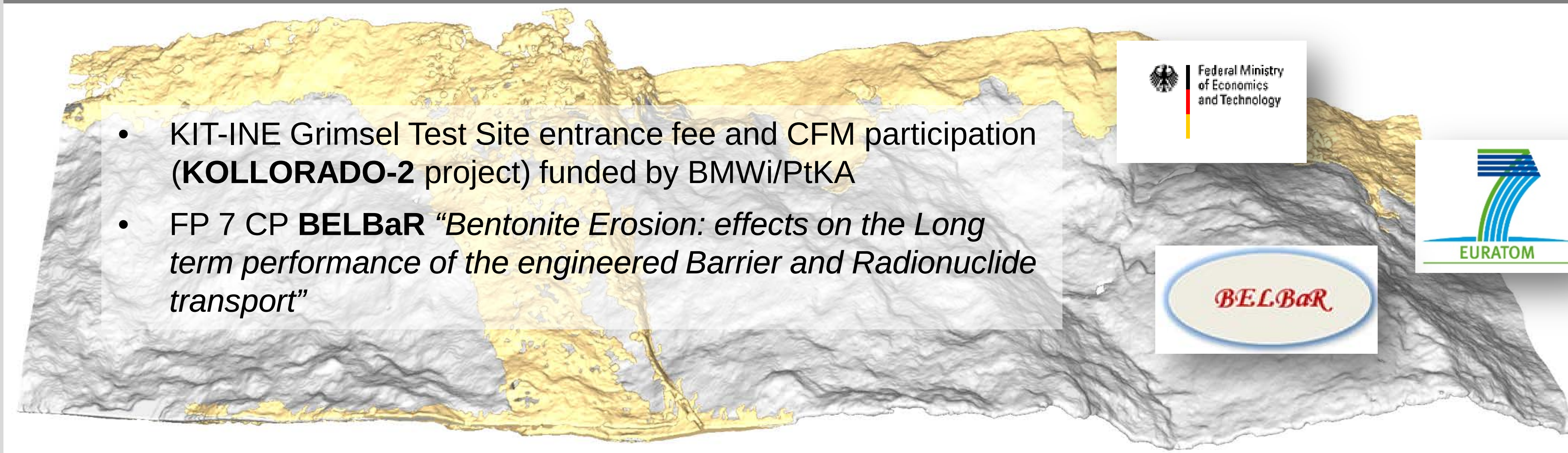
The latest results on colloid associated radionuclide mobility from the CFM project, Grimsel (Switzerland)

I. Blechschmidt, M. Bouby, S. Büchner, J. Brendlé, G. Darbha, H. Geckeis,T. Kupcik, R. Götz, W. Hauser, S. Heck, F. Huber, M. Lagos, A. Martin, T. Schäfer

INSTITUTE FOR NUCLEAR WASTE DISPOSAL (INE)



- KIT-INE Grimsel Test Site entrance fee and CFM participation (**KOLLORADO-2** project) funded by BMWi/PtKA
- FP 7 CP **BELBaR** *"Bentonite Erosion: effects on the Long term performance of the engineered Barrier and Radionuclide transport"*

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T. Schäfer, F. Huber , C. Walther, M. Lagos, G. Darbha, S. Büchner, **W. Hauser , M. Bouby, P. Höss, A. Pudewills, H. Geckeis, S. Heck**	*Karlsruhe Institute of Technology (KIT)* *Institute for Nuclear Waste Disposal (INE)*

New

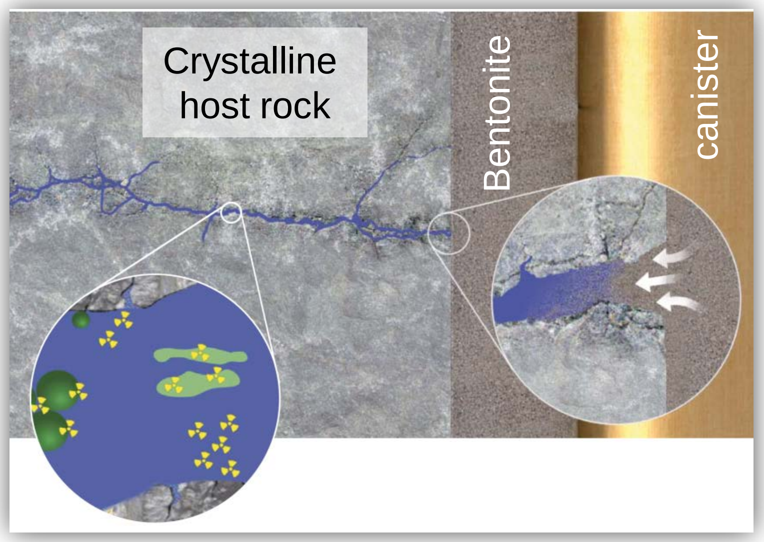
New

Outline

- **INTRODUCTION**
  - Conceptual Approach
- **RESULTS & DISCUSSION**
  - Colloid associated radionuclide transport
    - Hydraulics at Grimsel Test Site
    - Migration Experiments (Run 12-02)
    - Comparison of Laboratory and Field data
- **SUMMARY & FUTURE ACTIVITIES**

Conceptual Approach

- Research is dedicated to study
  - **Colloid formation/bentonite erosion**
  - **Groundwater/porewater mixing zone**
  - **Colloid migration (filtration)**
  - **Colloid associated RN transport**



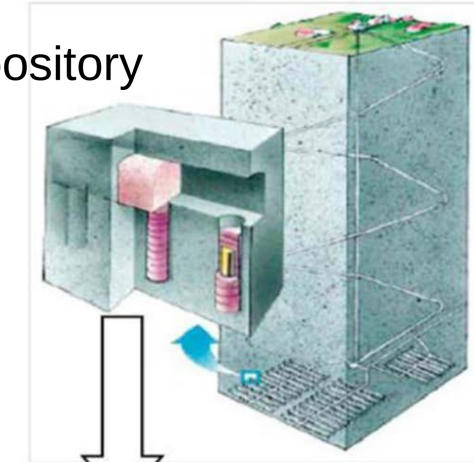
Laboratory Studies	Field Experiments	Modelling Studies
Colloid-RN interaction Colloid Generation Field test analysis	*In situ* test: formation & migration Migration: colloids, homologues, RN tracers	Solute, colloid and associated RN transport Colloid generation

Expected Outputs

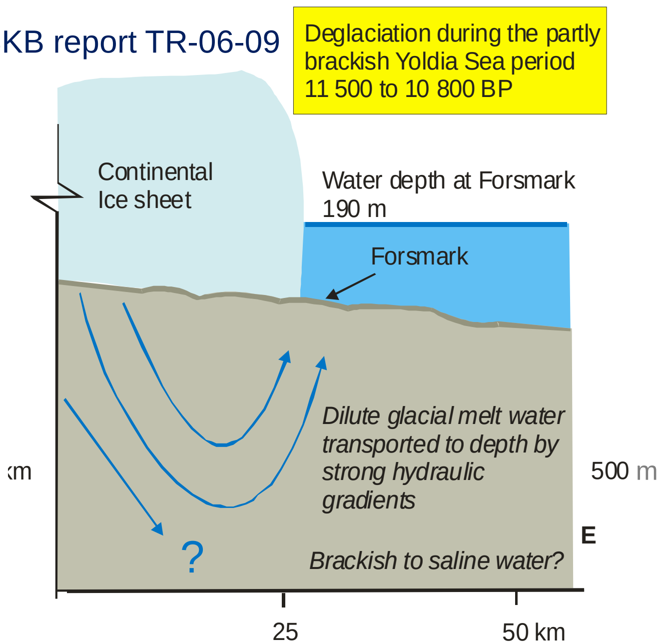
- **Significant increase in process understanding related to colloid formation at the bentonite/ host rock interface**
- **Provide PA relevant information on the colloid influence on RN migration/ retardation**
- **Gain experience in long term monitoring for repository surveillance.**

Normal evolution scenario for Sweden's KBS-3 repository

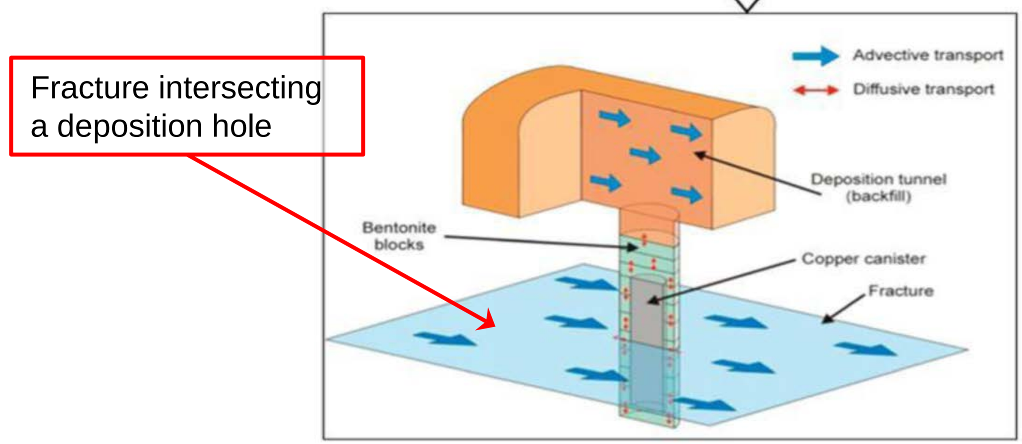
- Dilute water intrusion from melt waters during the glaciation stage will impact groundwater compositions at repository depth.



SKB report TR-06-09



SSM report 2011:08



- **Buffer erosion part of the normal evolution scenario (SKB report TR-06-09)**
- **Calculations of buffer material losses could lead to advective flow conditions in some deposition holes.**
- **By regression fit to erosion rate calculations 50 deposition holes will see advective conditions by 1 million year (SSM report 2011:8)**

What is the reference glacial melt water?

(SSM report 2011:22)

Table 2. Reference compositions for glacial melt waters.

