BENTONITE COLLOIDS

Formation and stability of colloids
Colloid-mediated radionuclide transport

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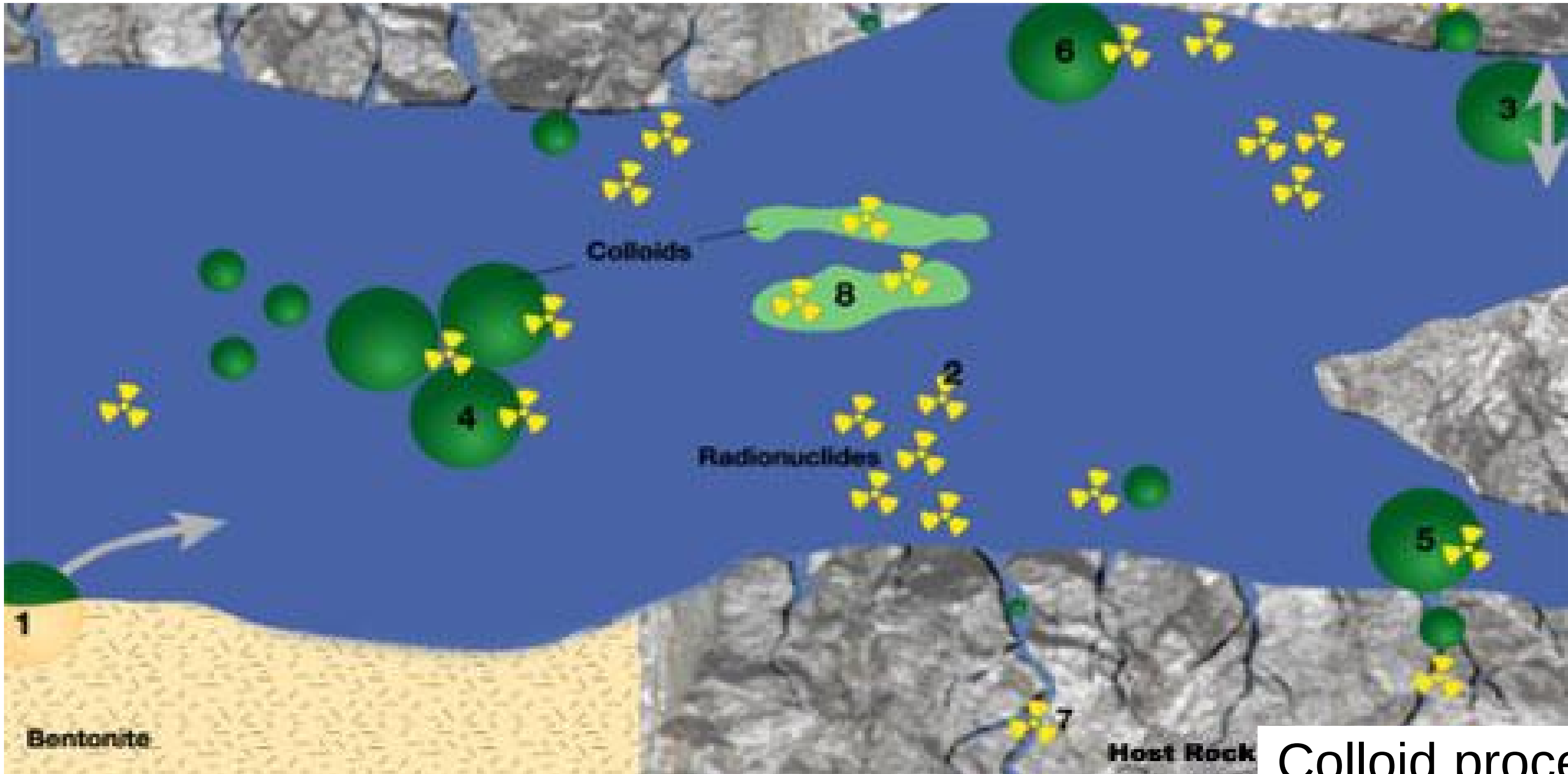


