EUROPEAN COMMISSION

Community research

BELBaR

(Contract Number: 295487)

DELIVERABLE (D-N°:6.12)

Reporting period: e.g. 01/09/13 – 28/02/15

Date of issue of this report: **18/02/2016**

Start date of project: **01/03/12**

Duration: 48 Months

Project co-funded by the European Commission under the Seventh Euratom Framework Programme for Nuclear Research &Training Activities (2007-2011)		
Dissemination Level		
PU	Public	

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Christophe Davies (EC) BELBaR participants		

BELBaR

Clay Colloids in Aqueous Systems

3-4 February 2016, Berlin, Germany

Venue: Seminaris CampusHotel Berlin

www.belbar.eu

Agenda

February 3

08.30	Registration
09.00	**Welcome and overview** - Patrik Sellin
09.20	**Mechanisms of erosion** - Tiziana Missana
10.00	**Colloid mobility -** Thorsten Schäfer
10.40	*Coffee break*
11.00	**Colloid Formation and stability -** Radek Cervinka
11.40	**Modelling of erosion and transport -** Patrik Sellin
12.20	**Treatment of colloids in a safety case -** Amy Shelton

12.50 *Lunch*
(at the conference premises, hosted by the project)

14.00	**Flow of Clays -** Jon Otto Fossum
14.45	**Back to the project on inorganic colloidal particles in Lake Brienz (Switzerland) ten years after -** Montserrat Filella
15.30	**Coffee break**
16.00-16.20	**Benchmarking Exercise of Clay Erosion in Artificial Fracture Tests** Tim Schatz
16:25-16:40	**Size of Clay Platelets, pH and Temperature Matter** Mo Segad
16:45-17:05	**Understanding the mechanisms of chemical erosion of bentonite- need for a holistic approach** Nuria Marcos

17.30 Poster session

List of posters see next page.
A buffet dinner will be served during the poster session.

February 4

9.00-9.20	**Irreversibility of bentonite colloid aggregation under different environments -** Ursula Alonso
9.25-9.45	**Influence of temperature on smectite clay gels** - Magnus Hedström
9.50-10.10	**Interaction pressure between charged plate-like particles in electrolyte solutions: An application of density functional theory with the solvent primitive model** – Ivars Neretnieks
10.15	*Coffee break*
10.40-11.00	**Detachment of colloids at the clay solid/liquid interface -** Rasmus Eriksson
11.05-11.25	**Sorption behavior of Np(V) onto clays from Russian and Indian deposits -** Anna Yu Romanchuck
11.30-11.50	**Study of radionuclides migration through crushed granite in presence of bentonite colloids -** Kateřina Kolomá
11.55-12.15	**Effect of clay nanoparticle mobility, desorption and redox kinetics on radionuclide mobility investigated in an underground research laboratory (Grimsel Test Site, Switzerland -** Thorsten Schäfer

12.20 **Lunch**
(at the conference premises, hosted by the project)

13:20-13:40	**Radionuclide transport in granite fractures in the presence of bentonite colloids: Summary of the studies carried out at Ciemat -** Tiziana Missana
13:45-14:05	**Modelling bentonite erosion -** Ivars Neretnieks
14:10-14:40	**Scaling of erosion from laboratory experiments to temporal and spatial extent of a repository** – Markus Olin
14.40	*Coffee break*
15:00	**Summary -** Jinsong Liu/Jarmo Lehikoinen
15.30	End of conference

The BELBaR project has received funding from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487

Posters

Title	Authors
Hydration and swelling behaviour of Febex bentonite observed by Environmental scanning Electron microscopy (ESEM	Friedrich, Schild, Wiedler, Schäfer
Determination of surface area of clay minerals by EGME method	Brázda, Červinka
Comparison of erosion behaviour of different clays	Alonso, Missana, Fernández, García-Gutiérrez
The electrophoretic mobility of montmorillonite Zeta potential and surface conductivity effects	Leroy, Tournassat, Bernard, Devau, Azaroual
Comparison of the stability behaviour of colloids obtained from different raw bentonites and clayey materials of interest in the frame of high-level waste repositories	Missana, Alonso, Fernandez, Lopez
Swelling of Ca/Na Montmorillonite at different temperatures physical insights with the primitive model	Thuresson, Jönsson, Karnland
Behaviour in the phase interface of colloid systems at high temperatures in new experiments o Josef mock-up type	Roll, Kuchovsky
Effects of bentonite colloids on the radionuclide migration in granitic rock	Hölttä, Elo, Suorsa, Honkaniemi, Niemiaho
Geomicrobiological aspects of clay colloids - culturable microorganisms	Mikes, Spacek
Generation and stability of bentonite colloids	Soursa, Hölttä
The effect of aperture variability and accessory minerals on the erosion of MX80 form a fracture intersecting a deposition hole	Reid, Lunn, Mountassir, Tarantino
Evaluation of actinide(IV)-Silica colloids mobility under repository conditions – the NUWAMA project	Hildebrand, Weiss, Zaenker, Kulenkampff, Lippmann-Pipke, Videnska, Cervinka
Differences in crystalline swelling properties of three montmorillonites in liquid water - influence of temperature, interlayer cation and layer charge	Svensson
Smectite free swelling and erosion in artificial fractures	Hedström, Hansen, Nilsson
Build-up of Accessory Mineral Layers during Erosion of Buffer Material	Schatz
Neptunium (V) sorption onto Montmorillonite and Bentonite colloids and the influence of colloids on Np(V) transport	Elo, Huittinen, Hölttä
Intercalation and Retention of Carbon Dioxide in a Smectite Clay promoted by Interlayer Cations	Fossum
Influence of physico-chemical, chrystallochemical and compositional properties of clay minerals on erosion processes	Fernández. Alonzo, Missana
Measuring free swelling of MX-80 Bentonite in a narrow channel using x-ray imaging	Harjupatana, Lämsä, Kataja
A novel Density functional theory (DFT) modelling on clay colloids: interaction forces and ion exchange	Yang, Neretnieks, Wold
Modelling bentonite erosion phenomena by coupling finite and discrete element methods	Molinero, Casas, Celigueta, Oñate, Bruno
Rheology measurements on smectite clay gels	Nilsson, Hedström
A large deformation model with strong chemical-mechanical coupling for bentonite to assess the bentonite buffer behaviour in spent nuclear fuel disposal conditions	Pulkkanen, Olin
Do montmorillonite particles form gels in aqueous suspensions	Eriksson
Electrolyte-mediated dissolution of montmorillonite in alkaline environments	Eriksson
Bentonite Erosion in an artificial fracture set-up under near natural conditions	Rinderknecht, Friedrich, Heck, Götz, Huber, Schäfer
Bentonite Erosion and Colloid Mediated Transport of Radionuclides in a natural shear zone at the Grimsel Test Site	Rinderknecht, Heck, Götz, Walschburger, Geyer, Hilpp, Fuß, Huber, Schäfer, Geckeis
Modelling the impact of fracture geometry on bentonite erosion	Florian Huber
Microstructure of bentonite and dilute water erosion	Matusewicz Olin Pulkkanen
Bentonite erosion experiments under dynamic conditions	Bouby, Heck, Hilpp, Geyer, Schäfer
Montmorillonite colloids. I: Characterization and stability of dispersions with different size fractions II: Dependency of Colloidal size on Sorption of Radionuclides III: Influence of colloidal size on the sorption reversibility of radionuclides	Norrfors, Bouby, Marsac, Wold, Lützenkirchen, Schäfer
Influence of organic matter (fulvic acids) on the coagulation and long term stability of clay colloids prepared under different chemical conditions	Bouby, Heyrich, Heck, Hilpp, Schäfer
The surface properties and CS adsorbtion of natural and acid-modified montmorillonites	Krupskaya, Zakusin
Detachment of colloidal particles from bentonites in water	Kaufhold, Dohrmann

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BELBaR 2nd Workshop

Clay colloid conference Participant list

First Name	Last Name, org.	Signature
Ursula	Alonso CIEMAT	
Muriel	Bouby, KIT-INE	
Lukas	Brazda, ÚJV ŘEŽ	
Jordi	Bruno AMPHOS 21	
Radek	Cervinka, ÚJV ŘEŽ	
Reiner	Dohrmann	
Outi	Elo	
Rasmus	Eriksson	
Montserrat	Filella UNIVESITY OF GENEVA	
Jon Otto	Fossum	
Frank	Friedrich KIT-INE	
Mireia	Grive AMPHOS 21	
Tero	Harjupatana JYU	
Allan	Hedin, SKB	
Magnus	Hedström Clay Technology AB	
Heike	Hildebrand HZDR	
Elina	Honkaniemi	
Florian Mathias	Huber KIT	
Pirkko	Hölttä	
Maria	Jansson	
Dr. Stephan	Kaufhold	
Kateina	Kolomá, ÚJV ŘEŽ, a.s.	

Anne	Kontula , POSIVA oy	
Victoria	Krupskaya	
Jarmo	Lehikoinen STUK	
Philippe	Leroy BRGM	
Jinsong	Liu	
~~Longcheng~~	~~Liu~~	
Nuria	Marcos , Saanio & Riekkola Oy	
Jiri	Mikes TERAMED	
Tiziana	Missana CIEMAT	
Jorge	Molinero AMPHOS 21	
Dr. Kakha	NADIRADZE	
Ivars	Neretnieks	
Ulf	Nilsson Clay Tech	
Karin	Norrfors , ÅF-Industry AB	
Ulrich	Noseck GRS	
Markus	Olin VTT	
Vladimir	Petrov MSU	
Veli-Matti	Pulkkanen VTT	
christopher	reid	
Franz	Rinderknecht KIT	
Michal	Roll CEG	
Anna	Romanchuk MSU	
Tim	Schatz	
Thorsten	Schäfer KIT-INE	
M.	Segad Meehdi	M. Segad
Patrik	Sellin	
Amy	Shelton RWM	
Marie	Skepö	Marie Skepö
Valtteri	Helsinki Suorsa University	

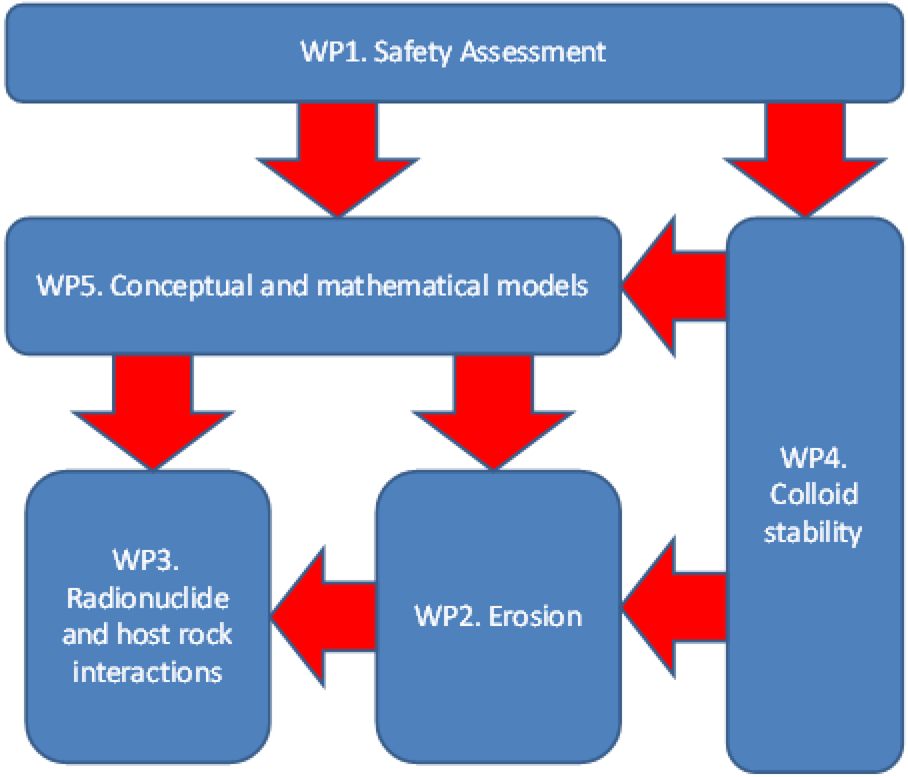
Daniel	Svensson	
Axel	Thuresson	
Stephan	Weiss HZDR	
Mary	Westermark SKB	
Irina	Vlasova MSU	
Guomin	Yang KTH	
Bo	Jönsson LTU	
Michal	Matusewicz	
Pavel	Špaček CHEMCOMEX	

BELBaR: *Investigation of erosion processes in bentonite engineered barriers systems of a repository in crystalline rock and their impact on the long-term performance of the repository*

BELBaR

- BELBaR is a Collaborative Project within the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities.
- The main aim of BELBaR is to increase knowledge of the processes that control clay colloid stability, generation and its ability to transport radionuclides.
- The overall purpose of the project is to come up with a new way of treating issues in long-term safety/performance assessment.
- The project started March 1, 2012 and has a duration of 48 months.
  - BELBaR will end February 28, 2016
- The project has 14 partners from seven European countries