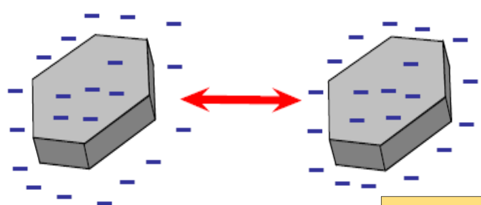
0.075mmol/L

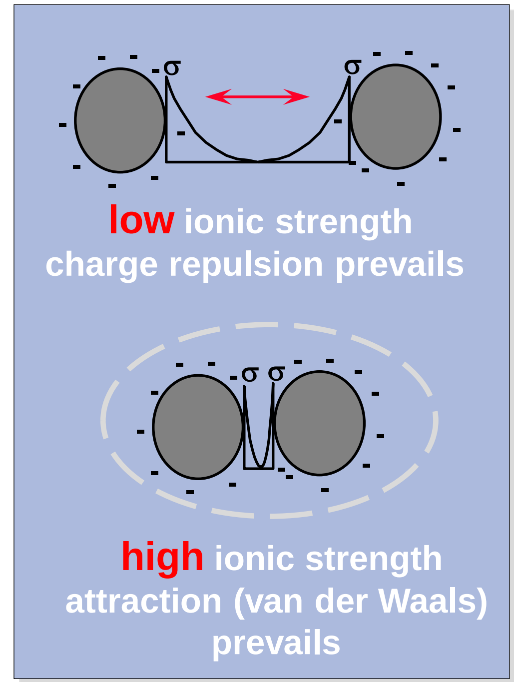
Sample	pH	Na	K	Ca	Mg	Cl	SO_4	HCO_3
	mg/L							
'Juvenile' glacial melt water	5.8	0.17	0.4	0.18	0.1	0.5	0.5	0.12
'Equilibrated' glacial melt water	9.25	0.17	0.39	3.0	0.1	0.5	0.5	5.43

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

Where do we find glacial melt water conditions? Grimsel Test Site (GTS)

	GTS groundwater Na-Ca-HCO_3 type
Pressure (bar)	1.4 – 33
pH	9.6 0.2
Ionic strength (mol/L)	0.0012
E_H(mV)	≤ -200
(Na^+, K^+, Rb^+, Cs^+)	0.7 mmol/L
Σ(Ca^{2+},Mg^{2+},Sr^{2+})	0.14 mmol/L
Fe_{ToT} (µmol/L)	0.003⁺
Total cell number (cells/mL)	4.0 0.4·10^3*
DOC (mg/L)	0.4 – 1.4





GTS ideal site to investigate experimentally effects of glacial melt water on buffer integrity & colloidal transport

⁺Frick et al. (1992); * Gillow et al. (1999)

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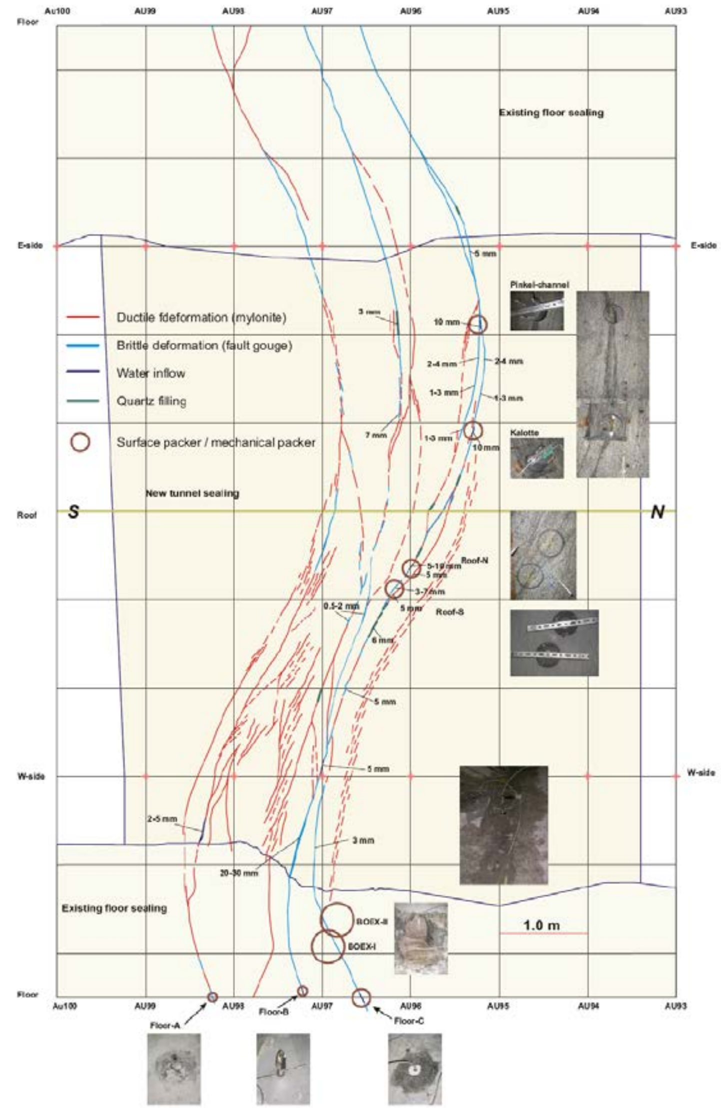
Migration (MI) shear zone (GTS, Switzerland)

(1730 m a.s.l., depth 450 m)

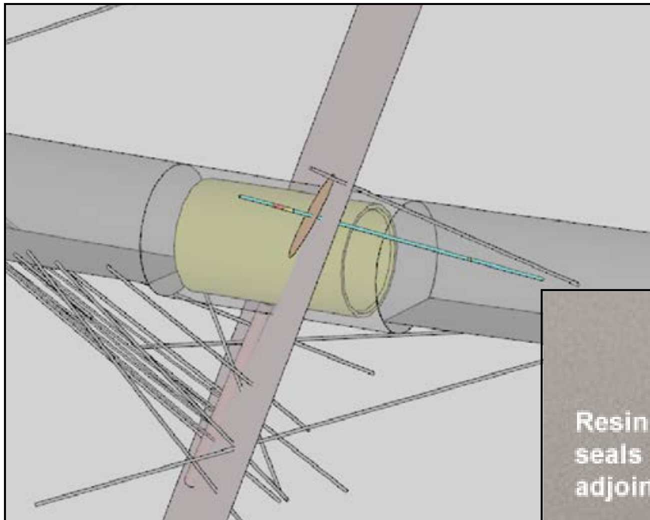
(1) Grimsel Test Site, (2) Rätherichsbodensee,
(3) Grimselsee and (4) Juchlistock.

- ✓ A zone with many discontinuities
- ✓ Signs of ductile and brittle deformation
- ✓ Some water inflow into the tunnel
- ✓ Core sample for lab experiments

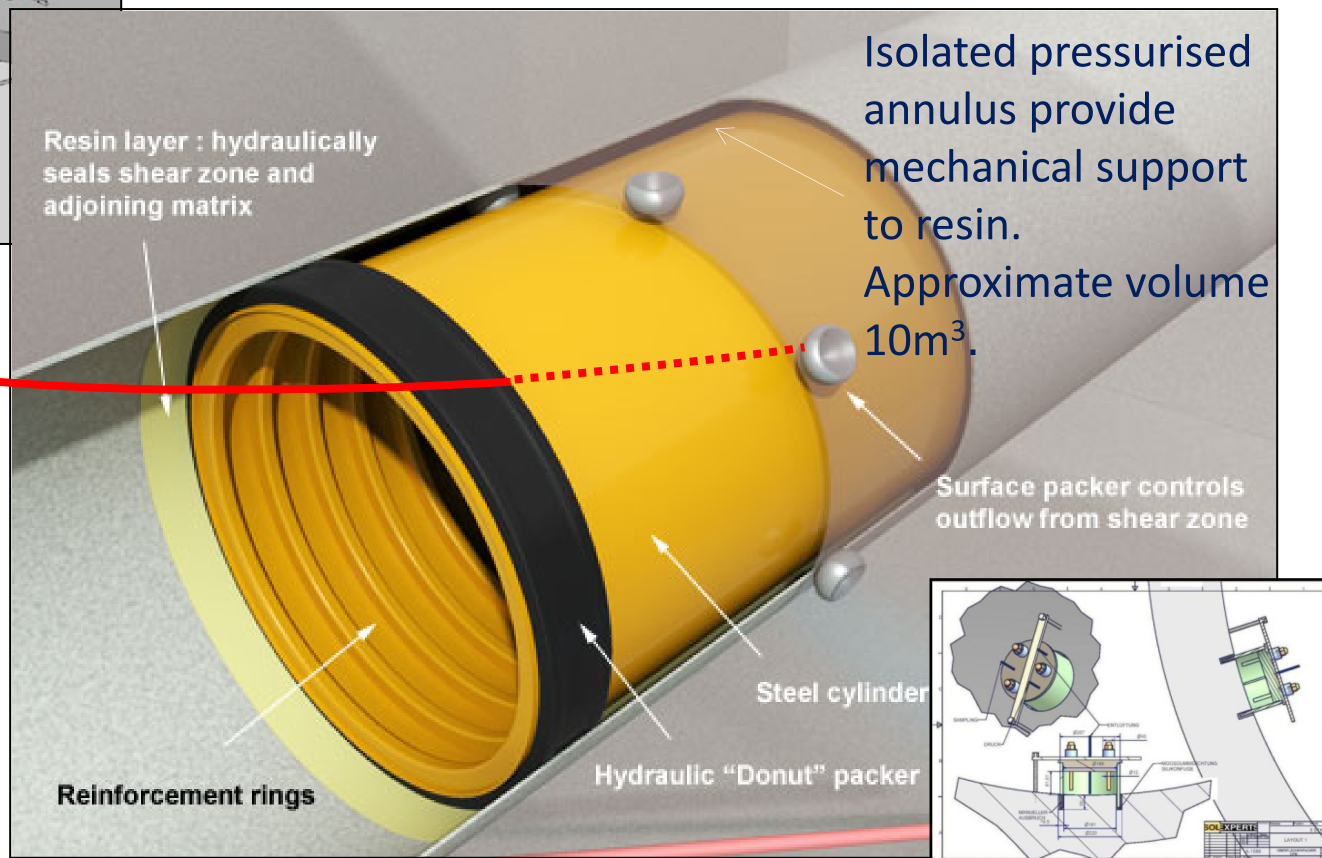


Tunnel sealing system and flow control

- Schematic of the site of the CFM in-situ experiment
- Schematic of the "*megapacker*" with its key elements and functionalities