Colloid processes at the bentonite/ granite interface

1. Generation of inorganic colloids (stable, mobile)
2. Dissolved radionuclides in ground water
3. Sorption/de-sorption of colloids onto/from rock surface
4. Sorption of radionuclides onto colloids
5. Filtration of colloids
6. Colloid size prevents penetration into pore space of rock
7. Diffusion of radionuclides into the pore space of the rock
8. Sorption of radionuclides onto colloids or incorporation of radionuclides into colloids

Stability of colloids

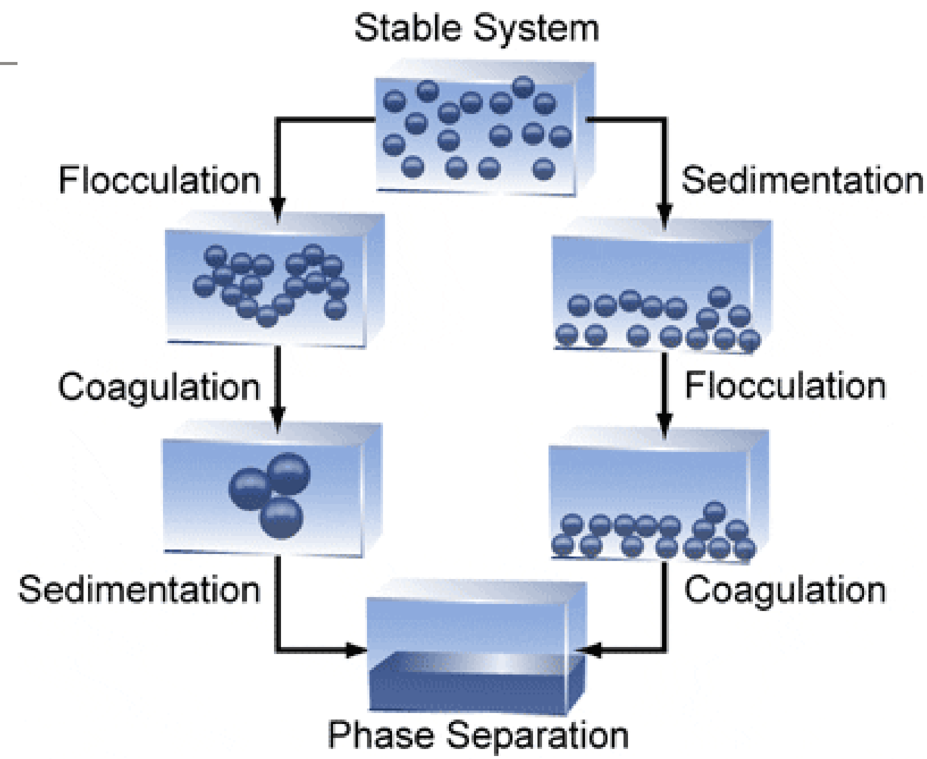
Solid particles are dispersed in liquid to form suspension.

Particle size from 1 nm to 1µm in one dimension.

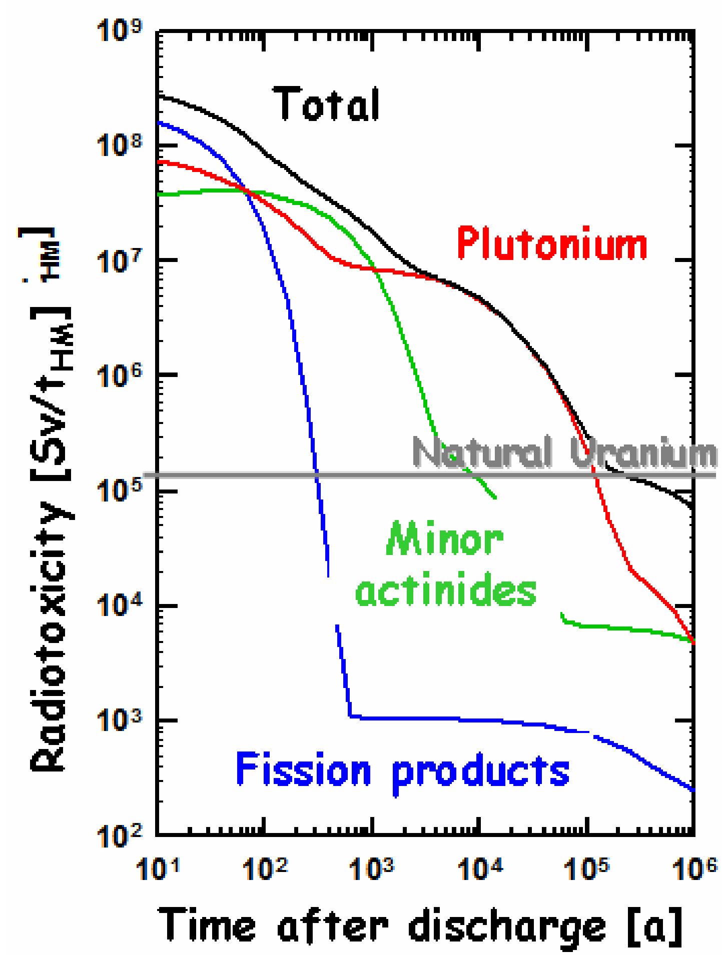
Surface charge →colloid transport significantly different to that of a solute.