Outputs – onset of project



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Partners

- SKB: Svensk Kärnbränslehantering, Sweden
- CIEMAT: Centro de Investigaciones, Energeticas, Medioambientales y Technologicas Spain
- NRI: Nuclear Research institute Rez plc, Czech Republic
- KIT: Karlsruhe Institut of Technology, Germany
- Posiva OY, Finland
- VTT:Technical Research Instuitute of Finland
- Clay Technology AB, Sweden
- University of Jyväskylä, Finland
- KTH: Kungliga Tekniska Högskolan, Sweden
- NDA: Nuclear Decommissioning Authority, United Kingdom
- B+Tech Oy, Finland
- University of Manchester ,United Kingdom
- Helsinki University, Finland
- Lomonosov Moscow State University, Russia

BELBaR

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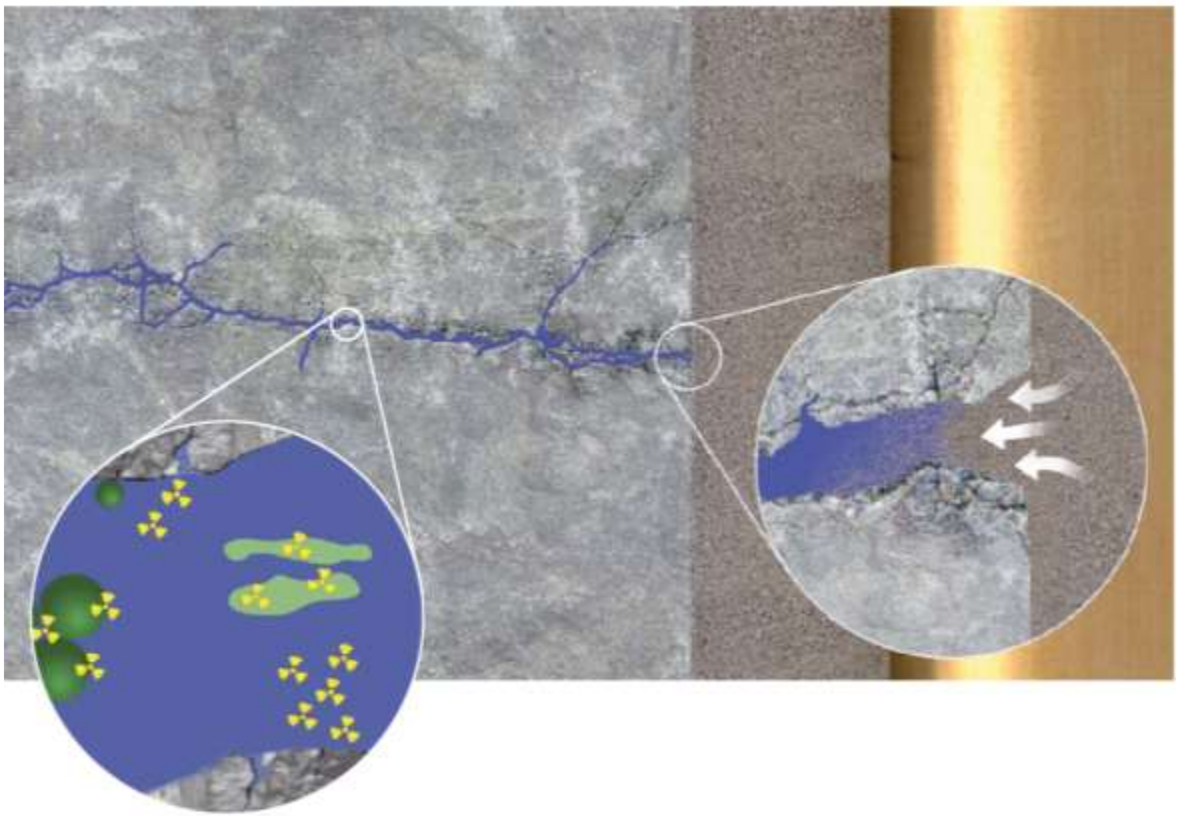
The problem to study



This meeting

- International symposium
- The target audience is the scientific community
- Present and discuss clay colloid issues
  - Results from BELBaR as well as from other studies
- Keynote presentations from externa experts

Agenda

- Today:
  - Overview of BELBaR
  - Invited talks
  - Oral presentations
  - Poster session
- Tomorrow:
  - Oral presentations
  - Summary

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007- 2011) under grant agreement no 295487.

Berlin, 3 February 2016

WP2
MECHANISMS OF EROSION

T. Missana
(CIEMAT)

Work Package 2: PARTICIPANTS and PMs

Work package number	2		Start date or starting event:				Project Month 1				
	Erosion										
Activity Type	RTD										
Participant	CIEMAT	MSU	KIT-INE	NRI-REZ	SKB	B+Tech	ClayTech	VTT	JYU	NDA	KTH
Person-months for the participant	18	6	6	10	1	28.5	9	16	11	1	1

11 participants, 7 countries

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OBJECTIVES

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WP 2

To **understand** the main mechanisms of clay particle erosion from the bentonite surface and try to **quantify** the (maximum) extent of the possible erosion under different *physico-chemical conditions*.

1. Assessment of bentonite barrier functionality the at the long-term, which could be compromised if a significant clay loss occurs.

WP 4

Conditions that favor colloid stability are also expected to favor colloid transport and erosion processes.

2. Interaction with RN and transport to the far-field of the repository.

WP 3

Safety Assessment (SA) demanded new data obtained to develop and validate models describing the bentonite barrier erosion.
Need to reduce uncertainties .

WP 1/5

BELBaR

OBJECTIVES

WP 1

Starting from the analyses of the state-of-the-art at the beginning of the project, the treatment of several topics was suggested:

- Mechanisms of erosion of clay particles from the bentonite surface: output of WP2.
- Improved models with new data: output of WP 5.

- Characteristics of the bentonite clay: role of divalent cations; other clay characteristics.

- Groundwater chemistry: role of divalent cations; ionic strength, mixed electrolytes;

- Groundwater/clay interactions: modelling inclusion in Safety Case;

- Groundwater velocity: dependence of erosion on water velocity;

- Clay extrusion paths: dependence of fracture geometry.

Wrap - up

Where we were at the beginning

Initial Objectives & Issue (NDA Report)

Where we are now

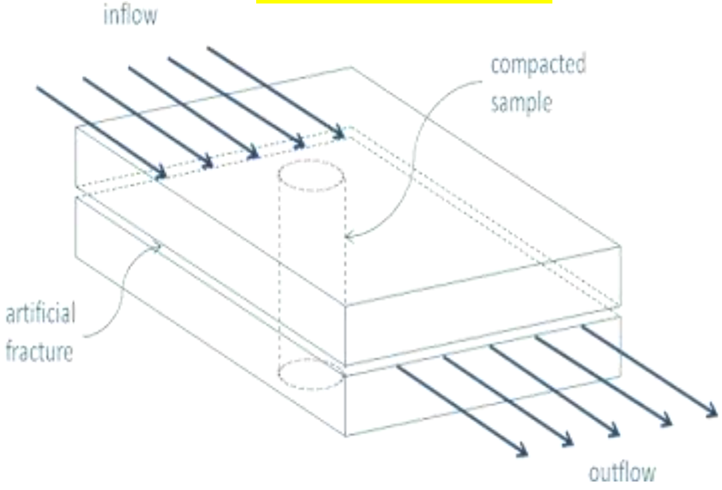
Accomplished Objectives
Remaining Uncertainties

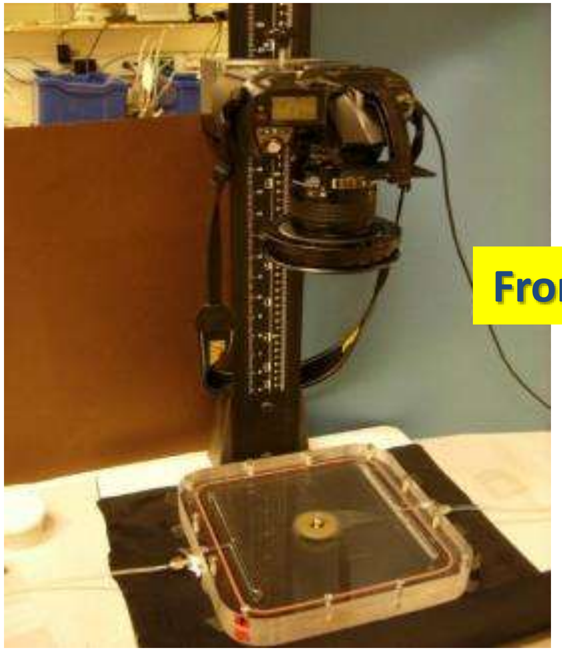
FINAL CONCLUSIONS FOR BELBAR

In this talk, a summary of the main results obtained by the organizations participating in WP 2. Source of information: deliverable and previous BELBAR Meetings.

Experimental sets-up

From B+Tech





From Clay Technology

Flow – trough artificial fracture.

Extrusion/erosion behaviour of bentonite buffer material at a transmissive fracture interface allowing the free-swelling of the clay. With this system, the effects of solution chemistry, material composition, flow velocity, fracture geometry (aperture, slope angle) and other parameters could be analysed. Benchmark exercise .

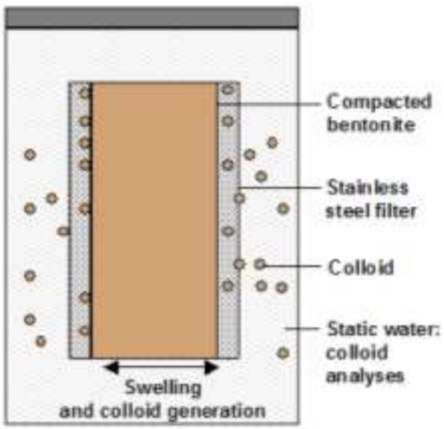
Experimental sets-up

(a)

Static system

CHEMISTRY

(b)

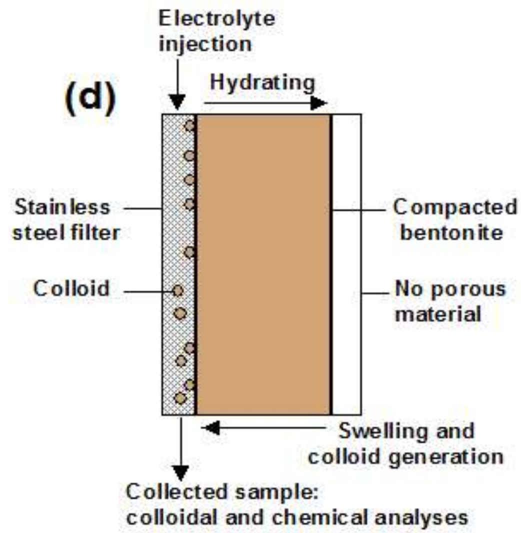


(c)

Dynamic system

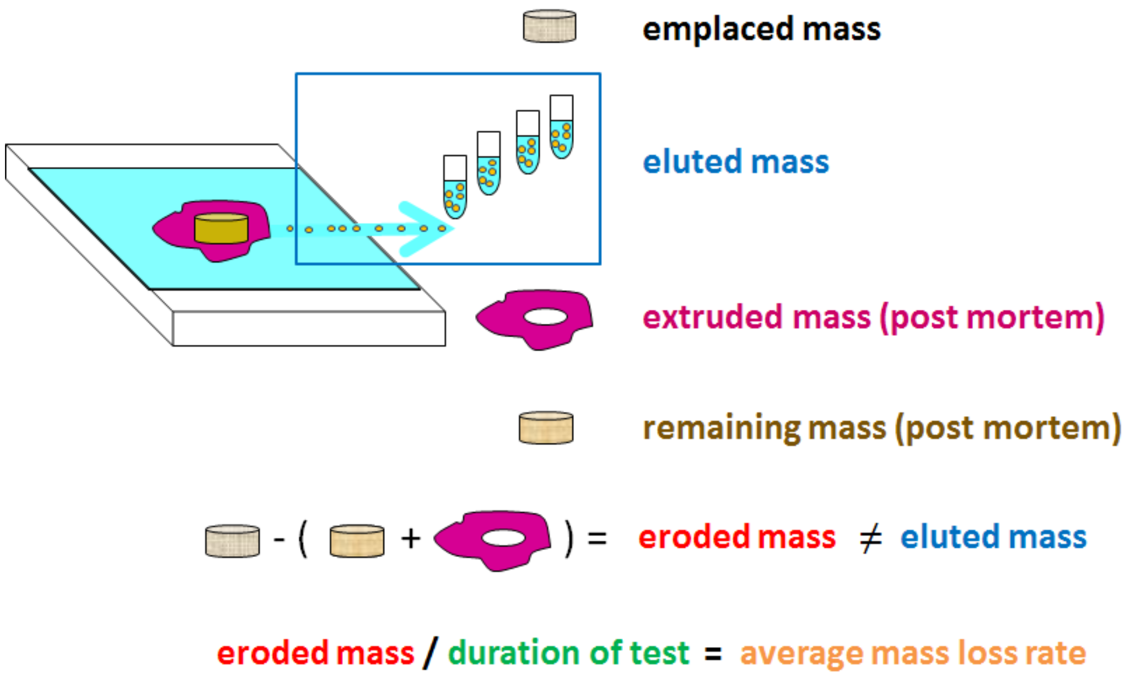
CHEMISTRY + FLOW

(d)



Experiments <u>maintaining the confinement of the clay</u> and allowing its hydration through the filters, with a pore size of 100 µm. The mass loss is limited to the particles dispersed in the liquid phase (the *eluted mass*) plus some particles retained in the sintered filters.