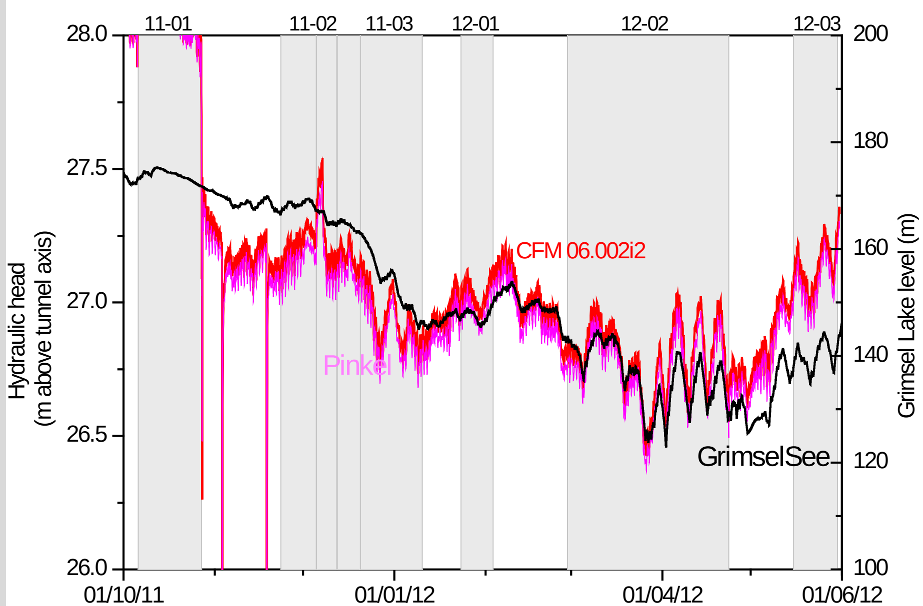


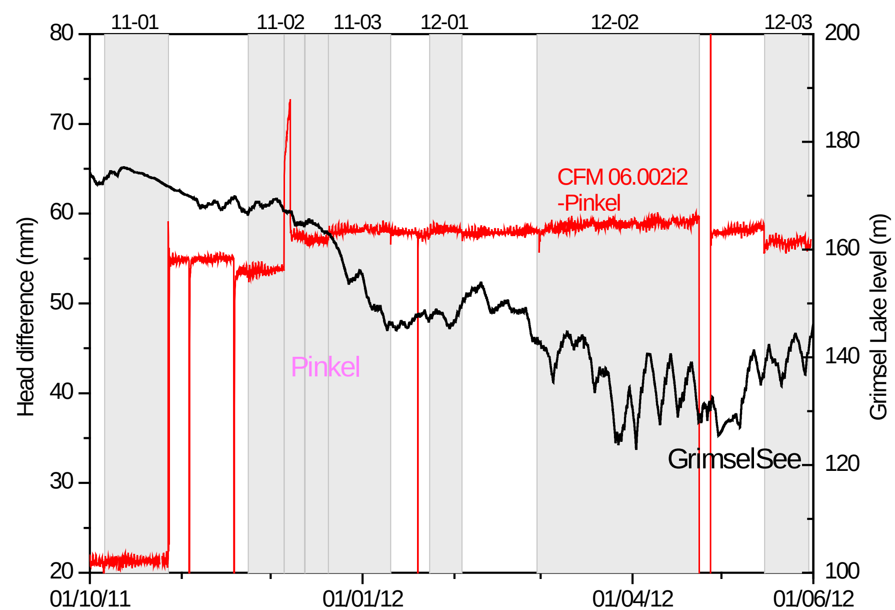
Extraction flow control and analysis



Hydraulic conditions established

- **Hydraulics of shear zone controlled by outflow from “Pinkel” surface packer.**
- **Under constant flow conditions:**
  - Head varies by ~1m over year due to influence of lake levels
  - Head difference/gradient is very stable <10mm
  - Gradient ~60mm/6m ~1%
- **Unique opportunity to study flow/transport at near repository conditions**





CFM project: Tracer Test Runs

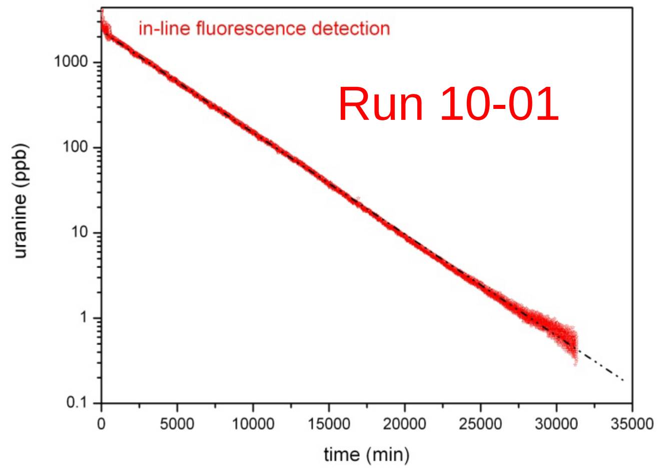
- With different combinations of **homologues** or **RN’s**, colloids and conservative tracers
- Injection into the MI shear zone in borehole CFM 06.002-i2 and extraction at the Pinkel surface packer

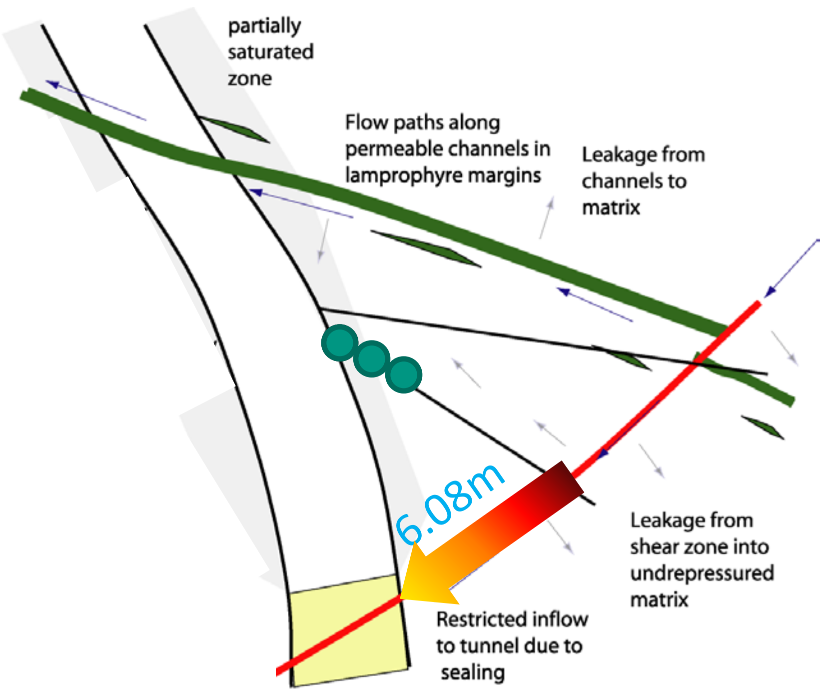
Run 08-01: direct tracer injection with 10 mL·min^{-1}; extraction flowrate 160 mL·min^{-1} (CRR configuration)

Run 10-01: tracer recirculation and 50 mL·min^{-1} extraction flowrate.

Run 10-03: tracer recirculation and 10 mL·min^{-1} extraction flowrate.

Run 12-02: tracer recirculation and 25 mL·min^{-1} extraction flowrate, slight injection with 0.33 mL·min^{-1}



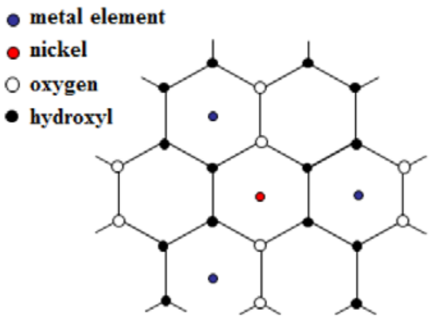


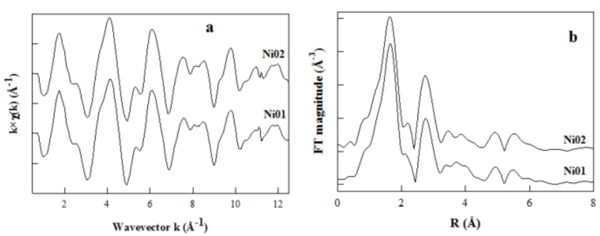
Injection Radionuclide cocktail: Run 12-02

- **Bentonite concentration:** **raw material equilibrated with GGW**
  - Total: 101.4 ± 2.5 mg/L
  - **8.9 ± 0.4 mg/L Ni-montmorillonite**, rest **Febex** derived colloids
- **Conservative tracer Amino-G:**
  - 1646± 8 ppb
- **ICP-MS & gamma- spectrometry data**

Tracer	concentration (mol/L)/ Total activity	Colloid association (min-max values)
^{22}Na	1.0-1.1·10^{-10} (1.17 MBq)	**0 - 3.5 %**
^{133}Ba	6.8-7.0·10^{-10} (1.97 MBq)	**24 – 34 %**
^{137}Cs	7.9-8.0·10^{-10} (785 kBq)	**97 – 98 %**
^{232}Th	5.3-5.6·10^{-9} (8 mBq)	**94 – 97 %**
^{237}Np	9.3-9.4·10^{-9} (119 Bq)	**0 - 1 %**
^{243}Am	7.0-7.4·10^{-11} (290 Bq)	**99 – 100%**
^{242}Pu	3.0-3.2·10^{-9} (190 Bq)	**99 – 100%**

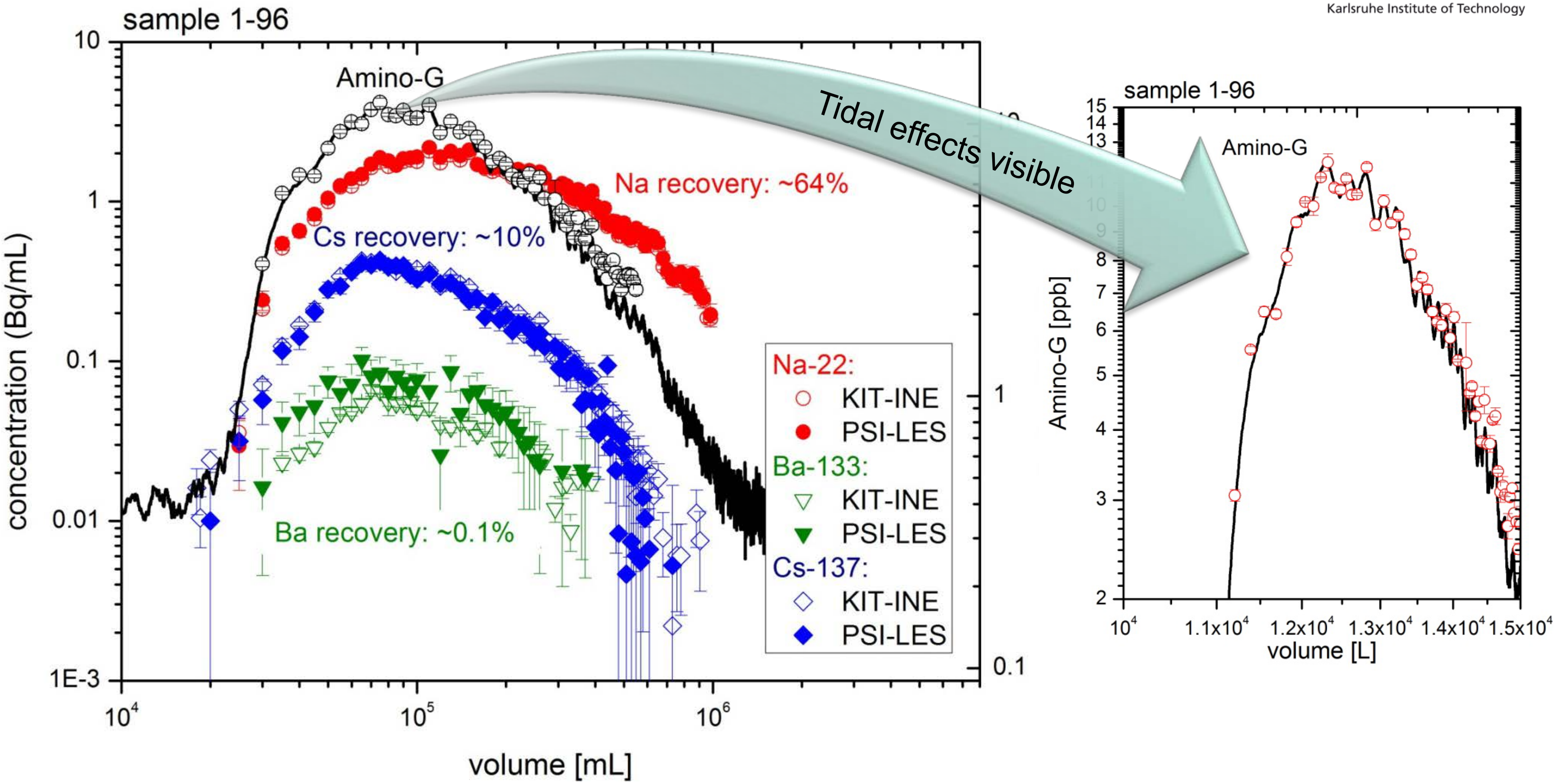
Ni- montmorillonite





Reinholdt, et al. (2013) Nanomaterials 3(1), 48.