High surface-to-volume ratio

Stability (zeta potential) dependents on salinity, particle size, pH.



Processes that deal with the stability of colloidal systems by DLVO theory (Derjaguin, Landau, Verwey and Overbeek)



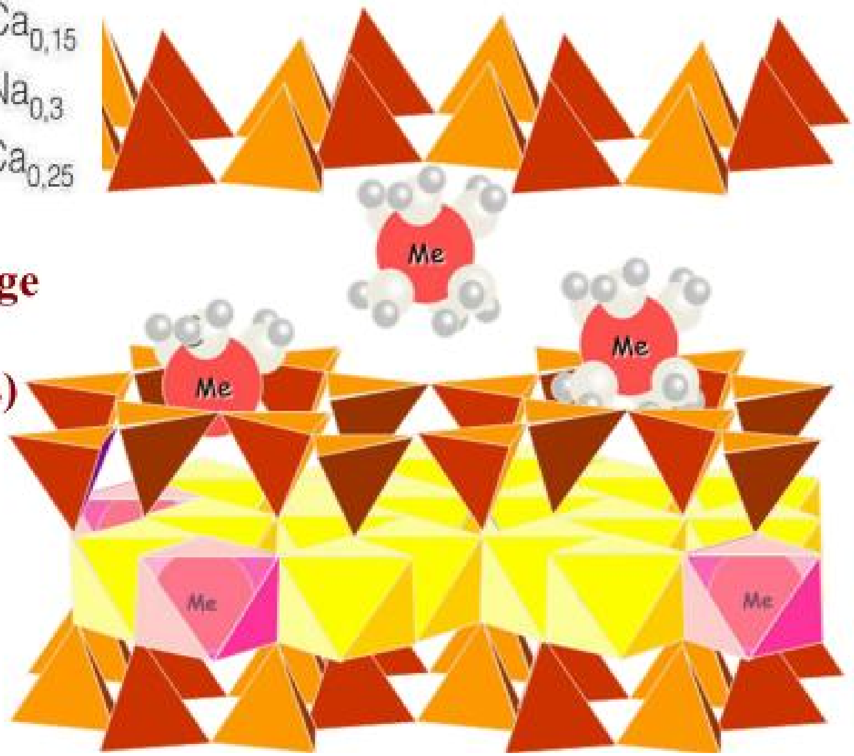
actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium
89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

2/1 MINERALS (b)

main data	dioctahedral minerals	trioctahedral minerals
2/1 MINERALS		
electric charge of the layer = 0,2-0,6 1T+1O+1T+Esp.Int.= 10—>18 Å Esp. Int : cations ± hydratés (Ca, Na) (Ch :10Å ; $2H_2O$:14Å ; EG : 17Å)	SMECTITES Al : montmorillonite, beidellite Fe : nontronite	SMECTITES Mg : saponite, stevensite, hectorite
electric charge of the layer = 0,6-0,9 1T+1O+1T+Esp.Int.= 10—>15 Å Esp. Int : cations ± hydratés (Ca, Na) (Ch :10Å ; $2H_2O$:14Å ; EG : 14Å)	VERMICULITES	VERMICULITES

montmorillonite	Si_4		O_{10}	$R^{3+}_{1,7}R^{2+}_{0,3}$	$(OH)_2$	$Ca_{0,15}$
beidellite	$Si_{3,7}$	$Al_{0,3}$	O_{10}	R^{3+}_2	$(OH)_2$	$Na_{0,3}$
saponite	$Si_{3,5}$	$Al_{0,5}$	O_{10}	R^{2+}_3	$(OH)_2$	$Ca_{0,25}$

