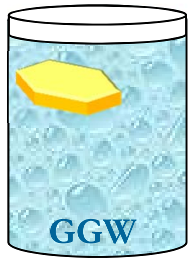
- SEM pictures

EXAMPLE 2

Al-fractograms evolution (size, recov.)



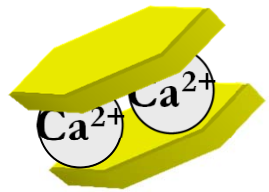
Bouby et al. GCA 75(13), 3866 (2011)



1- Slow agglomeration process over 3 years, reproducible

2- Explanations:

- Ca^{2+} ions induce agglomeration



- CCC = 10^{-3} M in $CaCl_2$ (Seher et al. 2010)

At 3.3 10^{-4} M, pH 9-10, W~ 100; colloid - colloid collision efficiency = 1%

→ *Slow clay colloid agglomeration not surprising*

KIT-INE Contribution into WP4: Colloid stability

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Systematic colloid stability studies: pH, low IS, OM

- **MX80 and FEBEX (delamination, rinsing-centrifugation)**
- **Glacial melt water types: pH~5 - 6 and pH 8-9**
- **Long time (starting in June for the rest of the project)**
- **Influence of the OM on the CCC**
  - PCS: fast coagulation studies (stability ratio W, CCC)
  - AsFlFFF/ICP-MS, LIBD, SPC: slow coagulation studies
- **Influence of Fe**
- **Tetravalent behavior**

99 years ago…!

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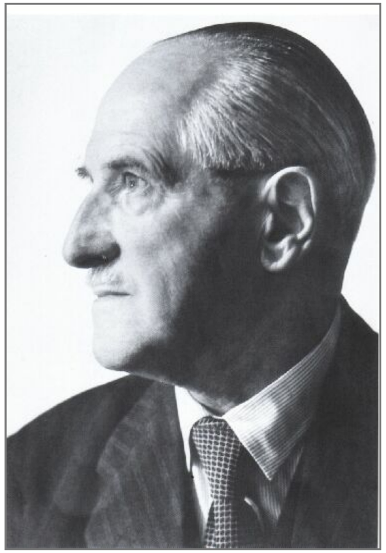

A BIT OF HISTORY

F. A. Paneth, (1887-1958) coined the term ``radiocolloid´´

``When a HNO_3 solution of Po is made alkaline with NH_4OH there is no apparent precipitation, but the solution which was previously dialyzable does not now show any Po in the dialysate, indicating the formation of a colloidal Po hydroxide ´´

Kolloid-Zeitschrift (1914), 13, 1- 4

I wish you all nice results to celebrate next year the first century on colloid studies!

Thank you for your attention!