Breakthrough curves: Run 12-02



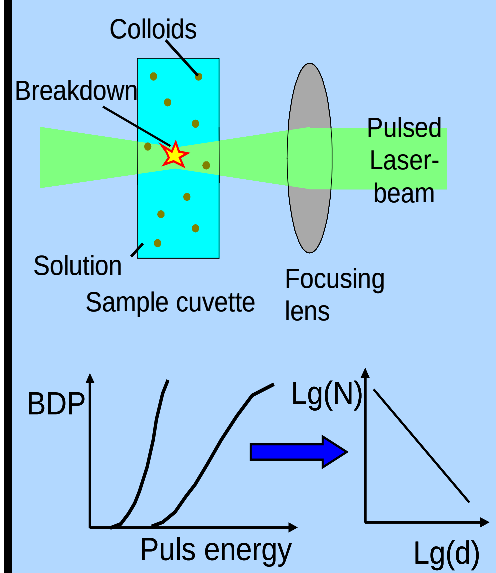
- ✓ Quantitative conservative tracer recovery (Amino-G)
- ✓ Dilution factor: ~137
- ✓ Very good match between PSI-LES and KIT-INE data for gamma spectrometry

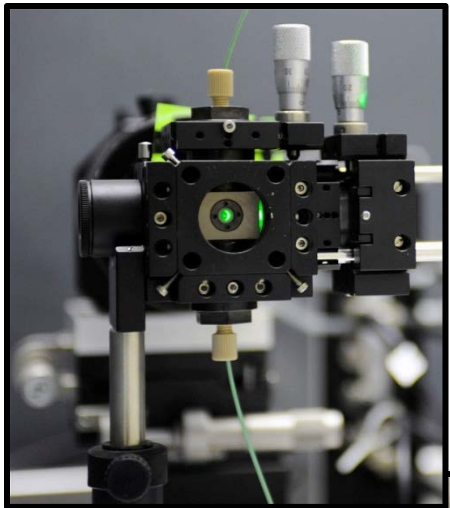
On-site in-line LIBD measurements

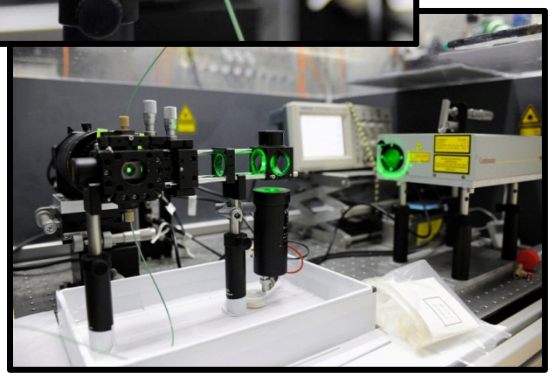
- The INE mobile LIBD system (MOB2)

Laser-induced Breakdown Detection (LIBD)

Single solid particles are ionized in the focus of a laser beam;
Breakdown plasma formation;
Breakdown probability ~ f(N, d)
Laser energy dependency ~ f(d)

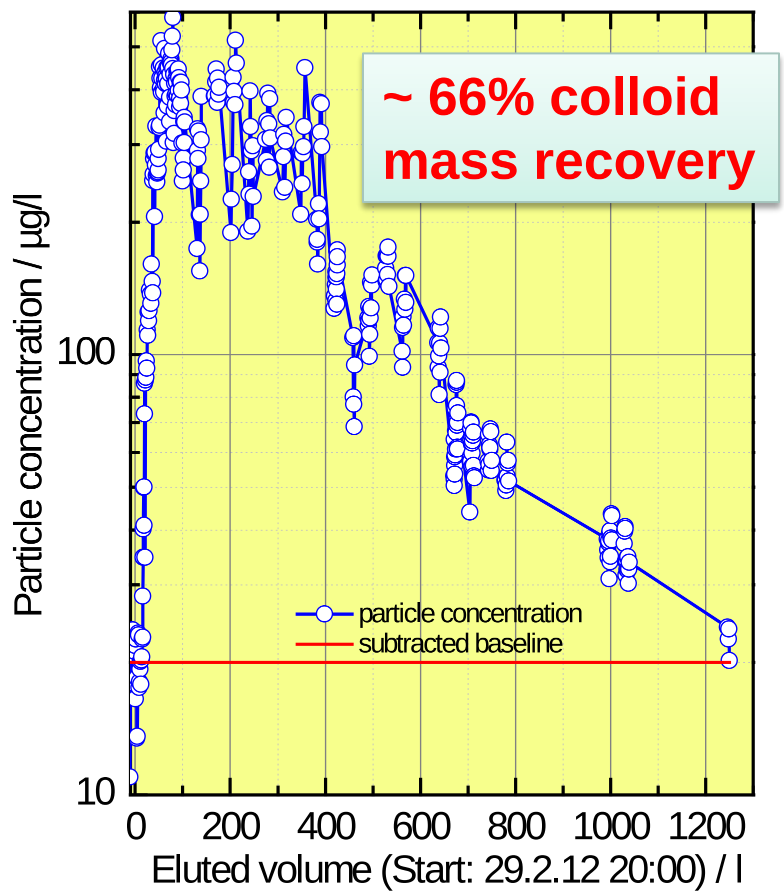




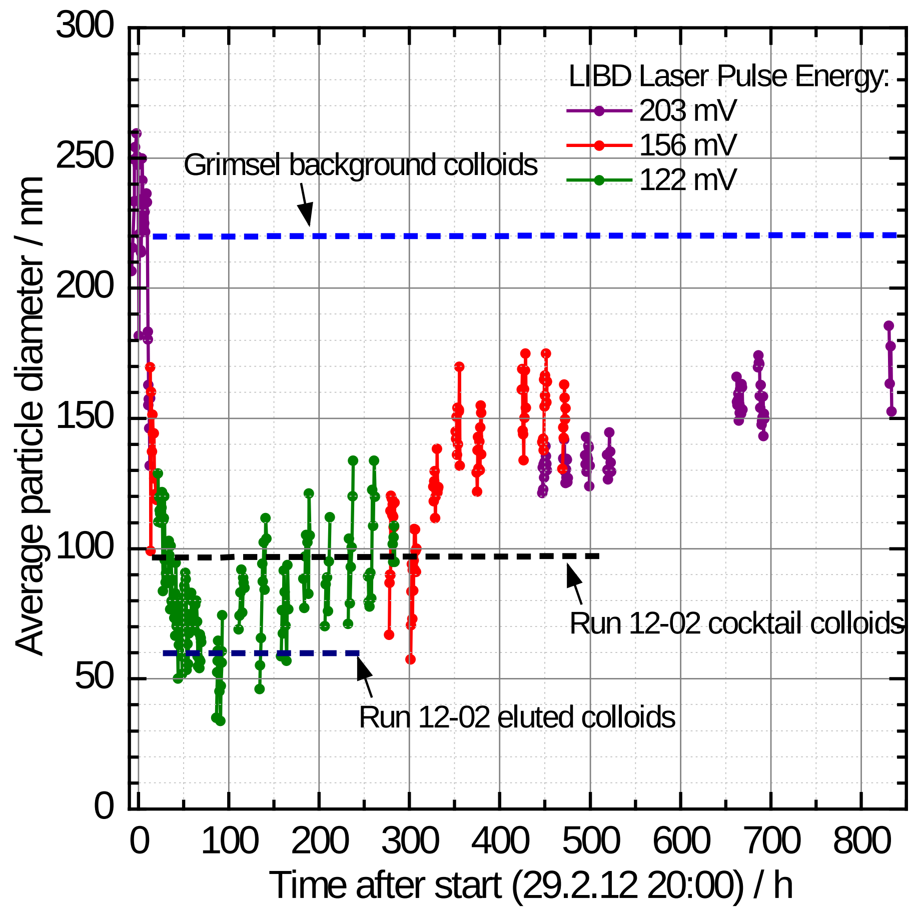


On-site in-line LIBD measurements

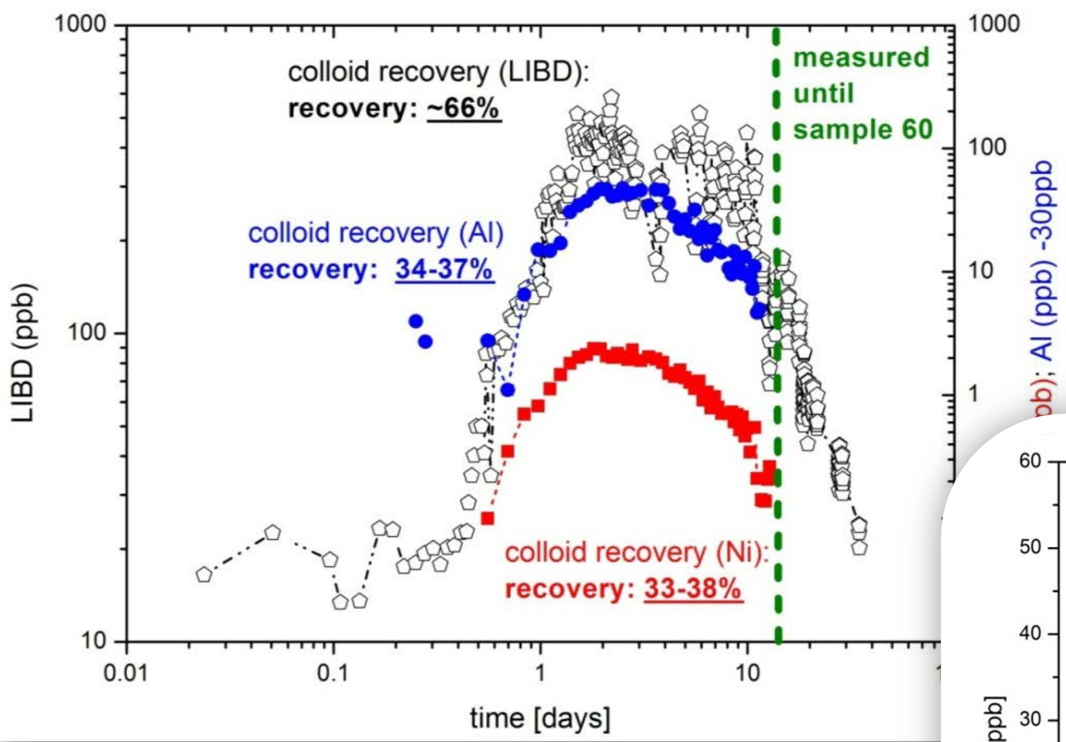
- Colloid mass recovery
  - Mobile LIBD (MOB2)