Experimental sets-up



- Eluted clay mass: PCS, turbidity, ICP-MS.
- Extruded, remaining: gravimetry.

EROSION OBSERVED IN DIFFERENT SYSTEMS: Given the differences in the type of experiments and the need of comparing the numerical results, obtained from the different organisations, it is important to make clear how the *"mass loss"* or the *"average mass loss rate"*, needed for <u>quantitatively estimating erosion</u>, is measured.

Mechanisms of erosion of clay particles from the bentonite surface

- **Clay must be hydrated enough, to allow the gel formation (which is the main colloids/particles source).**
- **Swelling pressure: driving force causing the gel intruding the fracture/pores of the rock; Particle detachment may occur when the driving force for water uptake (of osmotic nature) overcomes the attractive forces between the clay platelets.**
- **To produce an erodible gel layer, the bentonite must have a place to expand (for this reason the geometry of the fracture or the characteristic of the porous space in the rock are critical).**

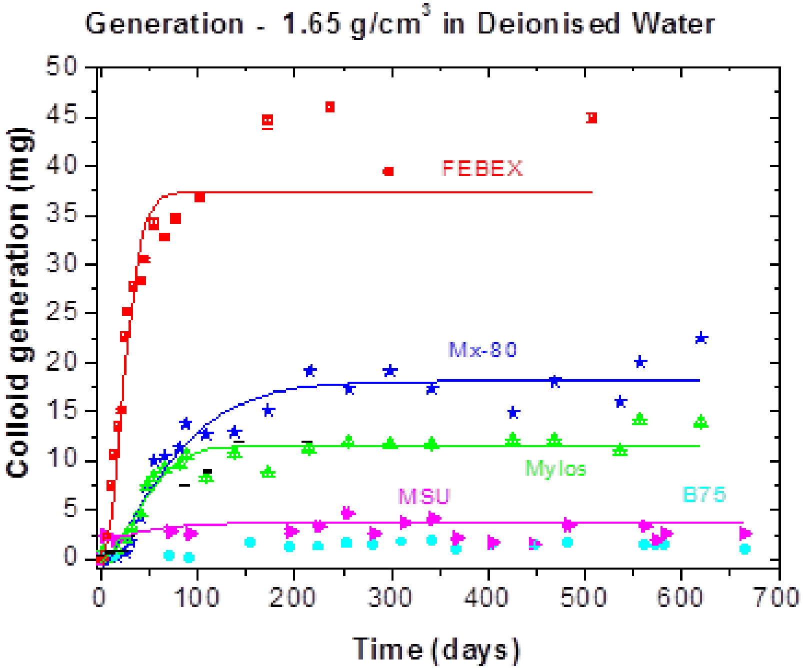
Repulsive electrostatic (double layer) forces separate particles, from the gel. Double layer depends on water (chemical forces); Conditions for particle "stability " necessary.

Water flow can shear off particles: (physical forces);

Mechanisms of erosion of clay particles from the bentonite surface

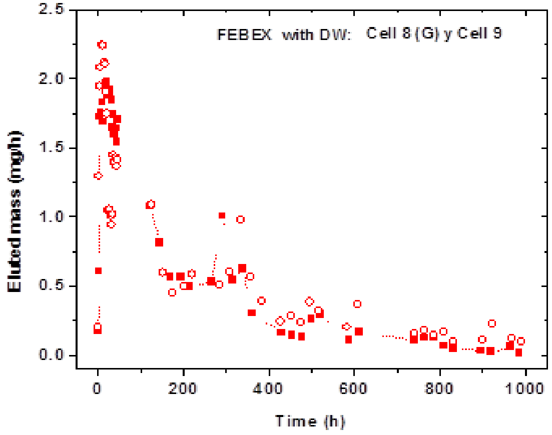
Is erosion "linear", continuous… (never-ending ?)

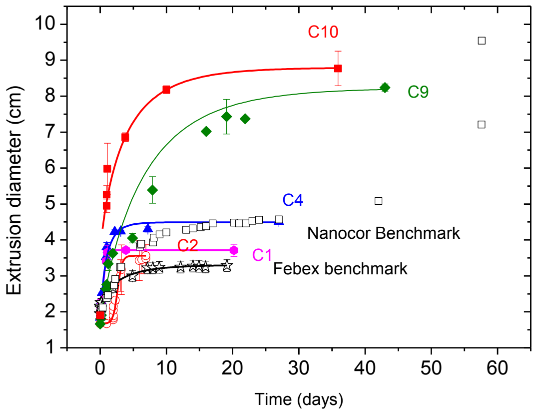
- **In CIEMAT's experiments in static system it has been observed that clay dispersion is not continuous.**
- **The eluted mass increased (linearly) with time after reaching a maximum value after a certain time. This (equilibrium) mass depended on different factors, for example the ionic strength of the water or the Ca content in the system, the type of bentonite, etc..**



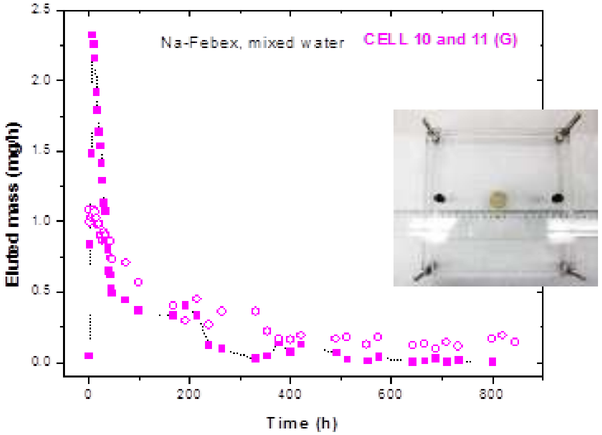
Mechanisms of erosion of clay particles from the bentonite surface

- In flow-trough artificial fractures the velocity of extruding phase into the fracture was not constant (as well as the eluted mass).
- With some exceptions (pure Na-smectite hydrated with DW, i.e. the most favorable case for erosion, the velocity of the bentonite within the fracture always decreased until reaching zero values, in many cases.





Eluted mass rates are not constant.
Point to be discussed.



Characteristics of the bentonite clay

What are the main clay properties enhancing/inhibiting erosion ?

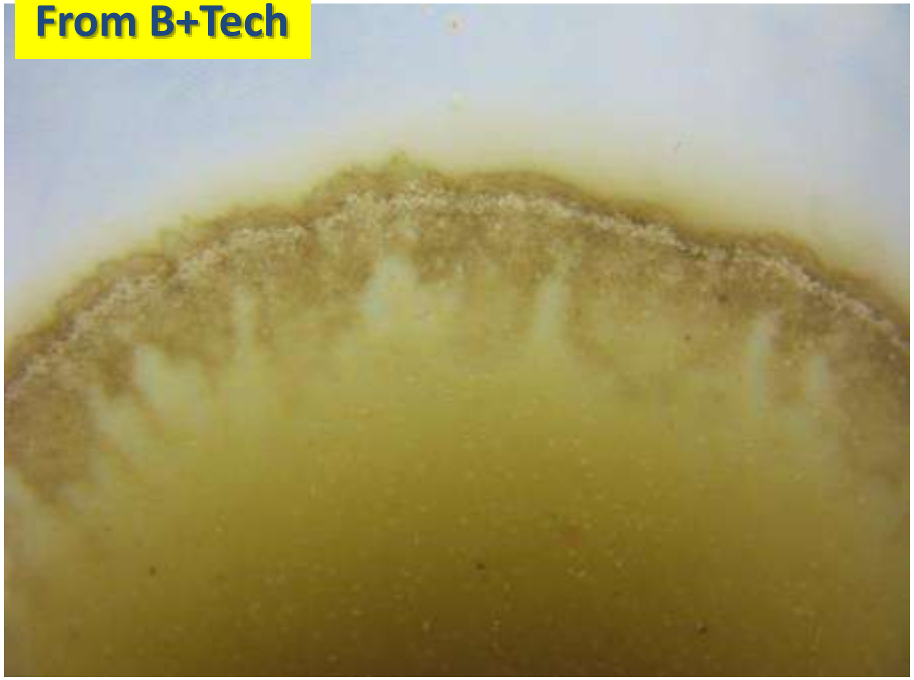
- **Eroding material is predominantly smectite;**
- **Type of smectite is important. Distribution between tetrahedral/octahedral charge is relevant (CIEMAT): montmorillonites in general more erodible than beidellites;**
- **Pure Ca-bentonite does not erode;**

General agreement

- **Na concentration above 20 % in the exchange complex is enough to make the clay erodible. In dispersed systems, a good correlation between colloids generated and Na has been found. However, the structure of bentonite even with exchanged Na-clay influences the erosion process.**
- **In respect to pure Na-clays, average mass loss rates for the *as-received* bentonites are at least an order of magnitude lower.**
- **Existence of minerals that may cause hetero-aggregation (kaolinite/oxides…) , inhibits erosion (relation between erosion and stability).**

Characteristics of the bentonite clay

From B+Tech



Horizontal artificial fracture test with sodium montmorillonite / sand. Sand layer formation at the extrusion/erosion interface is clearly visible.

Presence of accessory minerals (larger than the smectite particles) may slow down smectite and stop erosion because they remain behind and form bed layers.

However, no apparent attenuation of montmorillonite erosion observed with added accessory materials. The accessory mineral layer may (or not) be subject to erosion (not clear); in sloped fracture both smectite and minerals are removed.

Groundwater chemistry

What are the main chemical groundwater characteristics enhancing/inhibiting erosion ?

Groundwater chemistry plays a very important role on bentonite erosion. The conditions that favor clay colloid stability are expected to favor bentonite erosion; even though, they may not be enough for ensuring that the erosion process will take place.

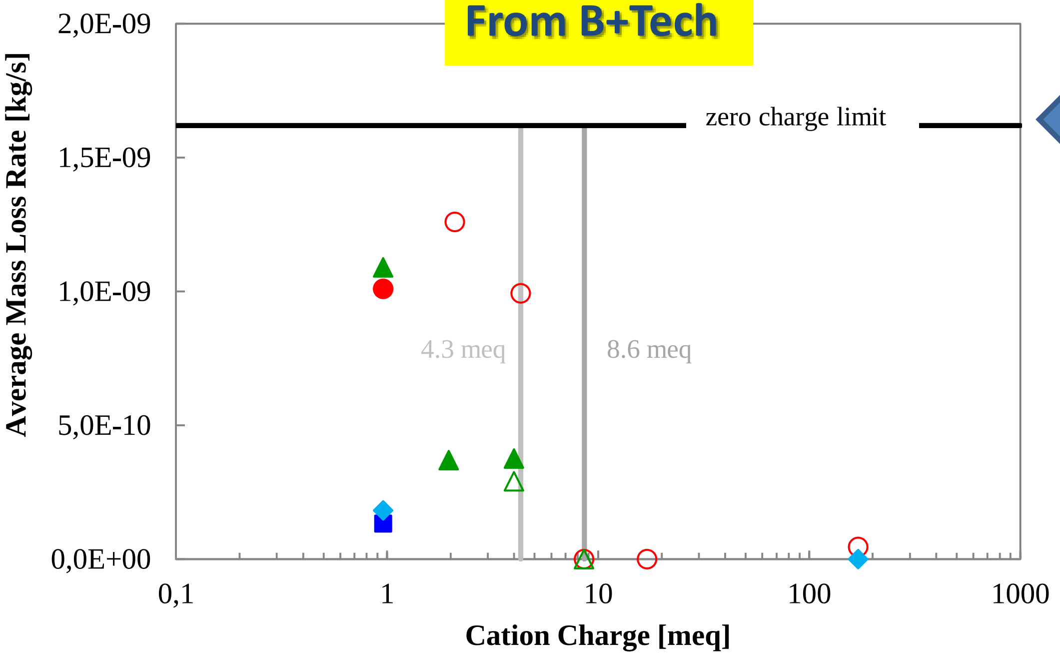
The maximum erosion is always recorded when deionized water (DW) is used. The values of mass loss rate obtained with DW can be surely used as (overly) conservative upper limits for the erosion of each type of bentonite.