Layer: low to intermediate electric charge
➔layers weakly linked,
Interlayer cations (exchangeable cations)
+ water (hydratation), ***or EG (in lab.)***
Swelling properties (expandable minerals).



Objectives

Formation and stability of colloids

- To determine the release and stability of inorganic colloids from MX-80 bentonite in different groundwater conditions
- To study bentonite erosion kinetics and mechanisms
- To test and apply colloid characterization methods

Colloid-mediated radionuclide transport

- To develop experimental methods (batch/dynamic, s/l separation)
- To study radionuclide sorption on colloids (sorption/particle size)
- To determine the effect of pH, ionic strength, solid–liquid ratio
- To study sorption reversibility/irreversibility (^{85}Sr, ^{152}Eu, ^{235}Np)

Experimental work/modelling

Colloid release and stability

Sample preparation

Mixture of solid material and liquid_→_storage

- **Bentonite** (MX-80, powder, compacted)
- **Reference groundwater**
  - Low salinity Allard, I = 4.2 10^{-3} M
  - Diluted OLSO, I = 0.001 – 0.1 M (OLSO, I = 0.517 M)
  - NaCl- and $CaCl_2$-solutions, I=0.001–0.1 M

Filtration

- 1.2 µm and 0.45 µm Isopore polycarbonate membrane

Characterization

- Colloidal particle size distributions and concentration
- Stability (zeta potential)

Colloid characterization

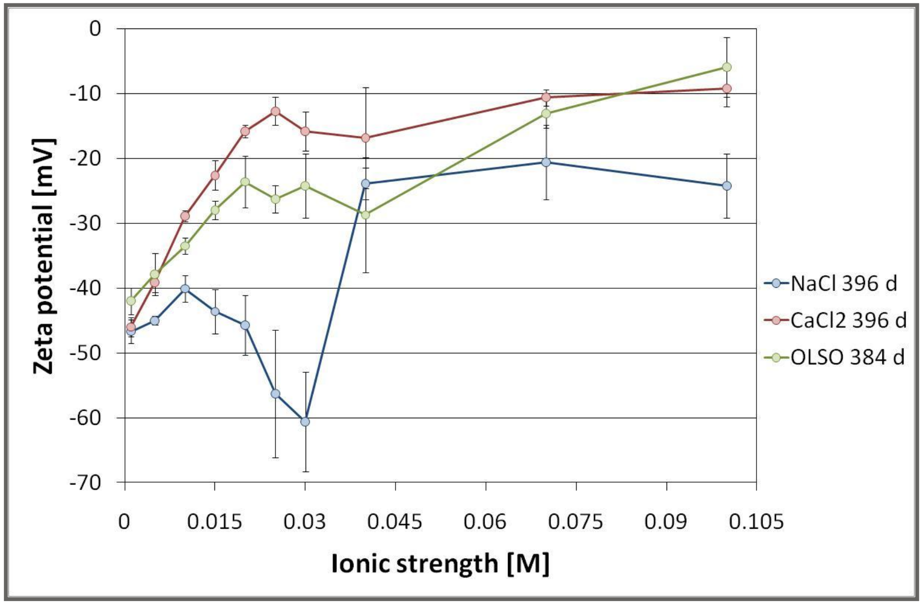
Dynamic light scattering (DLS, PCS)
(Malvern Zetasizer Nano ZS)
- Particle size distribution and particle concentration
- Zeta potential