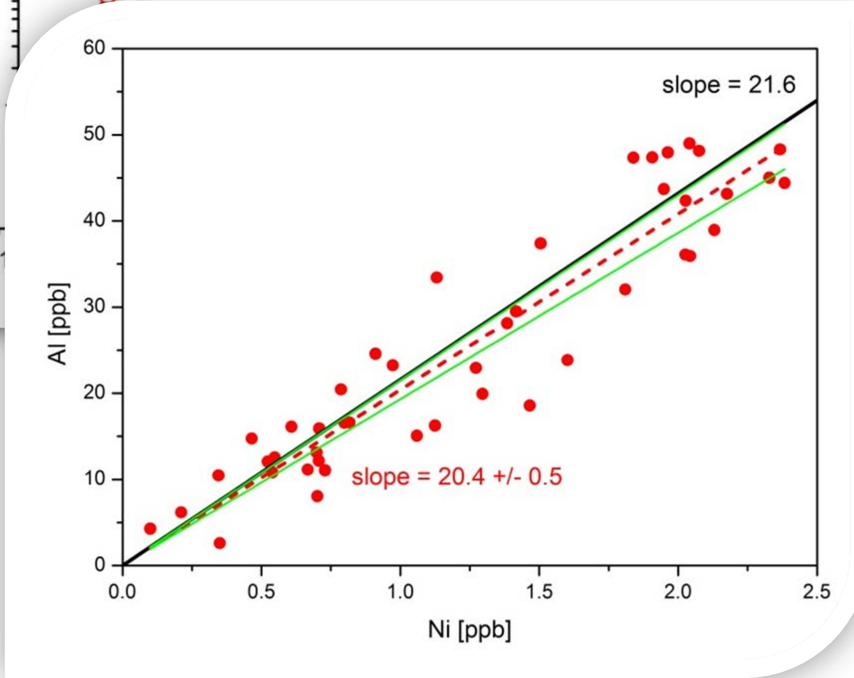


- Average colloid diameter



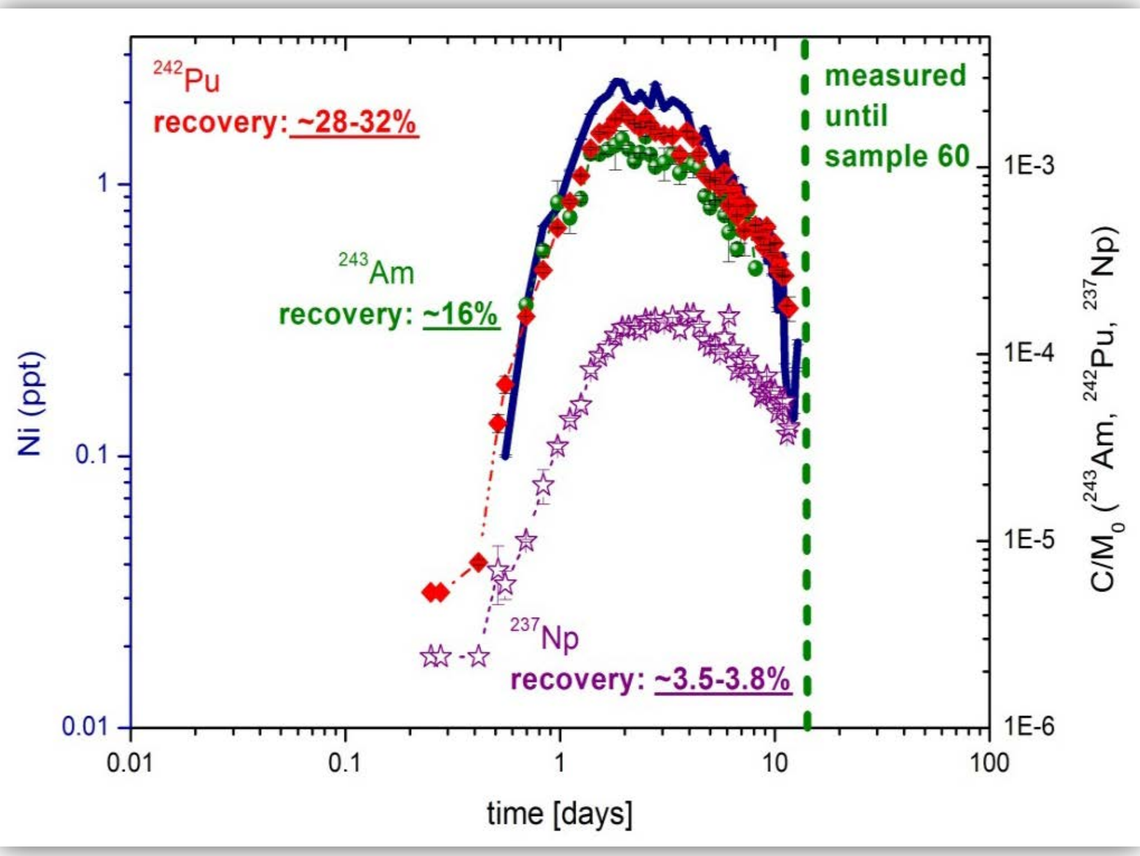
LIBD/HR-ICP-MS results: colloid recovery



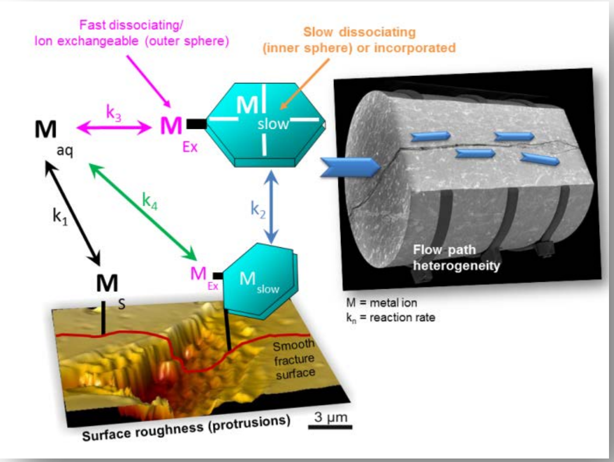


- ✓ **No significant additional colloid source of Aluminosilicates**
- ✓ **No preferential filtration or significant dissolution of synthetic montmorillonite.**

LIBD/HR-ICP-MS results: Am, Pu & Np recovery



- → **Process of colloid retention under glacial melt water conditions.**
- → **RN reversibility comparable to lab determined values?**



Colloid retention: Effect of surface roughness?

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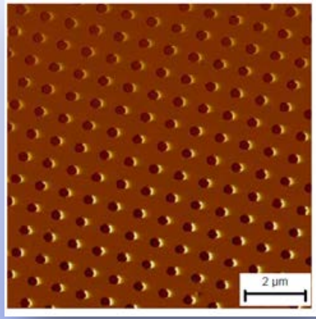
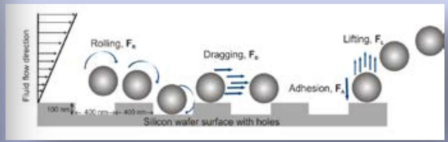
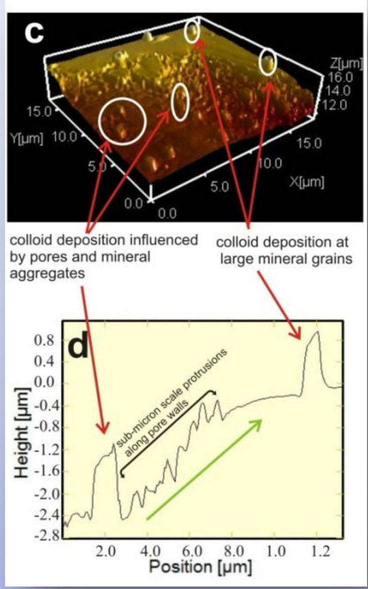
Roughness/ topography effects on Si wafer

Darbha et al. (2012) *Langmuir* 28, 6606.





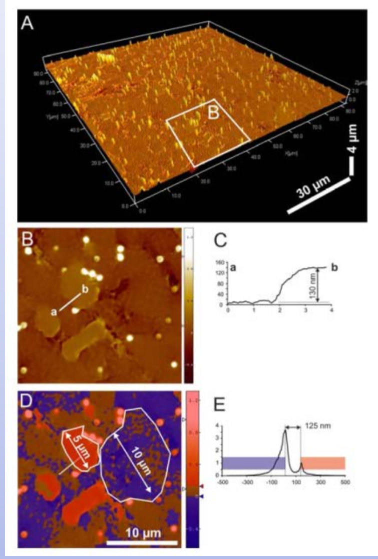


Impact of mineral aggregate surface topography on colloid deposition

Darbha et al. (2012) *Environ. Sci. Technol.* 46, 9378.

Deposition of colloids on rough rock surfaces

Fischer et al. (2012). *Am. J. Sci.* 312, 885.

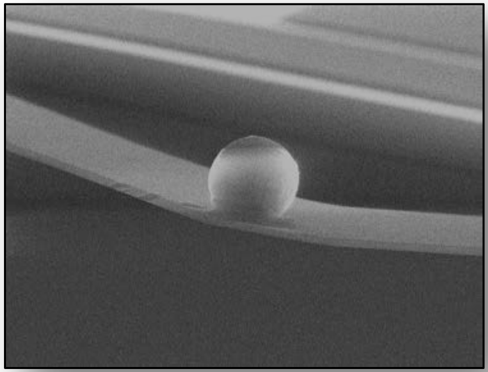


All work on Polysterene colloids….. what about more relevant probes?

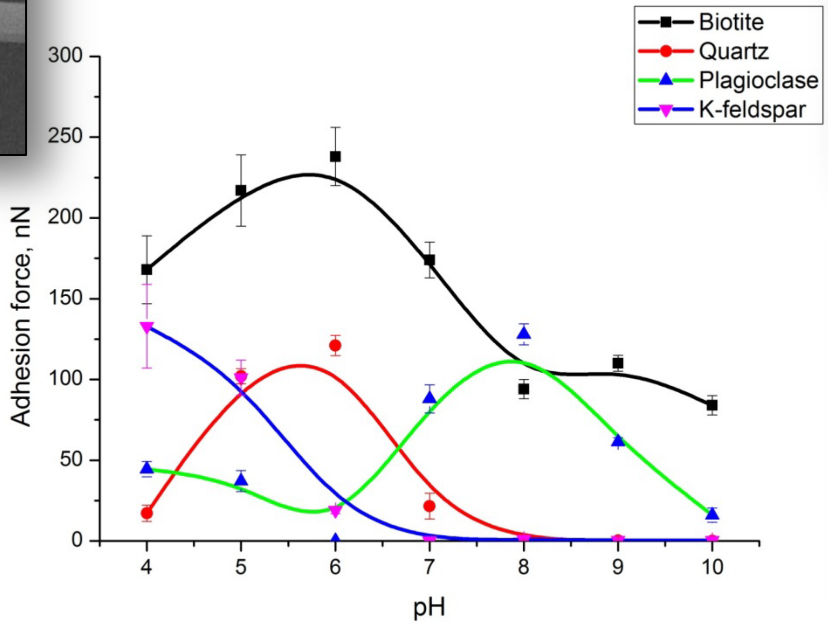
Atomic Force Microscopy: Colloid probe technique

- Interaction between Al_2O_3 colloid probe mimiking clay edge sites and mineral surfaces (Biotite, Plagioclase, K-feldspar, Quartz)

SEM of Al_2O_3 particle attached to cantilever

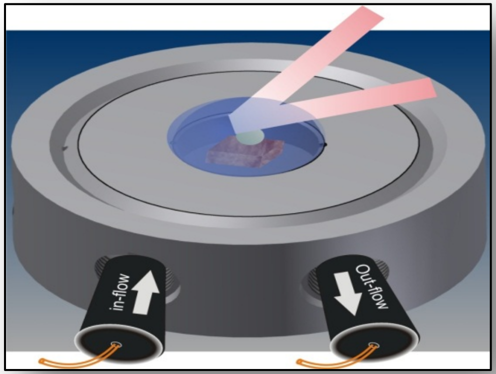


Parameters measured:
1. $F_{Adhesion}$
2. Snap-in force
3. Force-volume measurements

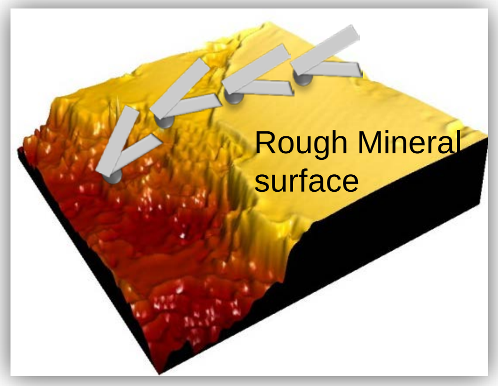


Adhesion is highest for biotite in comparison to any other mineral.