Ca in solution (I ~ 1 mM) inhibits erosion. The increase of ionic strength attenuates erosion;

Amongst crystalline waters, Grimsel groundwater is one the most favorable for colloid stability for its low salinity (1 mM). However, average mass loss is significantly lower than that of the limiting DW (30 %). The existence of more than ion influences erosion;

Groundwater chemistry

From B+Tech



MAXIMUM EROSION (DW)

A threshold electrolyte concentration exists, above which erosion does not occur, (this being related with also with the properties of solid).

This is a very important finding in the sense that chemical erosion can take place only under highly dilute solution conditions. The increase of ionic strength further attenuates erosion, up to the threshold limit where mass loss is not observable anymore.

Groundwater chemistry

- Threshold ≠ CCC. The critical coagulation concentration (CCC) determined in batch stability experiments, often overestimates the limits observed for erosion. Probably the CCC concept is not directly applicable to erosion experiments with natural bentonites and, in general, in those systems where more than one type of ion is present. Particularly, it is ill-defined when ion exchange processes occur.

Clay-groundwater interactions

Clay/groundwater interactions chemically affects both clay and groundwater.

- **Water/clay interactions may be very important for the evaluation of erosion and stability of colloids in a repository at a long-term.**
- **The soluble salts present in raw clays dissolved in contact with fresh water, causing an initial increase in salinity. Other dissolution/ precipitation processes may occur.**
- **Ionic exchange: continuous income of Ca from fresh groundwater may increase the Ca content in the exchange complex, decreasing the erodibility of the clay.**
- **The use of geochemical modelling can be useful to establish the evolution of both groundwater and bentonite surface and indicate the possible evolution on the erosion process as complement to stability models.**

Clay-groundwater interactions

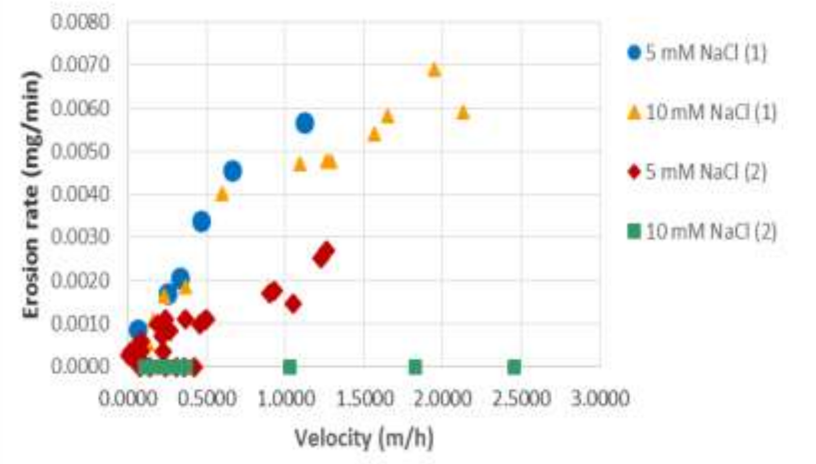
Reversibility ?

- **Hysteresis was observed in the erosion behavior passing form high ionic strengths to diluted ones. That means that smectite eroding at 10 mM NaCl, might be completely stable against erosion below the expected threshold value, if it has previously had a higher salinity present.**

The "history" of the system should be accounted for in evaluating erosion rates (Case of scandinavian scenario)

Similar in stability experiments: after aggregation in high ionic strength, bentonite colloids did not completely recover their initial size (or aggregation state) coming back to more diluted conditions. At least, during the experimental time.

From Clay Technology



Groundwater velocity

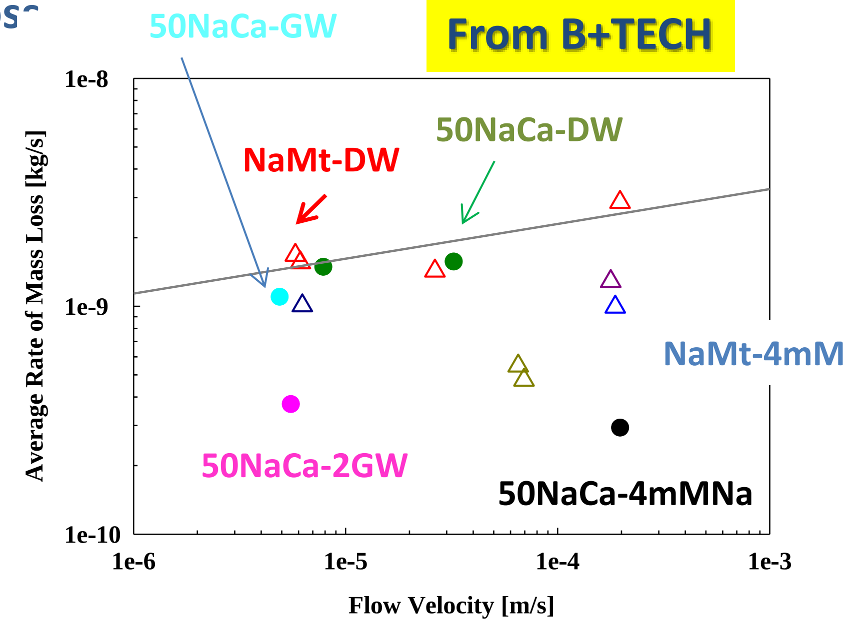
Are physical forces (produced by the water flow) relevant on bentonite erosion ? Are they more/less important then chemical forces ?

- **In largely erosive systems (ion concentration well below the CCC, or erosion threshold), the average mass loss rates seems to be (slightly) correlated with the flow velocity, the highest the flow velocity the highest the mass los-**

- **The observed variations are generally within the same order of magnitude.**

In other cases, the water flow velocity did not seem a relevant parameter or, at least, no clear trend between water velocity and erosion could be observed;

From B+TECH



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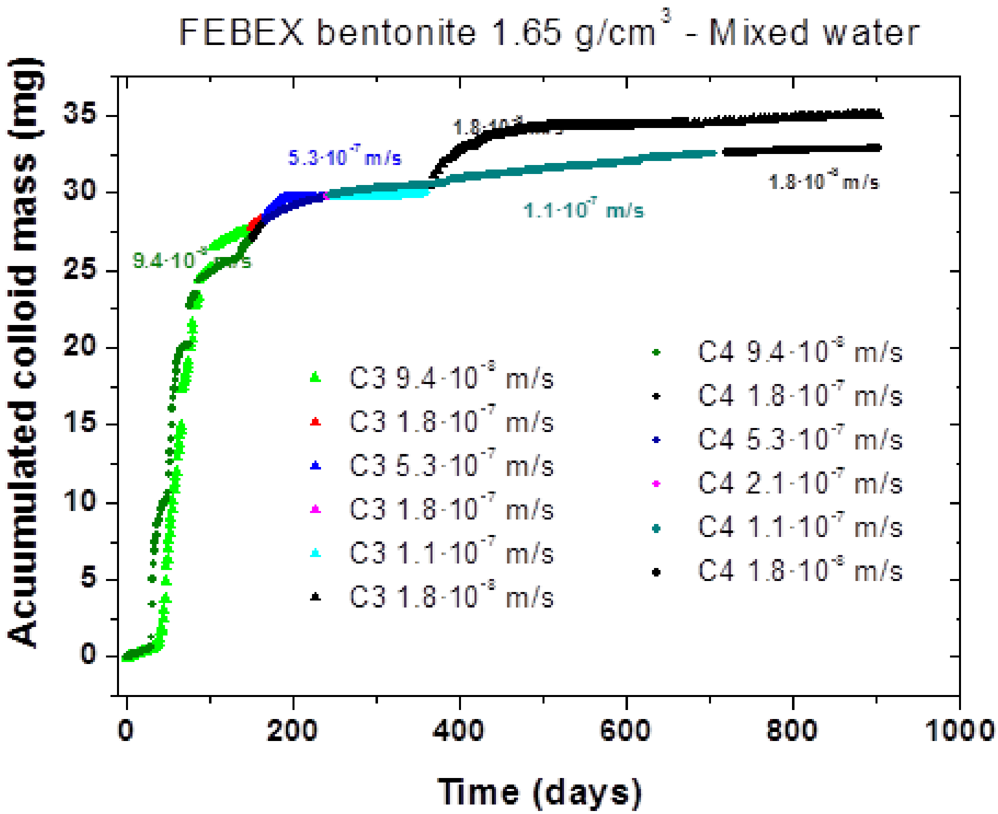
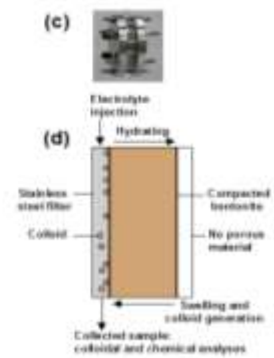
Groundwater velocity





Two different erosion cells under different flow conditions (changed periodically) showed practically the same erosion behavior.

Groundwater velocity

- The effects of groundwater velocity on the mass loss seem to be less relevant than those of groundwater chemistry and somewhat also related with the chemistry of the system.
- In some cases, it was reported that increased flow velocities lead to decreased effluent solids concentrations. This fact would suggest that a rate-limited erosion mechanism exist, at least within the range of tested flow velocities, and that hydrodynamic shear forces maybe not significant in the erosion process.

Thus this can be interpreted considering that the loss of smectite is governed by chemical dispersion/diffusion and that flow just mobilizes the particles present.

This would mean that chemical effects prevail over physical ones.

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Results

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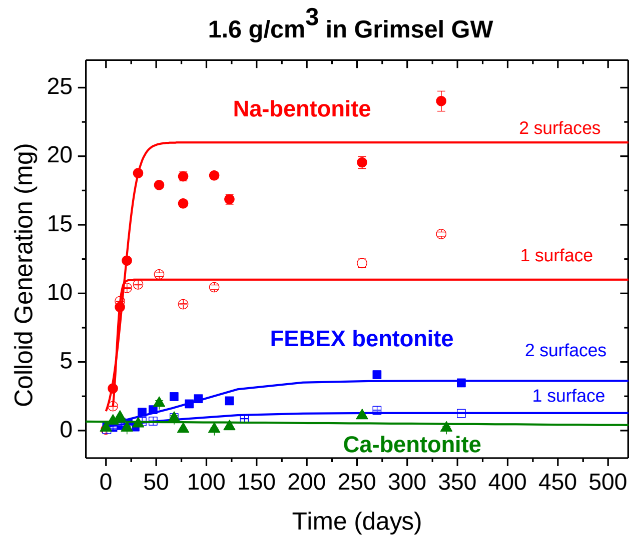
Clay extrusion paths

Does mass loss depends on the characteristics of the "extrusion paths": dimensions, geometry, roughness (mineralogy ?). Relations with filtration processes (WP3).

FRACTURE APERTURE

- **The effect is not completely clear.**

In static experiments, the erosion rate seemed to be roughly proportional to the area of the fracture (double areas double concentration of colloid in solution); consistent with a surface-area controlling effect on mass loss; difficult to determine under less erosive conditions.



One blind side: approximately half of eluted particles

Physico-chemistry of Actinides and Fission Products Unit

GOBIERNO DE ESPAÑA

MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

Ciemat

Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas

BELBaR

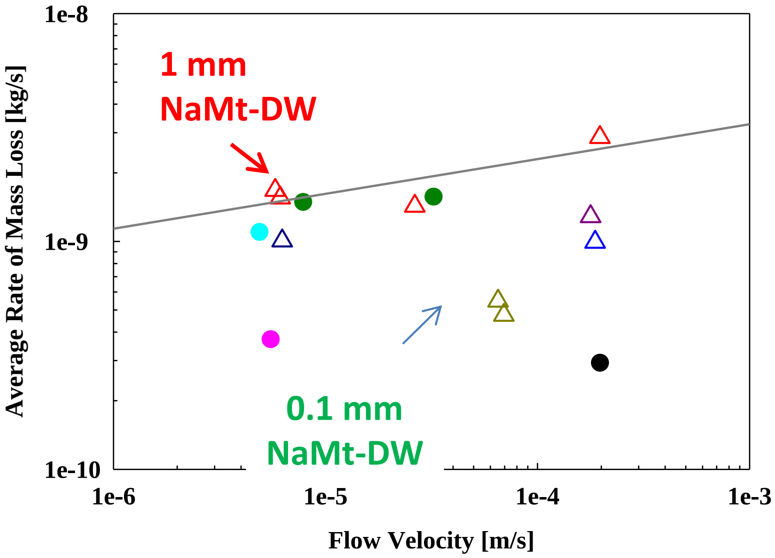
Results

EURATOM

Clay extrusion paths

Does mass loss depends on the characteristics of the "extrusion paths": dimensions, geometry, roughness (mineralogy ?). Relations with filtration processes (WP3).