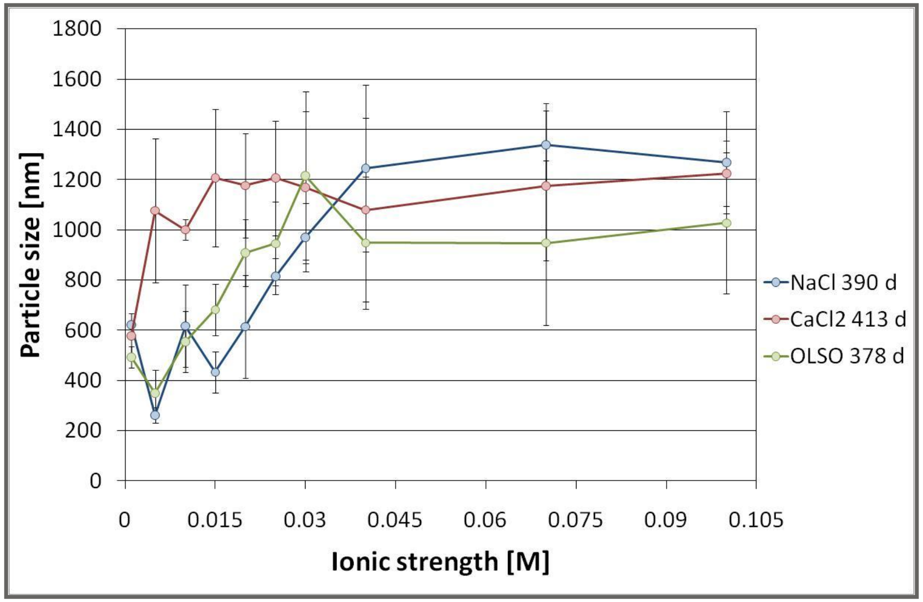
Asymmetrical flow field-flow fractionation (AsFlFFF)
- Particle size distribution

ICP- MS
- Elemental composition

Scanning electron microscopy (FESEM)
Atomic force microscopy (AFM)
XRD/SAXS
- Morphology

Stability of bentonite colloids





Zeta potential as a function of ionic strength in sodium chloride, calcium chloride and OLSO solutions after one year

Particle size as a function of ionic strength in sodium chloride, calcium chloride and OLSO solutions after one year

Sorption experiments

20 mL NaCl/$CaCl_2$-solution
150 µL Sr-85 or 120 µl Eu-152
1 g Bentonite powder
pH ~ 8 (Adjusted)

Shaking (1h/1-2 d/7 d)
Sentrifugation
(7500 rpm/30 min)

10 mL aliquot
Radioactivity measurement (5 min)
(Wizard® 3'' gamma counter)
Particle size and zeta potential determination