Continuous flow through-fluid cell for AFM experiments



Colloid probe technique



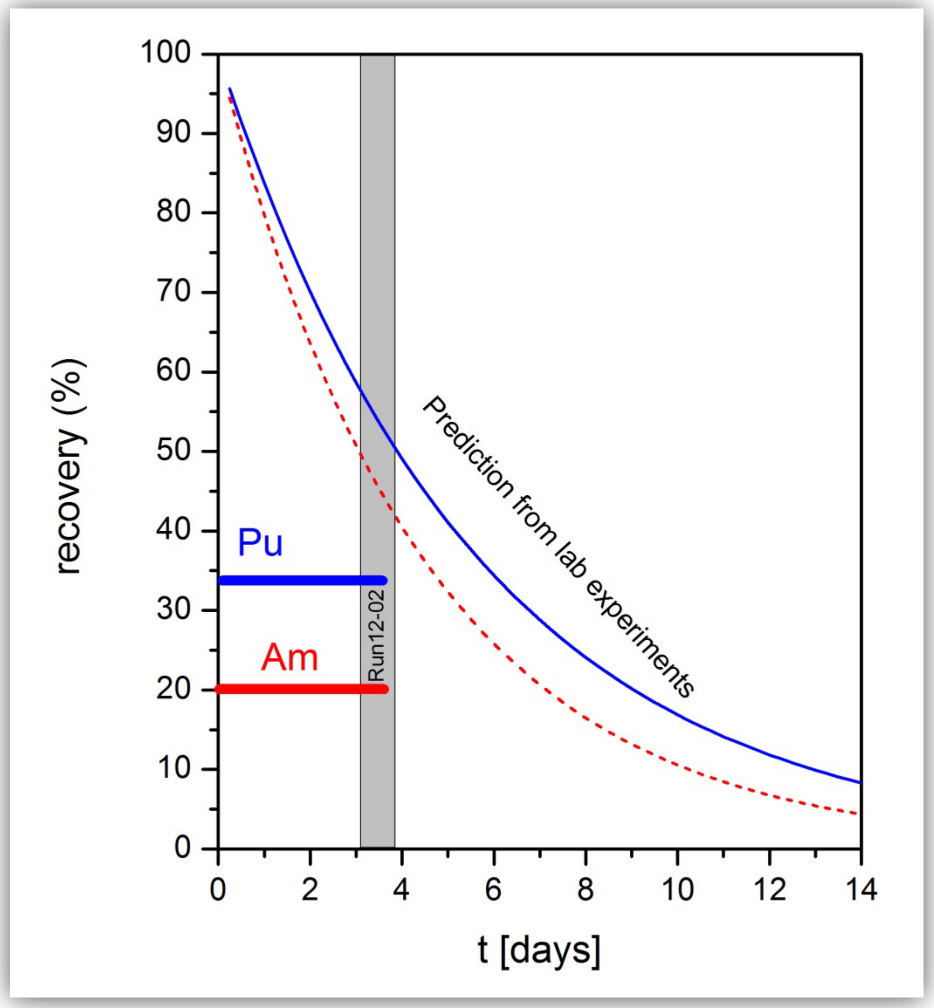
RN sorption reversibility: Comparison of lab & field tests

Laboratory experiment derived desorption rate

	Pu(IV)/Th(IV)	Am(III)
k_3 FEBEX*	0.0009hr^{-1}	0.0037hr^{-1}
k_3, Ni-montm.	0.0015hr^{-1}	0.0012hr^{-1}

Colloid retention from field experiments under glacial melt water conditions.

→ k_{coll} = 0.006h^{-1}



*Huber et al. (2011) *Appl. Geochem. 26, (12), 2226.*

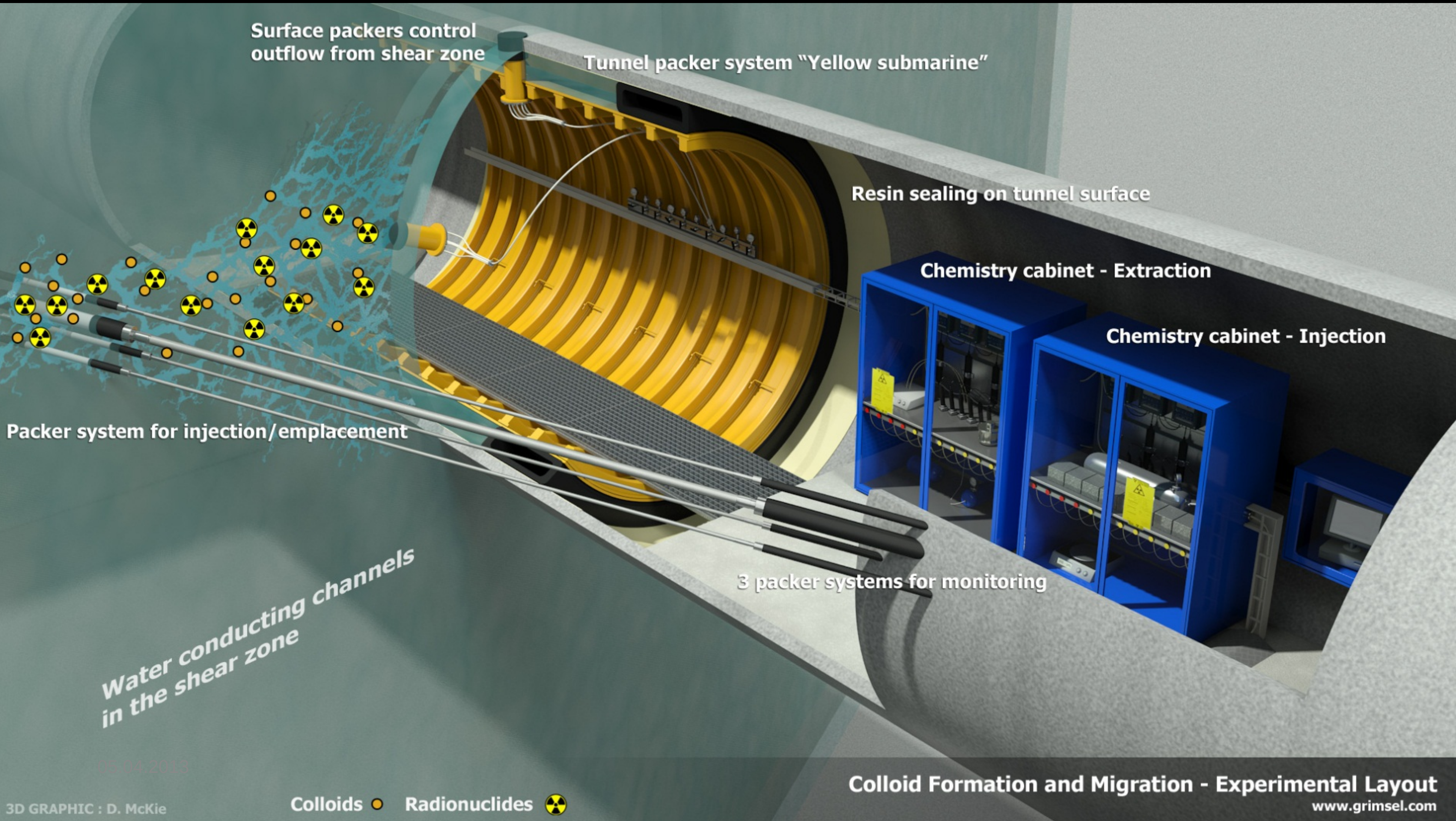
Conclusions

Karlsruhe Institute of Technology

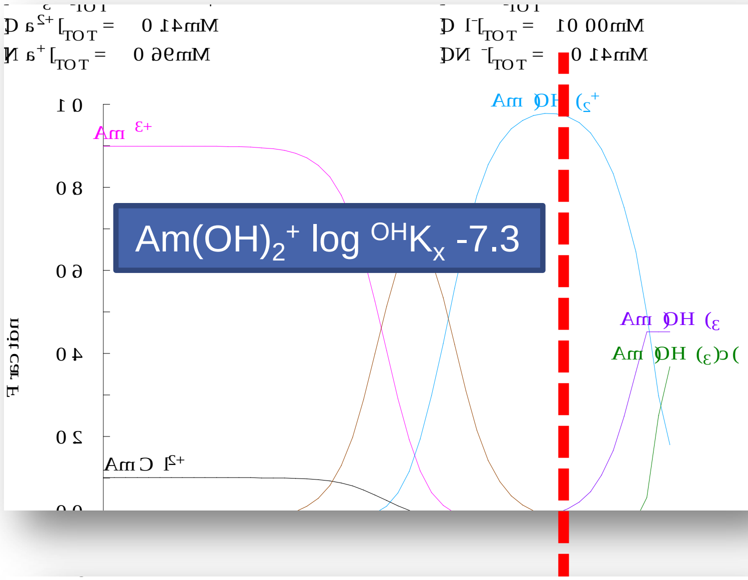
- Control of the hydraulic system has allowed further decrease in gradients and consequent increase in travel time.
- Flow velocity and gradient in shear zone more relevant to post-closure situation: 1% gradient and ~10^{-5} m/s while maintaining high recovery.
- In situ colloid/homologue tracer tests demonstrate:
  - Radionuclide/homologue colloid associated transport over increasing residence time detectable in the MI shearzone, proof of concept.
  - Radionuclide/Homologue recovery is lower for trivalent actinides compared to tetravalent actinides.
  - Reversibility kinetics faster than observed in batch type studies.
- The megapacker sealing system works well and is ready for the long-term in-situ experiment!

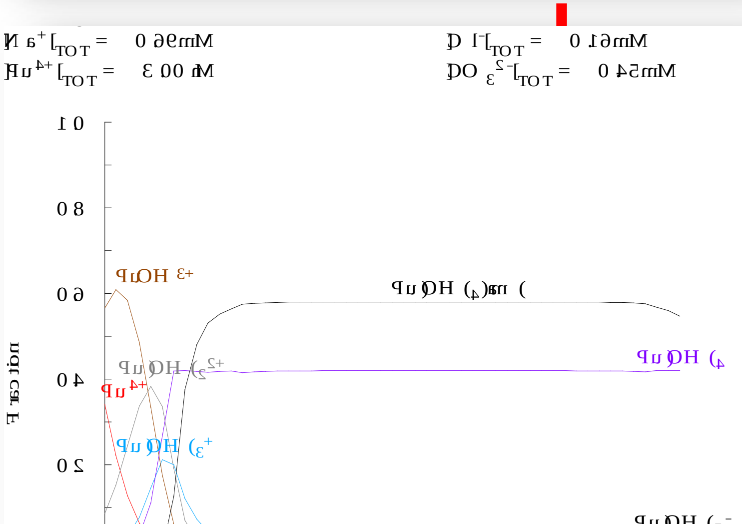
CFM project: next steps

Bentonite erosion/colloid generation directly from compacted bentonite instead of colloid suspension injection under realistic flow conditions.