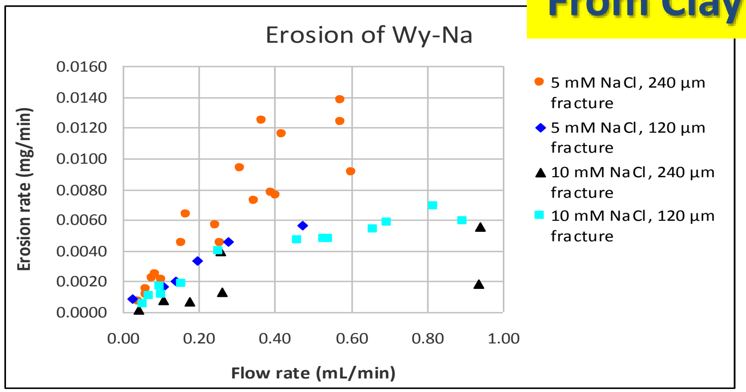
From B+TECH



From 1 to 0.1 mm nearly order of magnitude reduction in average erosion rates;

In other experiments this was not clearly seen.

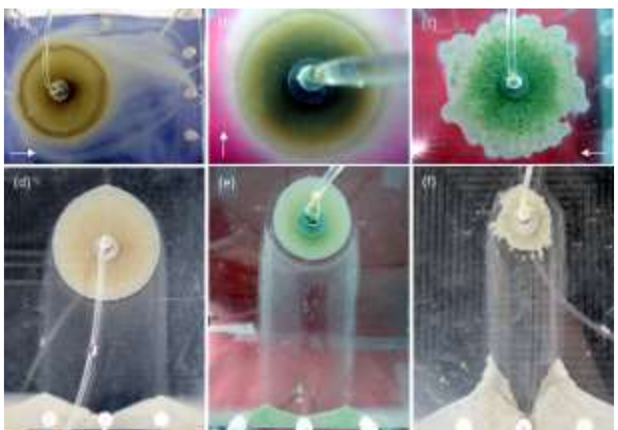
From Clay Technology



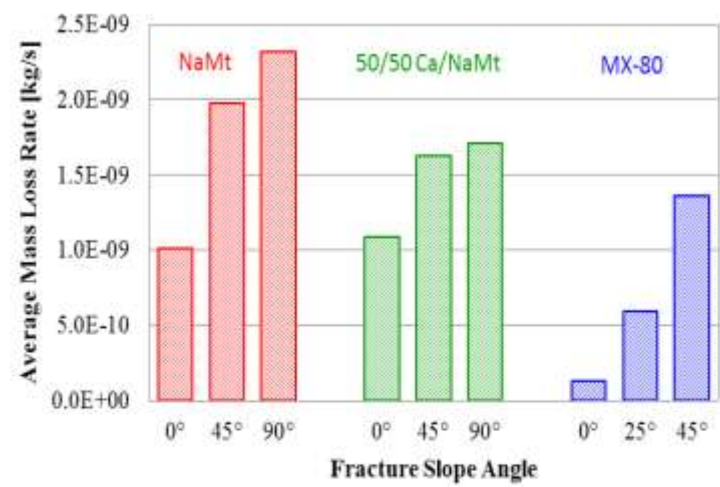
Clay extrusion paths

GEOMETRY: SLOPE ANGLE (& Gravity)

- **Artificial fracture tests 45° / 90: they showed a purely sedimentary mass loss mechanism compared to horizontal fractures, where the mass is released by dispersion.**
- **Average mass loss rates in sloped fractures, always larger than in horizontal case. (Larger slopes, increased mass loss rates). Such sedimentary-type mass loss was observed in sloped fractures under stagnant (no flow) as well as flow-through conditions.**



From B+Tech



Clay Extrusion paths

GEOMETRY: SLOPE ANGLE (& Gravity)

- Despite the mass loss mechanisms are different in the horizontal (dispersion and transport) and sloped angle fractures (structural collapse and sedimentation) they are both operational only under similar chemical environment, i.e with similar threshold for the ionic strength of the solution.

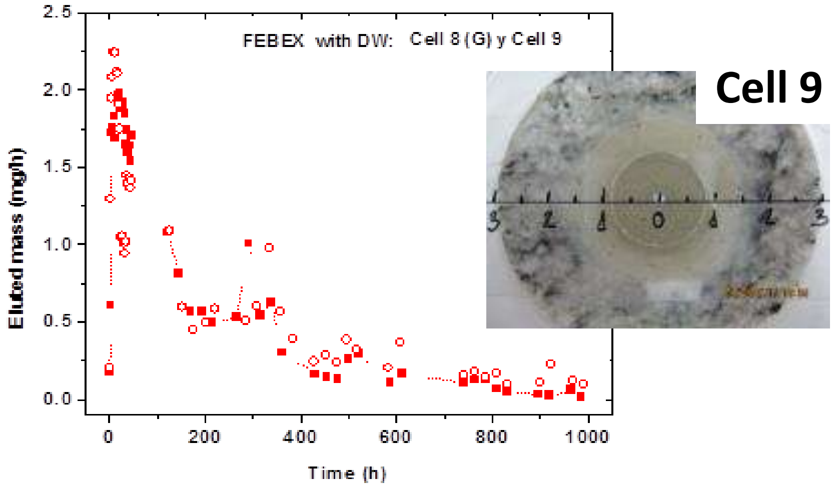
- Observations of mass loss at or above this threshold cannot be attributed to erosion, but rather to disintegration or breakdown of aggregates.

Clay Extrusion paths

SURFACE ROUGHNESS

- **Experiments were carried out by B+TECH to understand the effects of fracture roughness on mass loss. In the rough system, the average mass loss rate was found to be lower. Natural fractures are characterized by rough surfaces and probably buffer mass loss in rough-walled fractures may be significantly attenuated relative to that in smooth-walled systems.**

- **This is in agreement with previous studies of bentonite colloid migration in fracture;**
- **Nevertheless, "filtration" existed below a threshold value for water velocity. CIEMAT analyzed in horizontal flow through test with/without granite (<u>at high flow rates</u>). No large differences were observed.**



Clay Extrusion paths

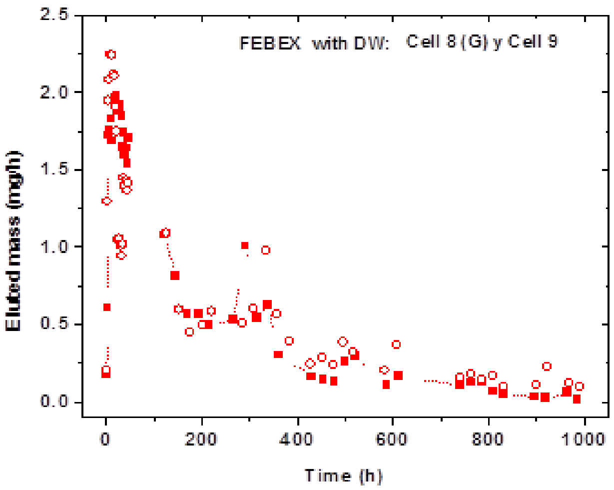
SCALING EFFECTS

- In order to try to assess the effect of scale through the experimental data, erosion tests with cells of different dimensions were carried out by B+TECH. The observed normalized average mass loss rates are in reasonable agreement.

MORE EFFORTS WHERE ?

Data obtained from different experimental sets-up leads to similar conclusions in regard to the different treated topics even if numerical values are sometimes not direcly comparable. Some additional work should be done on data representation as a whole, and on normalising procedures to fix the degree of uncertainty.

Time



NORMALISATION of Eroded Mass

If the eroded mass varies with time is not constant, the experimental time becomes a critical parameter ! Average mass loss rates with large errors.

Experimental times from less than 24 to more than 1000 hours

NORMALISATION of Eroded Mass

Data are recalculated considering the "final" radium of the clay (after extrusion)

Time dependent parameter; sometimes not very precise measurement, above all for raw materials.

Why not initial r ?

Numerically factor 2-3. Larger differences for highly erodible systems.

Extrusion Area (final radius ?)

CONCLUSIONS

- All the topics proposed at the beginning of the project related to erosion mechanisms have been analysed.
- The chemistry of both clay and groundwater are critical on the erosion behavior.
- Erosion will occur only below a threshold value for the ionic strength, depending on the clay and the solution, and basically under diluted solution conditions.
- The maximum mass loss is measured under both dynamic and static conditions with pure Na-smectite and deionized water. These maximum values will represent the upper and (overly) conservative limit for safety assessment consideration.
- The mass loss rates depend on ionic strength; they are about one order of magnitude lower for the as-received than for the purified Na-smectite.
- Ca-clays do not suffer any erosion but a quantity of Na in the clay exchange complex around 20-30 allows the clay to disperse. In solution 1 mM of Ca is enough to hinder erosion.

- In horizontal fractures the mass is lost from the extruded source material through dispersive release and transport. In sloped fractures structural collapse and sedimentation are the main processes causing the mass loss. However in both cases they are operational under a similar chemical threshold.

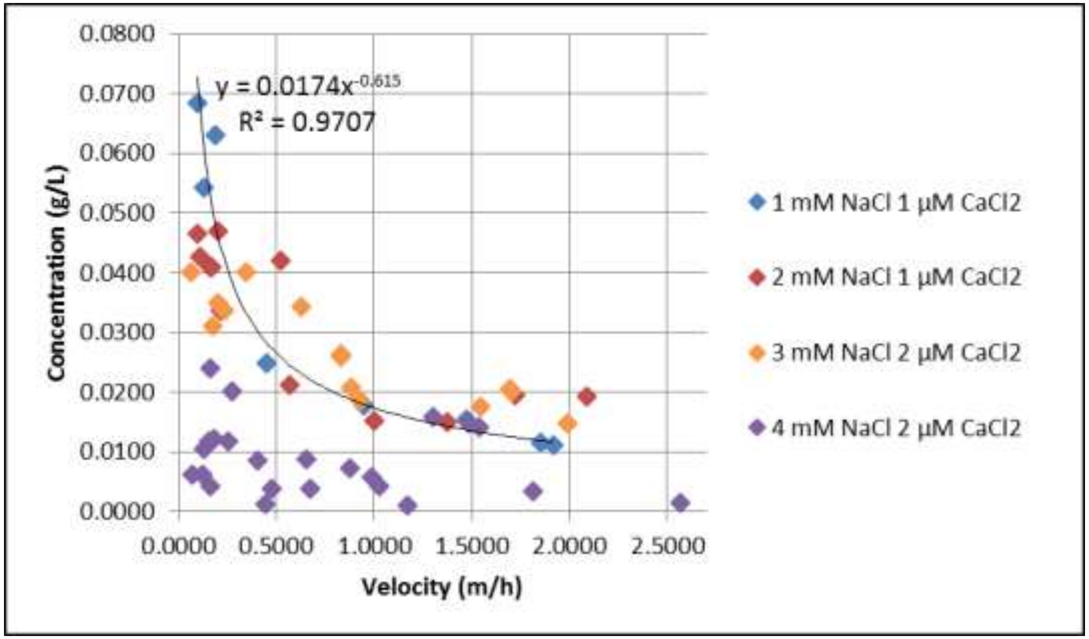
- The effects of groundwater velocity on the mass loss seem to be less relevant than those of groundwater chemistry and somewhat also related with the chemistry of the system. In highly diluted systems the mass loss appears to be correlated to flow velocity even if these variations are generally within the same order of magnitude. However, in less dispersive systems the water flow velocity do not seem to be a relevant parameter and no clear trend between water velocity and erosion has been observed in the different experimental tests.