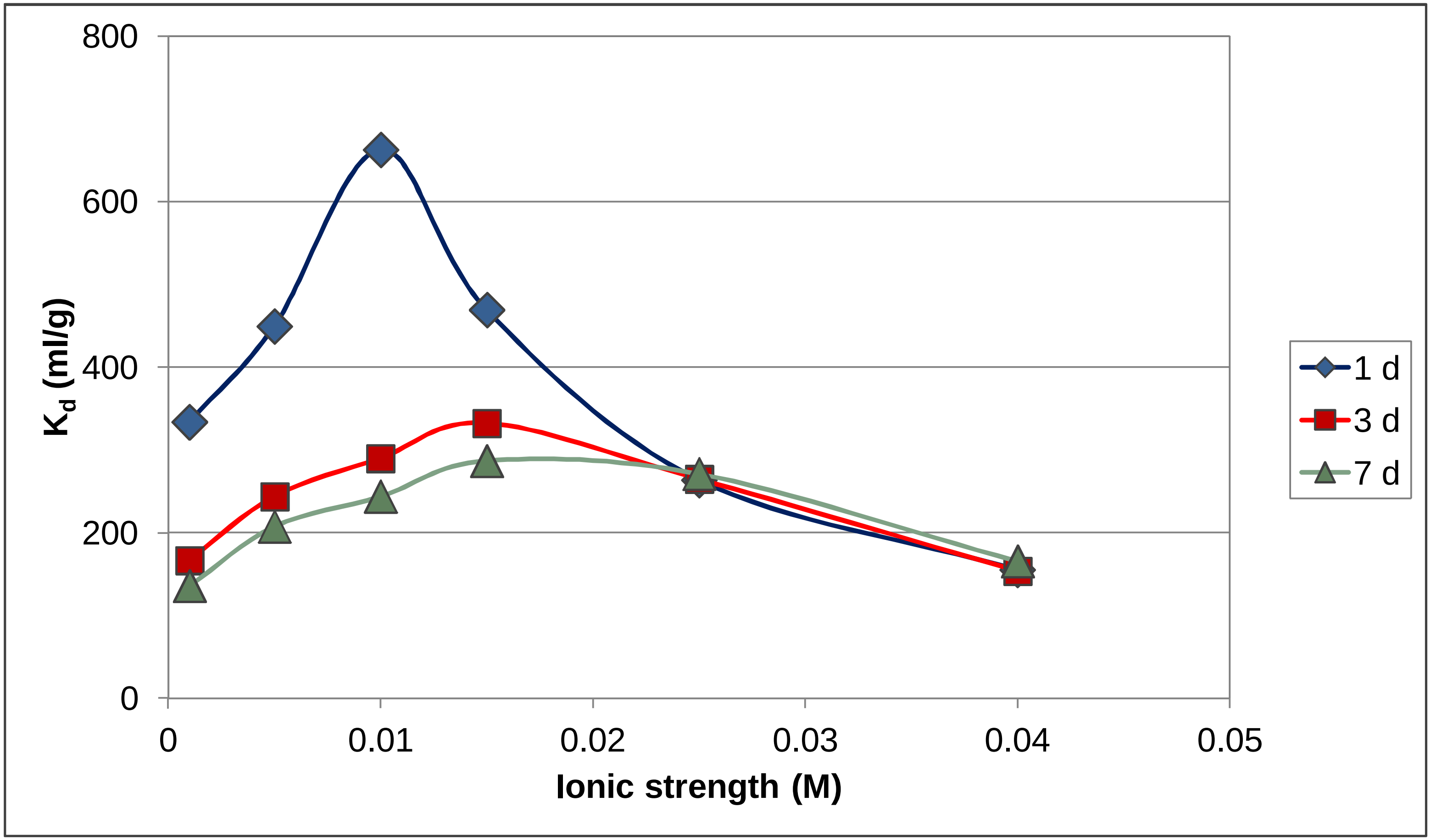
Filtration 1.2 µm (Isopore polycarbonate filter)
Radioactivity measurement (5 min)
Particle size and zeta potential determination (Zetasizer)

Filtration 0.05 µm (Isopore polycarbonate filter)
Radioactivity measurement (5 min)
Particle size and zeta potential determination (Zetasizer)

Drying and weighing of the filters

Desorption experiments

Sr-85 sorption



Conclusions

The stability of bentonite colloids depends strongly on the ionic strength and the valence of the cation, no substantial change during one year.

Low ionic strength (<0.04M in NaCl, <0.01 M in $CaCl_2$ or <0.015 M in OLSO) favors the formation of stable colloids

Colloids are smaller and more stable in monovalent (Na^+) than in divalent (Ca^{2+}) dominated solutions

In 0.001 M: 85 % adsorbed on the solid phase, 10 % adsorbed on the colloidal fraction (0.05 – 1.2 μm) and 5 % on particles larger than 1.2 μm

In 0.1 M: 100 % adsorbed on the solid phase

Under prevailing saline groundwater conditions in Olkiluoto colloids are instable but the possible influence of glacial melt waters has to be considered

Plans for 2012

Colloid formation and stability experiments

Development of static and dynamic bentonite erosion experiments

To test and apply colloid characterization methods

Colloid concentration determination: a standard series made from MX-80 bentonite and Al determination (ICP-MS)

Sorption experiments (Eu-152, Np-235, Bentonite powder and colloids (pH, ionic strength)

Plans for 2012

EU FP7 BelBAR

Colloid mobility and colloid/rock interactions in columns and in a natural fracture (0.9 m x 0.9 m) will be examined in Kuru Grey granite block used earlier to study fracture flow and radionuclide transport experiments.

Sorption experiments will be developed to study the radionuclide sorption reversibility in static and dynamic conditions.

Grimsel Test Site Phase VI, Colloid formation and migration (CFM)

Thank you

McCarthy, J. and Zachara, J. *Environ. Sci. Technol.* ***23*** (1989) 496