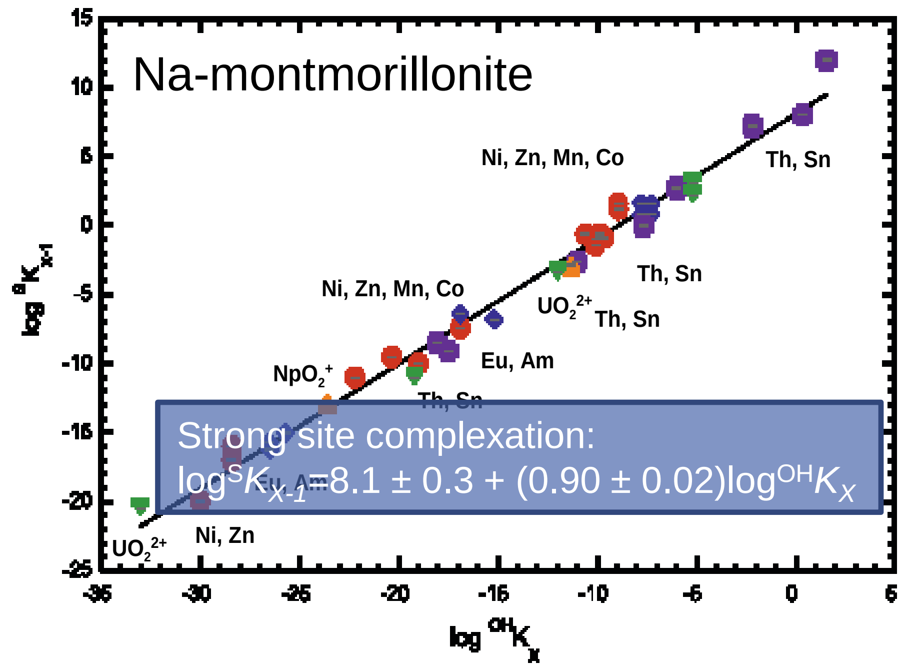


Colloid radionuclide reversibility





Bradbury&Baeyens, GCA, 69, 2005, 875



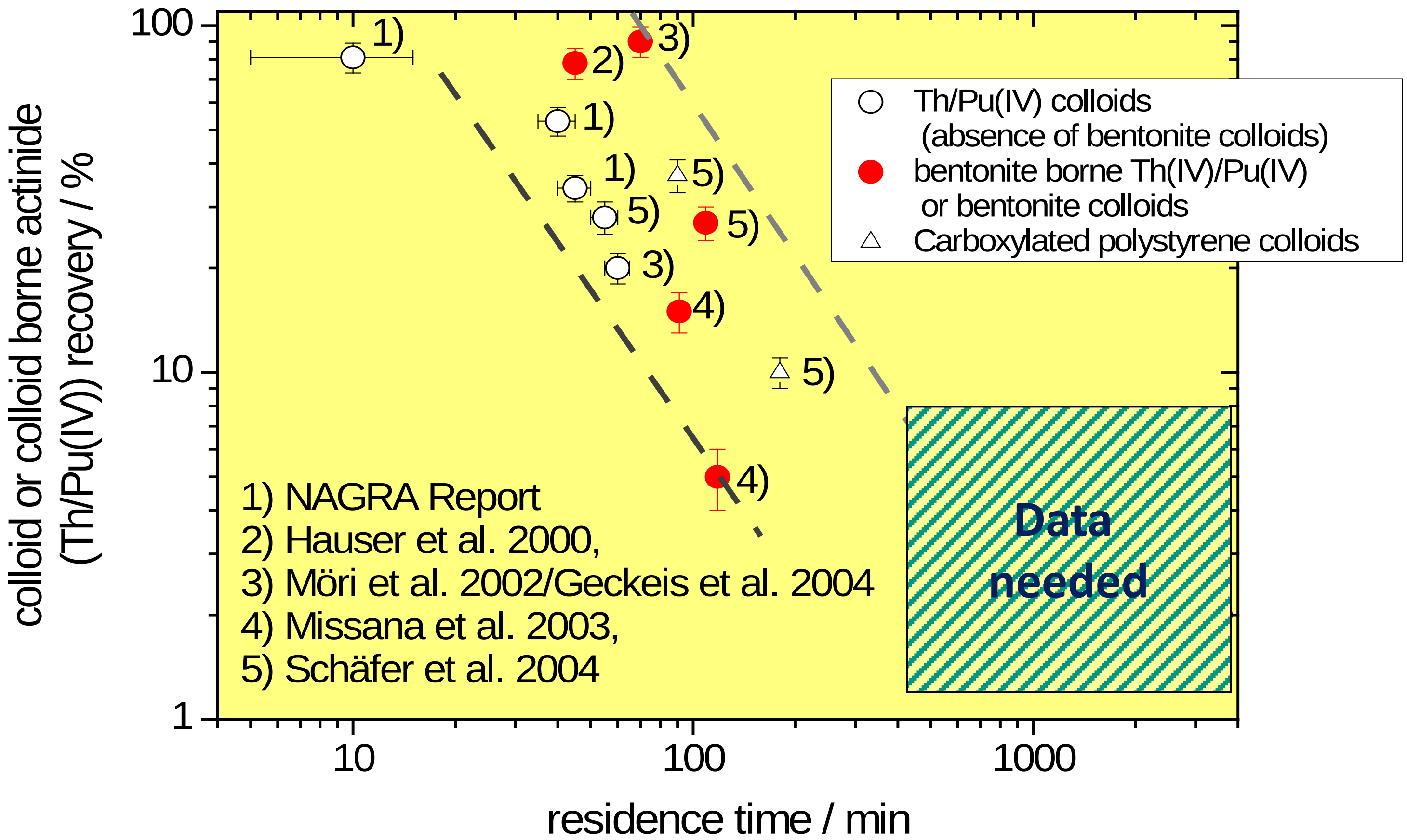
- A good linear correlation between the logarithms of strong site binding constants on montmorillonites, $^SK_{x-1}$, and the logarithm of the aqueous hydrolysis constants, $^{OH}K_x$, were found over 35 orders of magnitude.
- All of the modelled surface complexation data for the 11 metals considered were included in a single plot.

$\equiv SOAm(OH)^+$ log $^SK_{x-1}$ -6.8

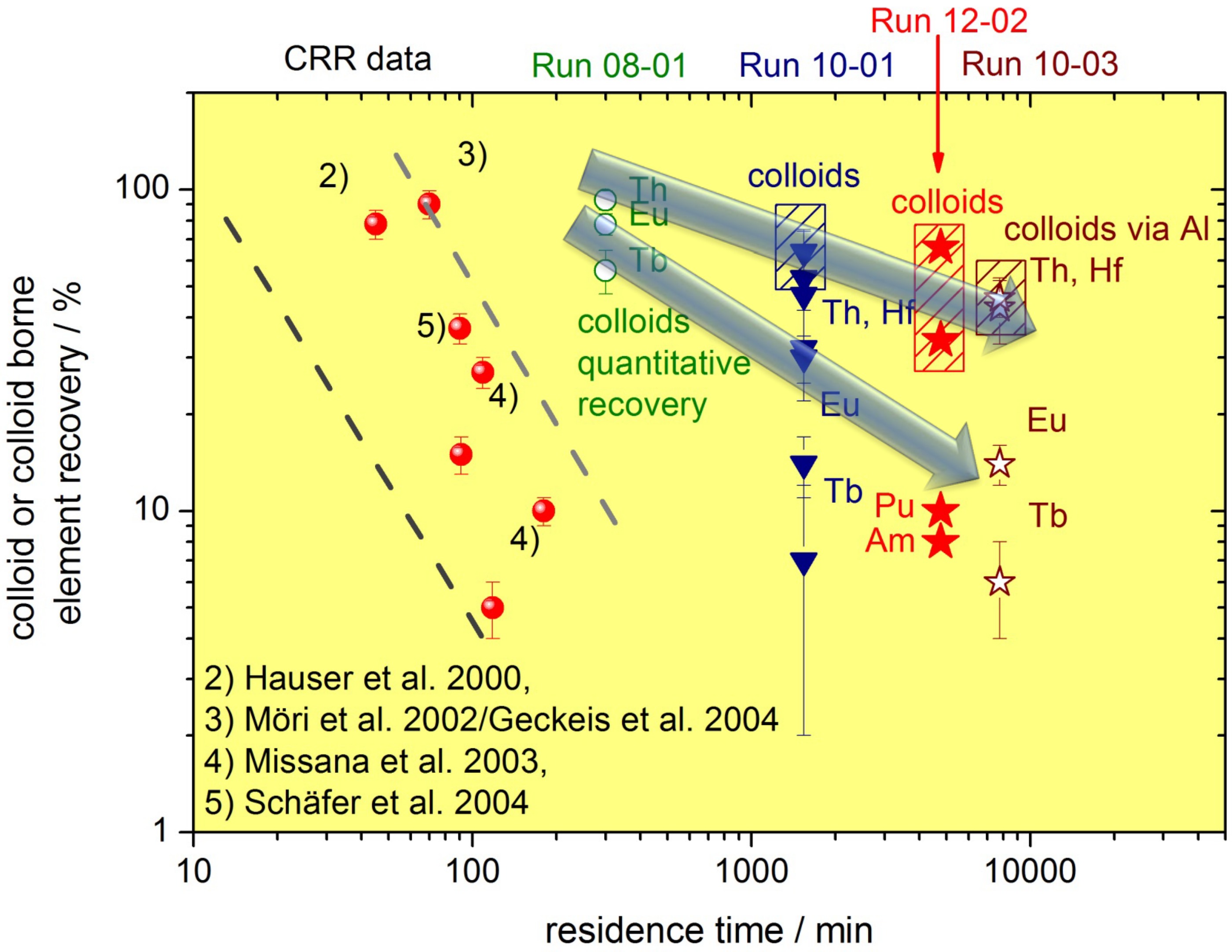
$\equiv SOTh(OH)_3^0$ log $^SK_{x-1}$ -9.1

What did we know after CRR at the start of CFM?