- Some additional effort needed on data representation and normalising procedures to fix the degree of uncertainty.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Thanks for your attention

Groundwater chemistry


0.0800
0.0700
0.0600
0.0500
0.0400
0.0300
0.0200
0.0100
0.0000
Concentration (g/L)
y = 0.0174x^-0.615
R² = 0.9707
0.0000
0.5000
1.0000
1.5000
2.0000
2.5000
Velocity (m/h)
1 mM NaCl 1 µM CaCl2
2 mM NaCl 1 µM CaCl2
3 mM NaCl 2 µM CaCl2
4 mM NaCl 2 µM CaCl2

BELBaR Project

Colloid formation and stability

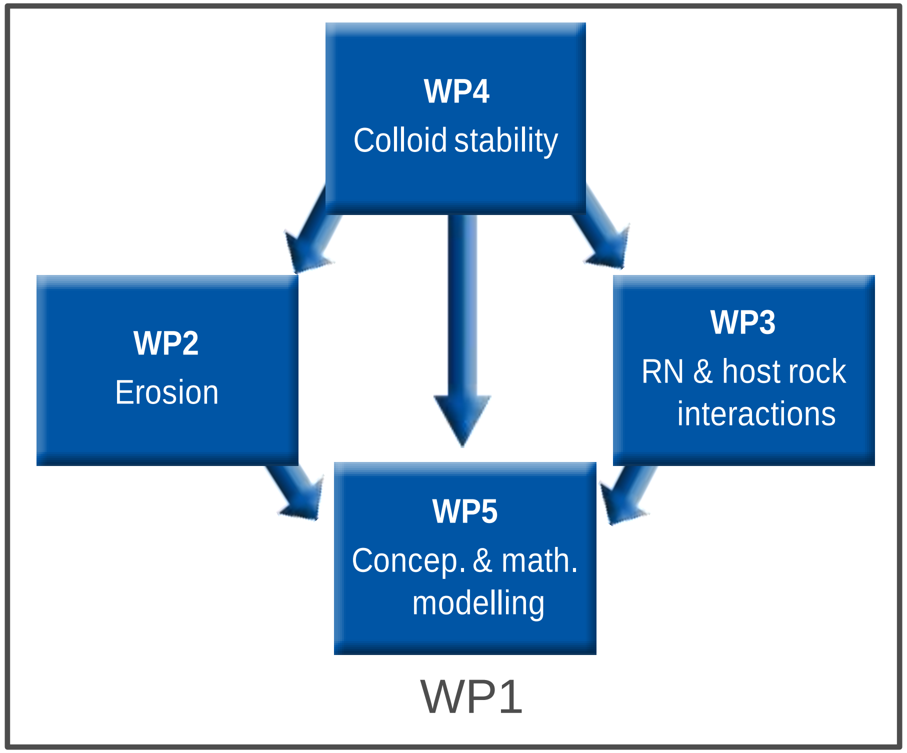
Summary of results from WP4

(CIEMAT, KIT-INE, ClayTech, KTH, B+TECH, SKB, ÚJV)

Edited by Radek Červinka
ÚJV Řež, a. s., 2016

BELBaR Final Workshop
Berlin, 3-4 February, 2016

WP4: Objectives



1) **Clay colloid stability studies under different geochemical conditions with respect to ionic strange and pH**

Reason for different behaviour of different clays - trend or correlation between the bentonites characteristics and its stability

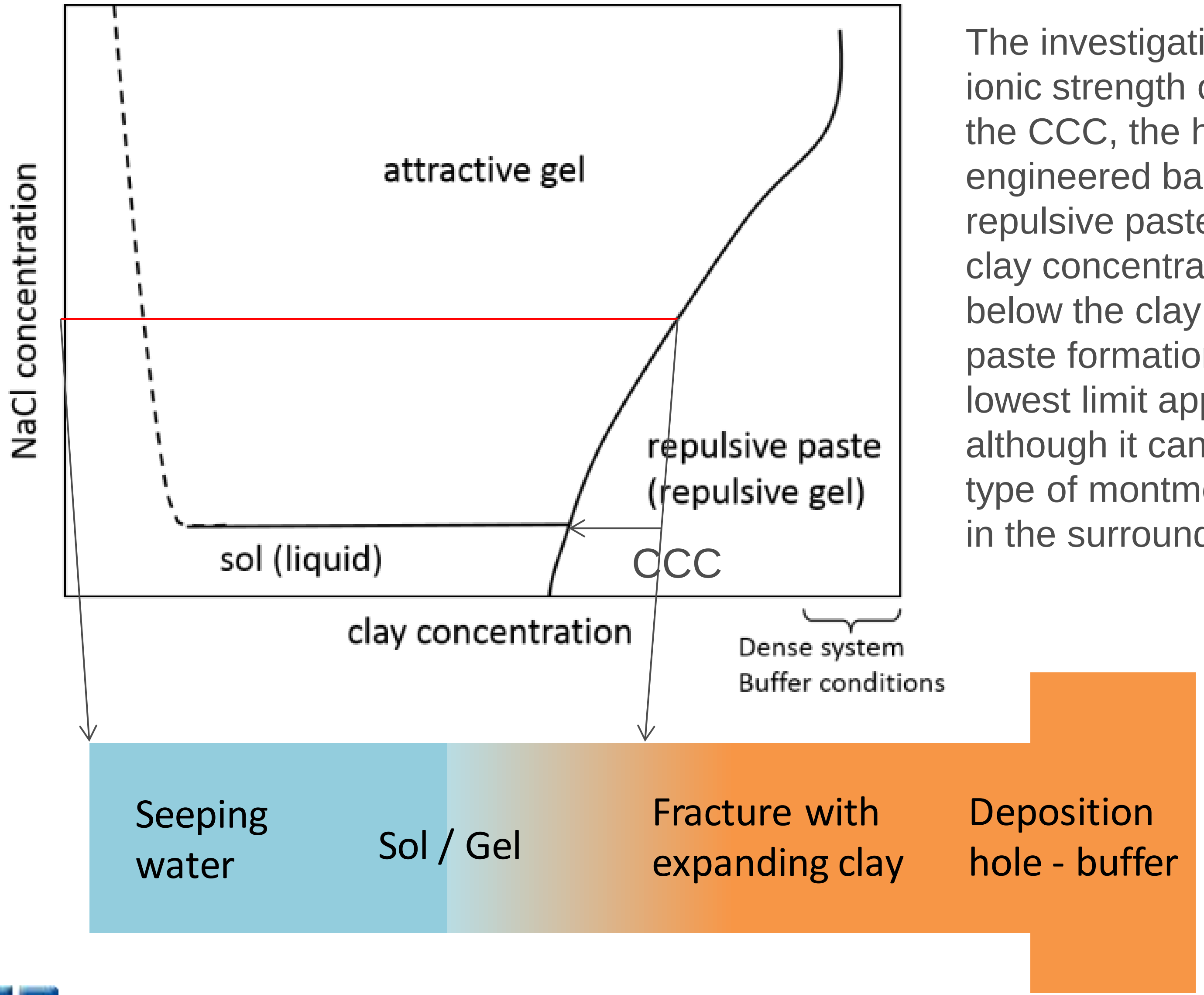
2) **Critical coagulation concentration, coagulation kinetics, (ir)reversibility of coagulation process**

If we are at the boundary, close to conditions which are favourable for clay colloids coagulation, the aggregation process can be very slow.
If the hysteresis of coagulation process take a place, the aggregation or disaggregation of clay colloid will not undergo in the same dimensions.

3) **Role of complexing agents (organic / humic substances) on clay colloid stability**

Interaction between the clay colloids and organic molecules greatly influences its stability

WP4: Phase (state) diagram of Na-montmorillonite



The investigations suggest that, provided the ionic strength of the ground water is above the CCC, the highly compacted clay in engineered barriers will act as a swelling repulsive paste and expand. Once the lowest clay concentration at the swelling front is below the clay concentration required for paste formation, the clay will form a gel. The lowest limit appears to be about 60 g/l, although it can be higher depending on the type of montmorillonite as well as the salinity in the surrounding system.

Oral presentation (Feb. 4): Influence of temperature on smectite clay gels – Magnus Hedstrom

WP4: Bentonites characterization

- For further stability studies and characterization five different bentonites were selected
  - FEBEX bentonite, Spain (Huertas et al., 2000)
  - IBECO bentonite, Mylos, Greece (Koch, 2008)
  - MX-80 bentonite, Wyoming, USA (Müller-Vonmoss and Kahr, 1983)
  - Bentonit 75 (denoted as B75), Rokle, Czech Republic (Konta, 1986)
  - Russian bentonite, Khakassia (Sabodina et al., 2006).

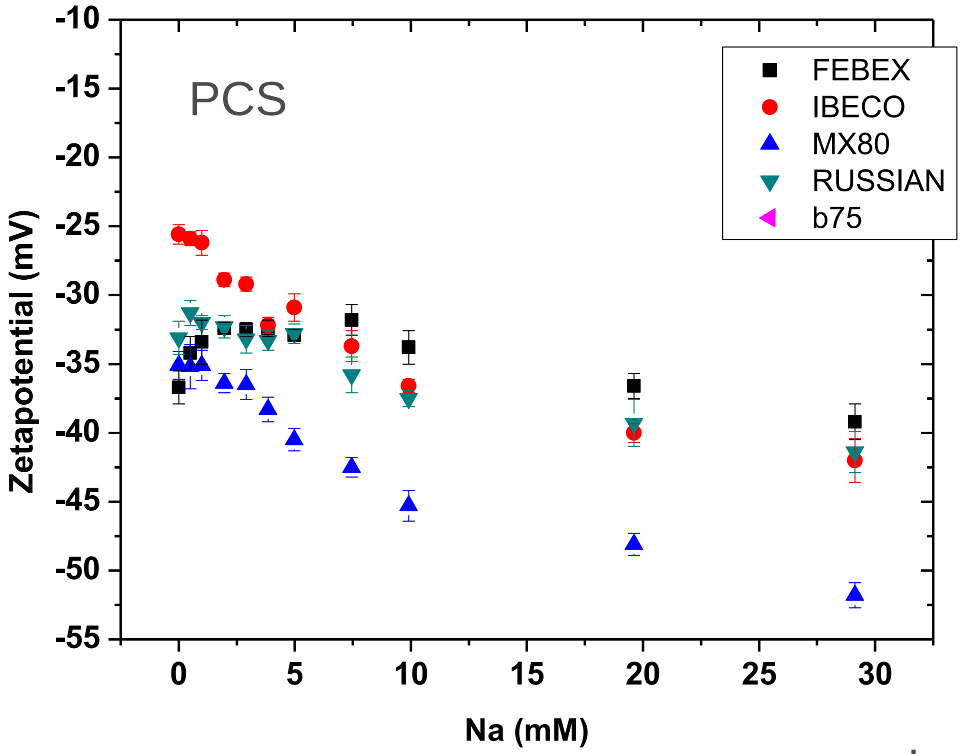
- A complete geochemical and mineralogical characterization was carried out (Fernandez, 2013)
  - mineralogy, especially clays content, cation exchange capacity and occupancy of cations on exchange positions, water content, porewater chemistry, charge distribution and cell formula

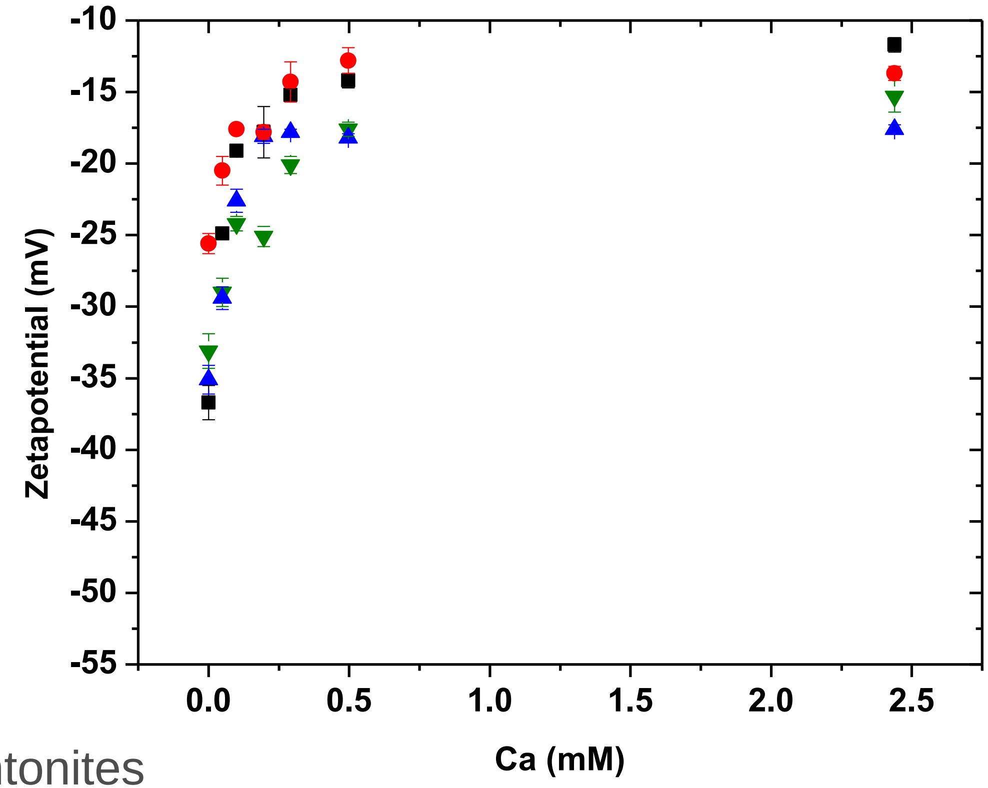
- Reason for detailed characterization of bentonites
  - One of the possible causes of the difference in the stability / erosion behaviour could be related to the different mineralogy (mainly clay minerals and its properties) of the different bentonites (tri-octahedral vs. di-octahedral clays, different exchange complex, different charge density, different charge location)
  - Try to find a trend or correlation between the bentonites characteristics and its stability

Fernandez, A.M. (2013): Mineralogical, geochemical and pore water characterization of different bentonites. CIEMAT Report June 2013, 40 pp. Madrid, Spain.

WP4: Role of inorganic compounds

- Stability studies (effect of cations, anions, pH, admixtures – illite, kaolinite, Al_2O_3) measuring CCC (test-tube coagulation tests), particle size by PCS or PCCS and zeta-potential
- It has to be noted, that CCC tests must be evaluated taking exchange into account (uncertainties for raw bentonites)

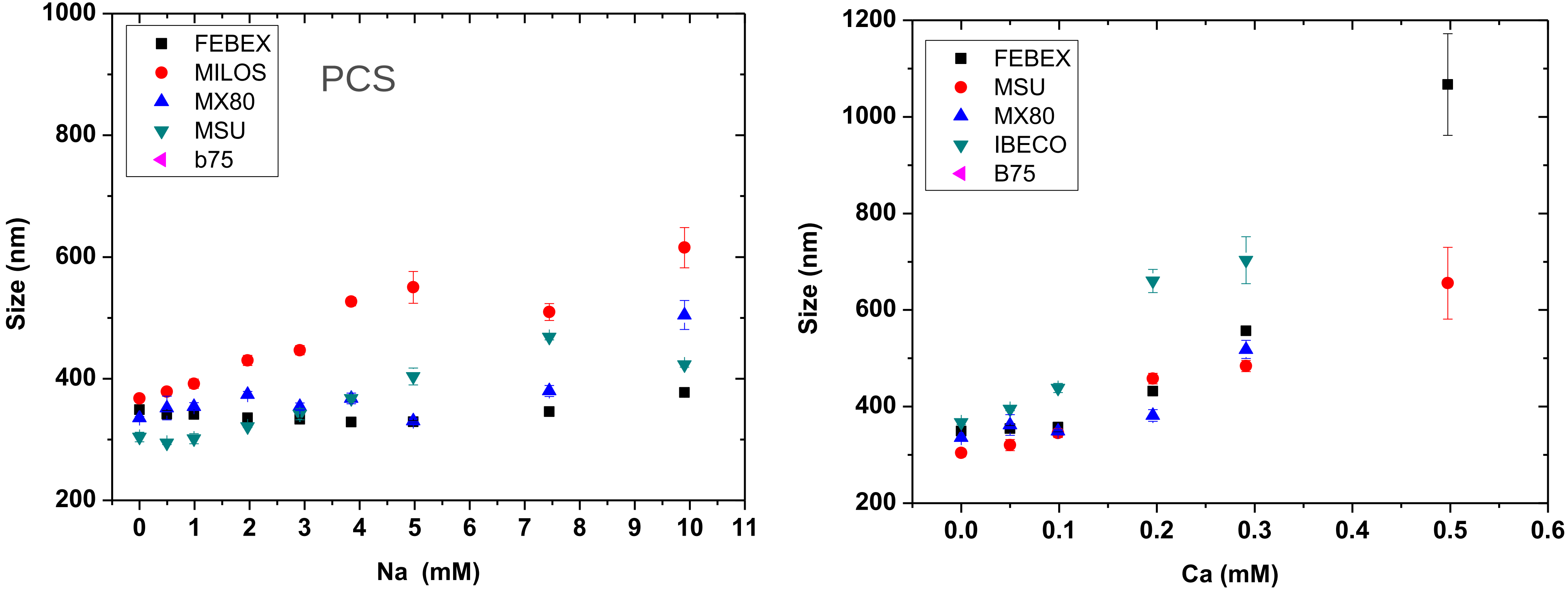




raw bentonites

Červinka et al. (2016): Final report on experimental results on clay colloid stability WP4. Deliverable D4.11. BELBaR.

WP4: Role of inorganic compounds

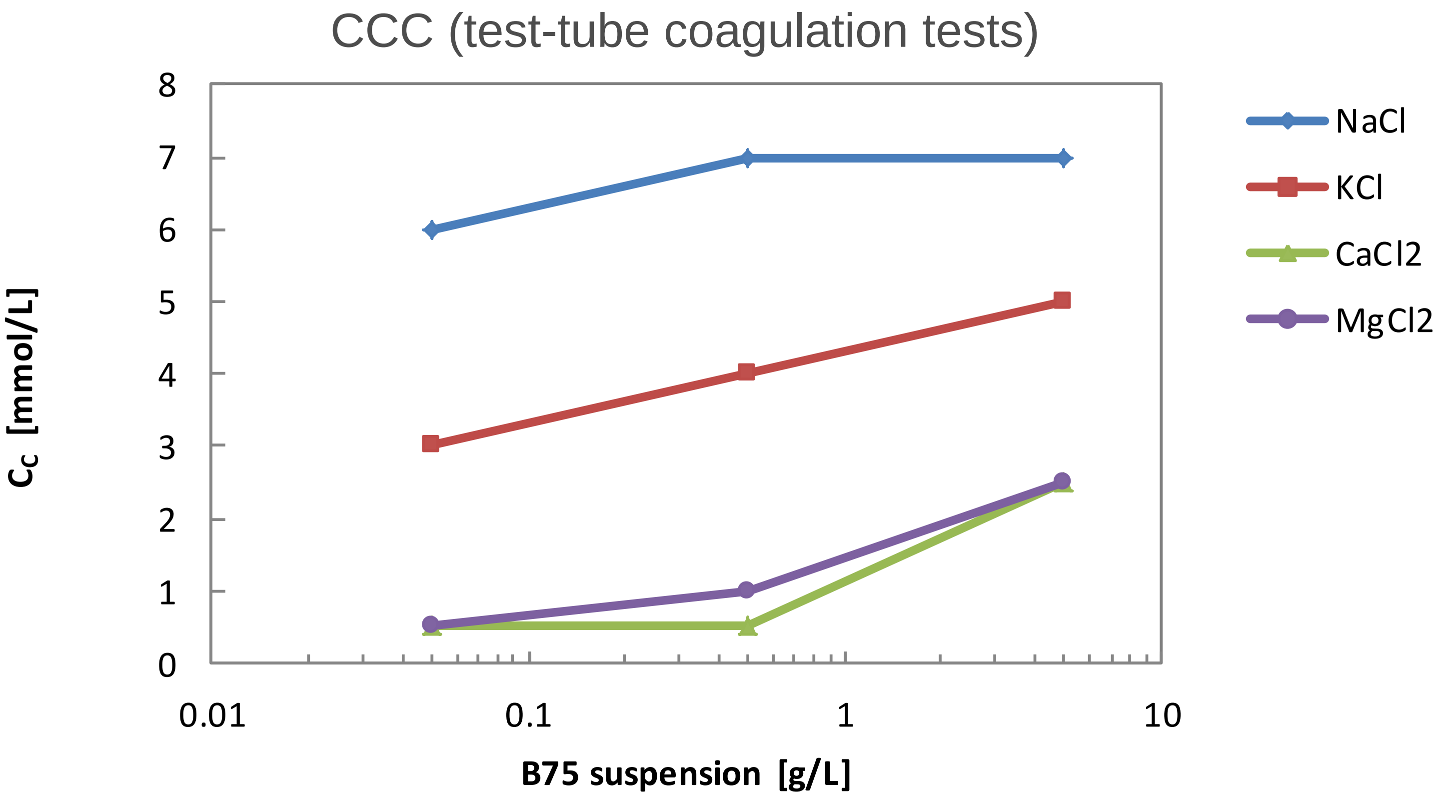


raw bentonites

Clay colloid aggregation is triggered by the presence of Na (10 mM) or Ca (0.1-0.2 mM) in solution indicating that they will not be stable with higher concentration of these ions.

Červinka et al. (2016): Final report on experimental results on clay colloid stability WP4. Deliverable D4.11. BELBaR.

WP4: Role of inorganic compounds



Importance of divalent cations. The effect of increasing CCC with the solid content (concentration of bentonite in suspension).

Sodium and potassium, and magnesium and calcium act in similar way during the coagulation process and in real systems (e.g. natural groundwater) their effect can be simplified to the effect of M^{1+} (Na+K) or M^{2+} (Ca+Mg) cations, where M^{2+} are more effective in coagulation, see D4.7 (Hedström et al., 2014) and D4.8 (Alonso et al., 2015).

Hedström M., Gondolli J., Červinka R. (2014): Status report on the effects of various anions. Deliverable D4.7. BELBaR.

Alonso U., Missana T., Mayordomo N., Fernandez A.M., Gondolli J., Červinka R. (2015): Status report on the effect of different bentonite types (Rokle, Mx-80, Febex, etc) on clay colloid stability. Deliverable D4.8. BELBaR.

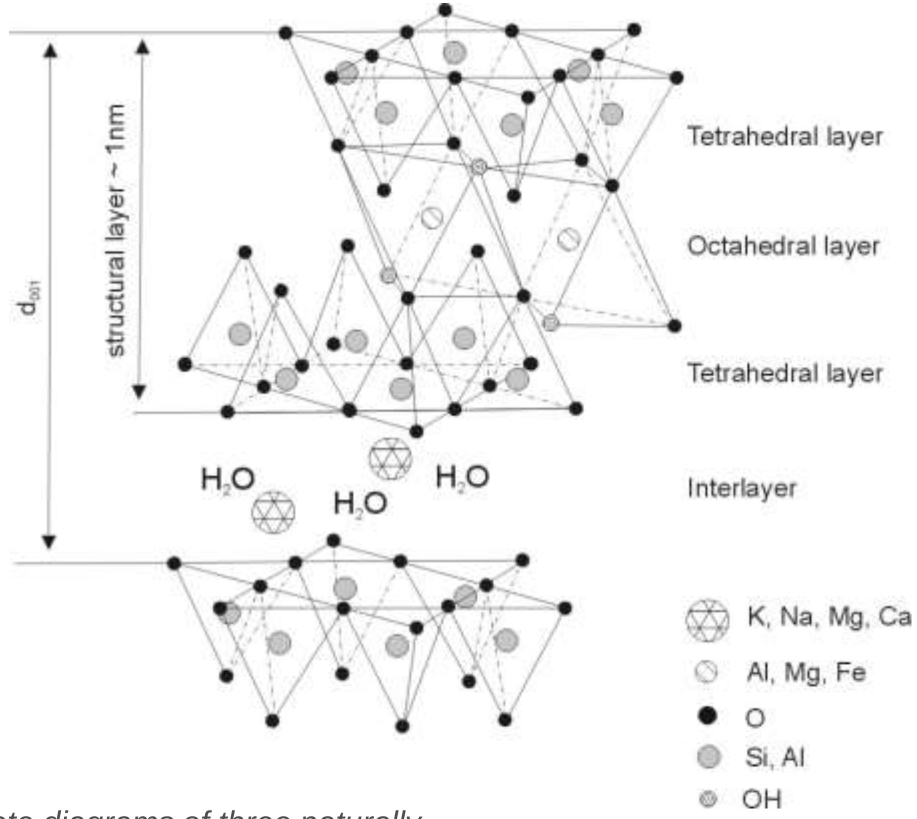
WP4: Role of inorganic compounds

Estimated CCC varies among Na-montmorillonites from different origins. Hansen and Hedström (2014) performed stability experiments at a larger number of different NaCl concentrations, give the following CCC values: Wyoming Na-montmorillonite, Wy-Na (from MX-80), **20 mM** (up to 6% w/w); Milos Na-montmorillonite, Mi-Na (from Deponit CA-N), **6-8 mM** (up to 4% w/w) and for Kutch Na-montmorillonite, Ku-Na (from Asha 505), ~**4 mM** (up to 4% w/w).

In general, those clays having the charge located in the tetrahedral layer forms larger colloids: these particles sediment easier being less stable than others even in DW. For more details see paper in preparation (Missana et al., 2016).

Karnland et al. (2006) SKB TR-06-30.

	Wy-Na1	Wy-Na2	Mi-Na1	Mi-Na2	Ku-Na
CEC [eq/kg]	0.87	0.88	0.97	1.09	1.04
σ [C/m²]	−0.11(1)	−0.11(1)	−0.12(3)	−0.14(0)	−0.13(5)
Tetr. Charge [e]	−0.11	−0.05	−0.15	−0.27	−0.38
Octa. Charge [e]	−0.54	−0.60	−0.57	−0.55	−0.42
Total Charge [e]	−0.65	−0.65	−0.72	−0.82	−0.79



Hansen E., Hedström M. (2014): Colloidal pastes, gels and sols: State diagrams of three naturally occurring montmorillonites (to be submitted).

Missana T., Alonso U., Fernandez A.M. (2016): Stability behavior of natural clays: the importance of physico-chamical characteristics of the clay. In preparation.