Geckeis et al. (2004) ***Radiochim. Acta 92, 765;*** **Möri et al. (2003)** ***Colloids Surf. A 217, 33;*** **Schäfer et al. (2004)** ***Radiochim. Acta 2004, 92, 731; Missana, et al. (2003) J. Contam. Hydrol. 2003, 61(1-4), 17.***



Synopsis of migration experiments



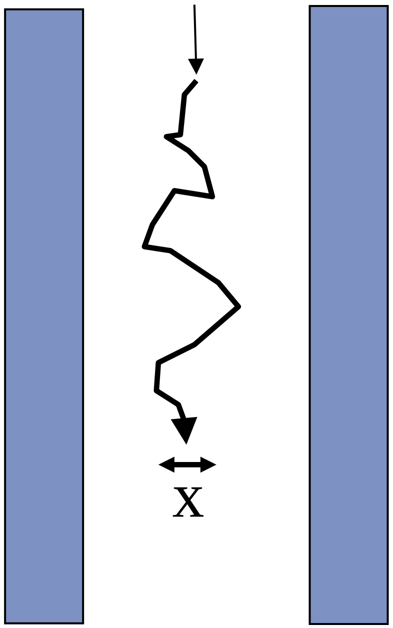
Conclusions (2/2)

- **URL activities on radionuclide migration** (matrix diffusion & colloid migration) constitute an **up-scaling of laboratory experiments** and is an important part of the **confidence building and uncertainty reduction**.
- **Testing and development of conceptual and numerical models** of processes potentially relevant to radionuclide transport through rock.
- **Experiments related to long-term processes**, post-operational phases, e.g. bentonite buffer/backfill stability are necessary to obtain **mechanistic understanding of empirical correlations currently used in conceptual models under realistic conditions**.
- **Instrumentation experience** gained under real-site conditions especially on the **reliability of long-term monitoring** systems will **foster technical innovation and will therefore improve monitoring**.

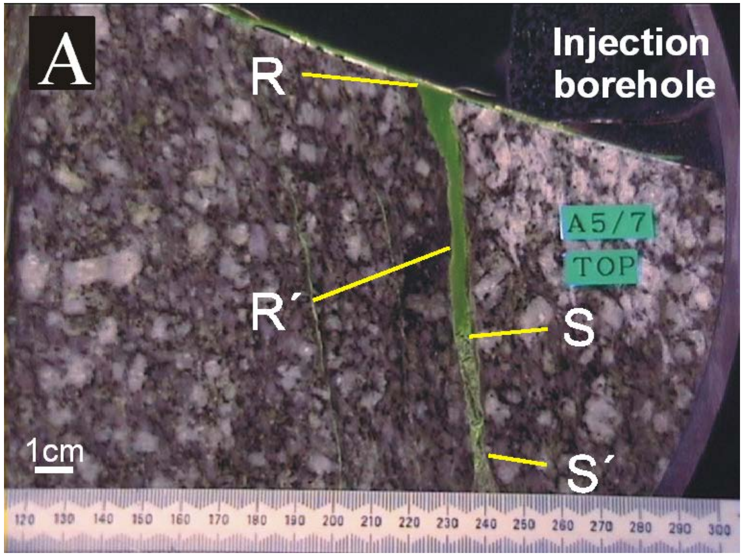

thank you for your attention

Backup slides

Why higher colloid recovery observed in CFM dipole compared to CRR dipole?



$$x = \sqrt{2D\tau}$$



τ=5 h (Run 08-01)	Diffusion-coeff. / m^2/s	X mm
colloid (d_p=200 nm)	$2.5 \cdot 10^{-12}$	0.3
solute	$1 \cdot 10^{-9}$	6.0

MI- shearzone:

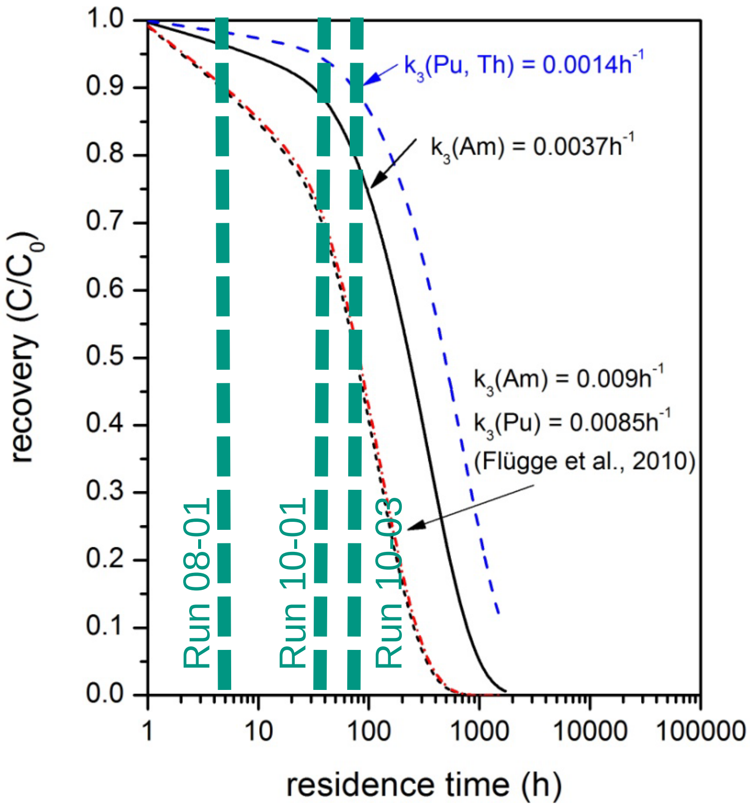
Aperture distribution: 1-24 mm

average aperture: 4.2 mm

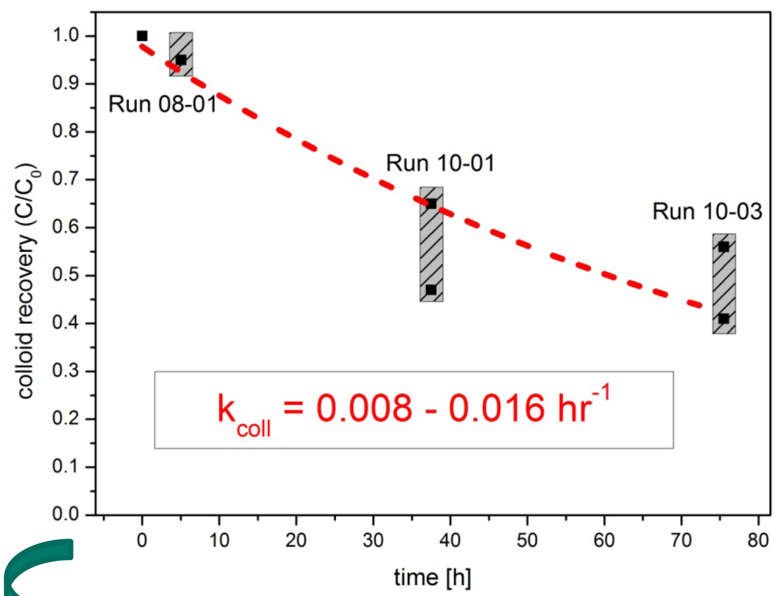
Zvikelsky, Weisbrod, *Water Res. Res.* 2006

Does the field migration data fit to laboratory desorption experiments?

	Pu(IV)/Th(IV)	Am(III)
k_3 „high C“	$0.0014hr^{-1}$	$0.0037hr^{-1}$
k_3, „low C“	$0.0085hr^{-1}$	$0.009hr^{-1}$



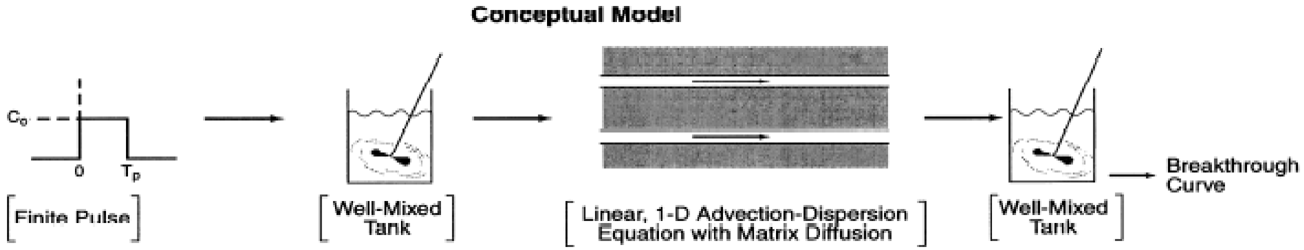
Colloid „filtration“ rate



There is colloid – FFM interaction

Modeling approach (collaboration Paul Reimus)

Reimus, Pohl, Mihevc, Chapman, Papelis, Lyles, Kosinski, Niswonger, Sanders (2003). *Water Resources Research* , 39(12), 1350.



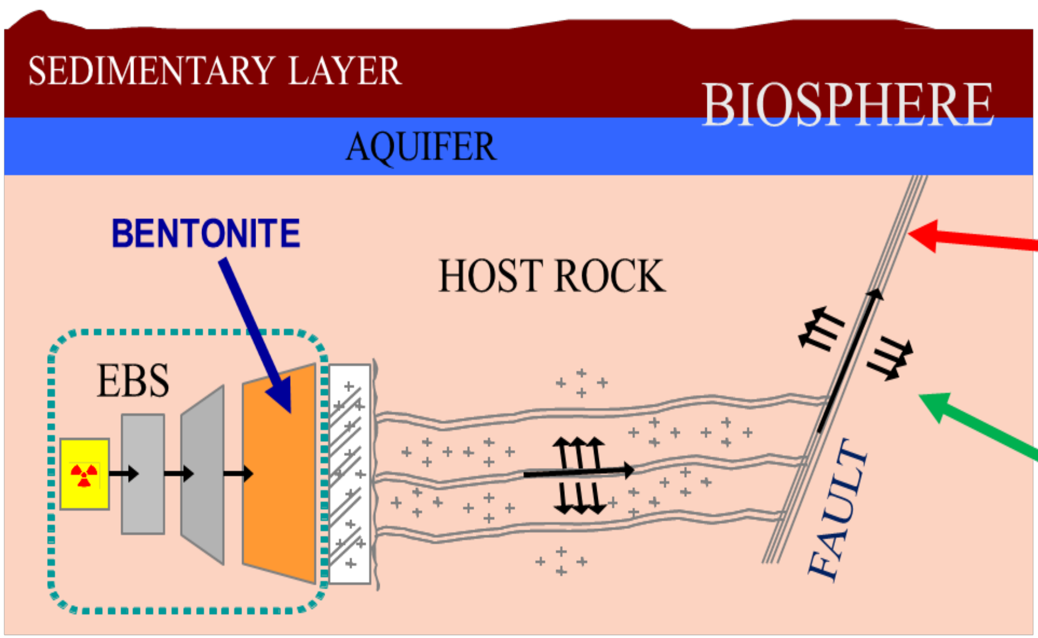
RELAP (Reactive Transport Laplace Inversion) semi-analytical model (Reimus et al., 2003) with the following steps:

1. First, accurately describe the input function
2. Fit the **uranine breakthrough** curves by **adjusting mean residence time** and **Peclet number** in advection – dispersion equation with convolved input function (no matrix diffusion assumed)
3. Fit **colloid breakthrough** curve starting with uranine parameters and adjusting these, using **filtration rate constant and retardation factor** as necessary
4. Fit **homologue curves** using colloid fit with addition of **first order desorption reaction terms**

Experiments on: RN-transport & Retardation

Simulate the long-term behaviour of contamination plumes containing radionuclide's in the repository near-field and the surrounding host rock:

- **Matrix diffusion**
- **Advective transport (colloid facilitated RN migration)**



Modified from JAEA TRU-2 report (2005)

Advection – Radionuclide migration with or without colloid facilitated transport

Matrix diffusion – delays migration of soluble radionuclides

CFM project: next steps

Bentonite erosion/colloid generation directly from compacted bentonite instead of colloid suspension injection under realistic flow conditions.