WP4: Role of inorganic compounds

- Series of test-tube tests
  - The C_c of Na^+ and Mg^{2+} were determined in the series of test-tube coagulation tests
  - Bentonite B75 in Na^+ as suspension in distilled water (only for 50 mg/l)
  - Different electrolytes ($NaCl$, $NaNO_3$, Na_2SO_4, Na_3PO_4 and $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$)

Salt	c_c (mmol/l)	$c_{c(cation)}$ (mekv/l)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
NaCl	5	5	6.3	not measured	not measured
$NaNO_3$	6	6	6.0	5	870
Na_2SO_4	3	6	6.1	2	approx. 1000
Na_3PO_4	no coagulation at given phosphate concentrations				

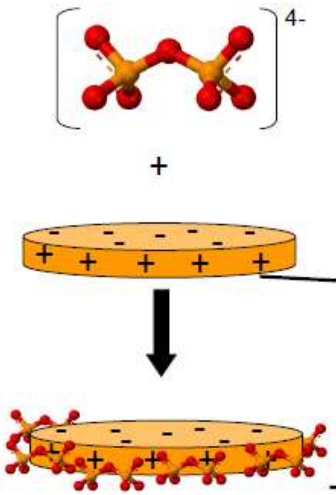
Salt	c_c (mmol/l)	pH	First lower concentration below c_c (mmol/l)	PCCS ϕ_h (nm)
$MgCl_2$	0.5	6.7	0.1	790
$Mg(NO_3)_2$	0.5	6.4	0.1	500
$MgSO_4$	0.5	6.1	0.1	476

ϕ_h - mean hydrodynamic diameter

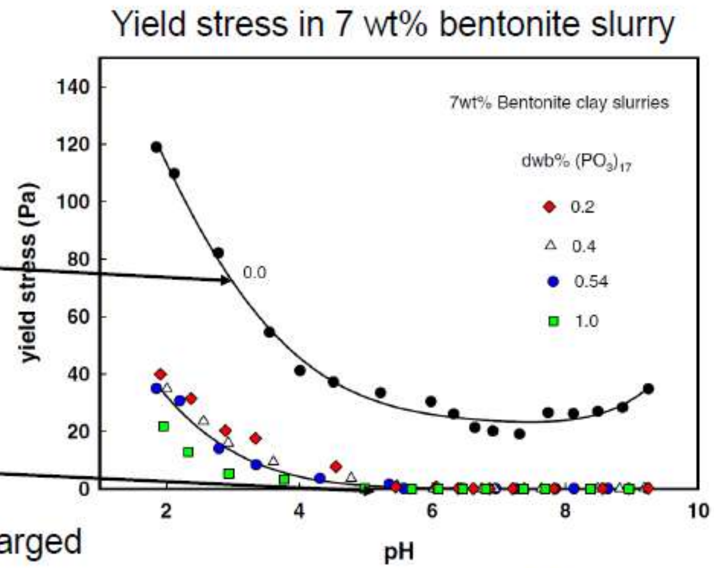
Hedström M., Gondolli J., Červinka R. (2014): Status report on the effects of various anions. Deliverable D4.7. BELBaR.

WP4: Role of inorganic compounds

- **Changing anion has only minor effect on the CCC, provided that the anion does not directly influence the overall clay particle charge, as in the case of polyphosphates and to some extent OH-, see D4.7 (Hedström et al., 2014).**
- **Exploring the influence of interacting anions may be of less direct practical significance for the safety assessment of a repository for spent nuclear fuel, but are of utmost importance for the understanding of the chemical-physical forces that hold gels together. The effect of polyphosphates on the gelling provide evidence that the gels are formed from edge(+)–face(-) attraction.**



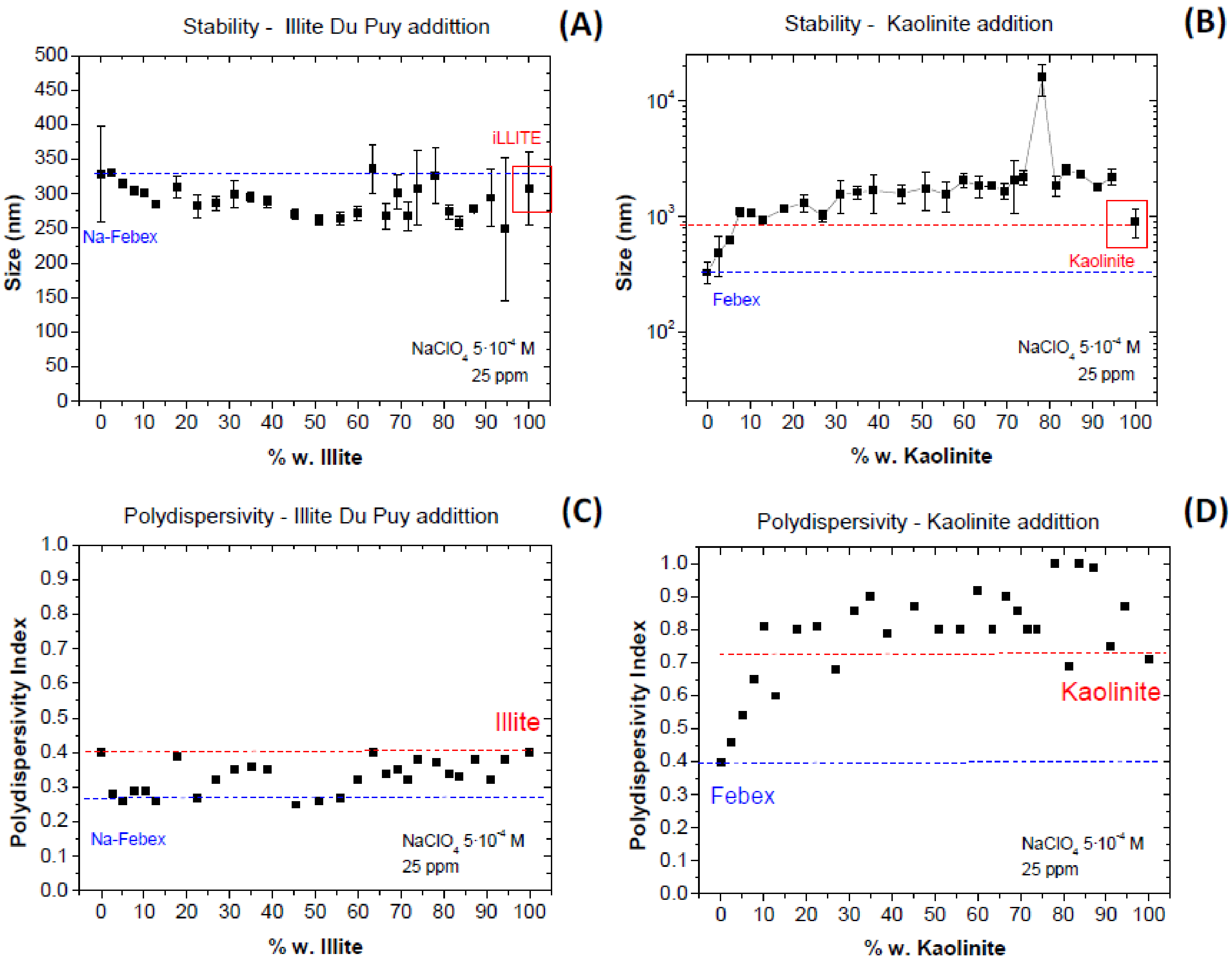
Both edge and face negatively charged
gel → sol



Goh *et al.* (2011).

Hedström M., Gondolli J., Červinka R. (2014): Status report on the effects of various anions. Deliverable D4.7. BELBaR.

WP4: Role of inorganic compounds



The interaction of smectite with mineral like kaolinite or Al_2O_3 produces the aggregation of particles that, alone under the same chemical conditions would be stable; this means that the presence of certain minerals not only inhibits the clay colloid generation “by dilution” of the smectite, but also may affect the properties of the smectite itself making the system unstable, D4.8 (Alonso et al., 2015).

Alonso U., Missana T., Mayordomo N., Fernandez A.M., Gondolli J., Červinka R. (2015): Status report on the effect of different bentonite types (Rokle, Mx-80, Febex, etc) on clay colloid stability. Deliverable D4.8. BELBaR.

WP4: (Ir)reversibility of coagulation process and hysteresis

- The disaggregation process of illite and smectite clays has been shown to be not completely reversible because the aggregation process is usually very rapid (minutes) but the kinetic of disaggregation, until reaching a complete disaggregated state, largely depends on the initial conditions of the experiments. The disaggregation process is more rapid in more diluted suspensions, D4.4 (Missana et al., 2014).
- During the investigations the effect of hysteresis was observed with different methods. The rheometry measurements showed that the attractive forces in the gels increase with aging. One week of resting produce significantly stronger gels than those tested after 24 hours, D4.9 (Hedström et al., 2015).

Average yield stress from the rheological measurements on Ku-mmt gels (from Asha 505)

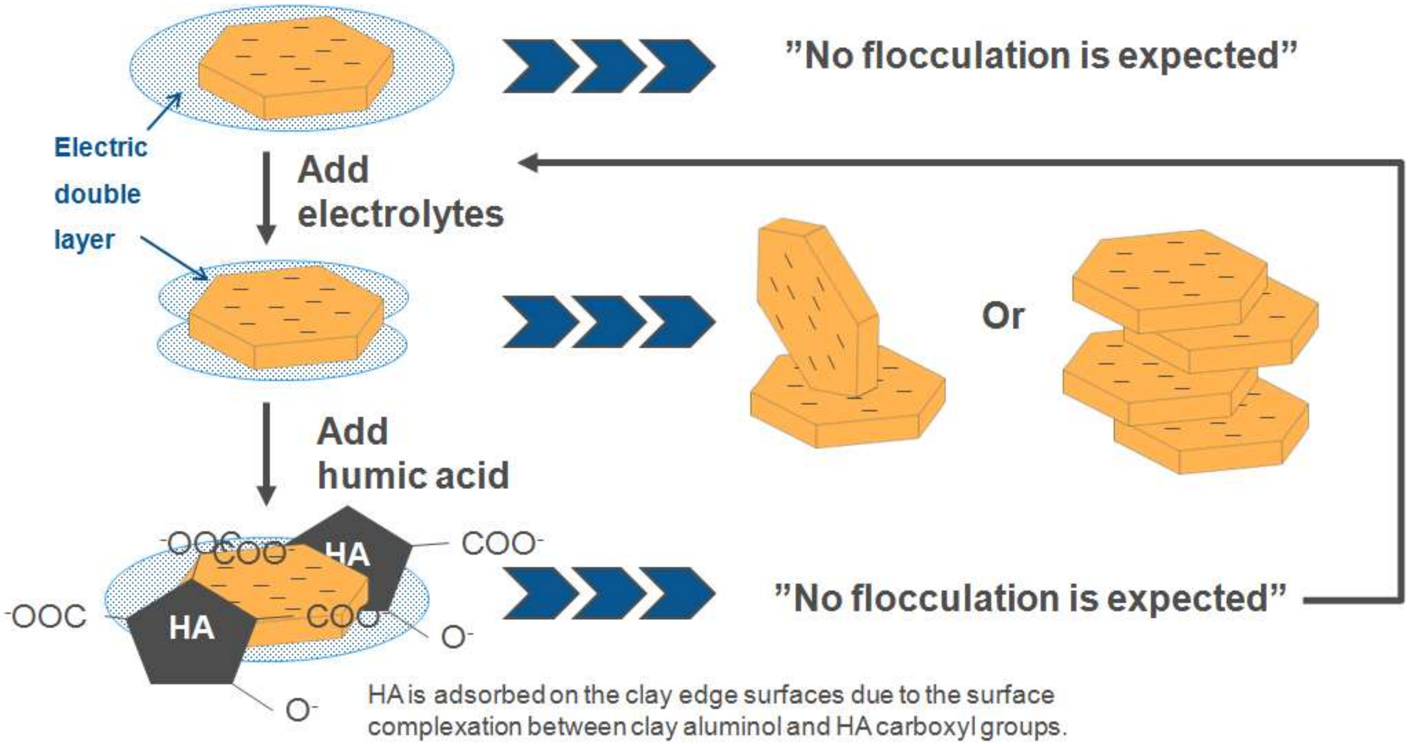
	Average maximum yield stress (Pa)			
C_{mmt} / [NaCl]	10 g/l, 24 h	10 g/l, 1 week	20 g/l, 24 h	20 g/l, 1 week
5 mM	0.4	1.1	4.4	7.7
10 mM	1.5	2.8	5.3	8.0
20 mM	-	-	9.2	8.9
50 mM	2.5	3.5	8.5	-
100 mM	2.6	3.9	10.0	-

Missana T., Alonso, U., Mayordomo, N., Benedicto A. (2014): Report on the reversibility of the coagulation process. Deliverable D4.4. BELBaR.

Hedström M., Nilsson U., Eriksson R. (2015): Rheology of attractive and repulsive montmorillonite/bentonite gels. Deliverable D4.9. BELBaR.

WP4: Role of organic compounds

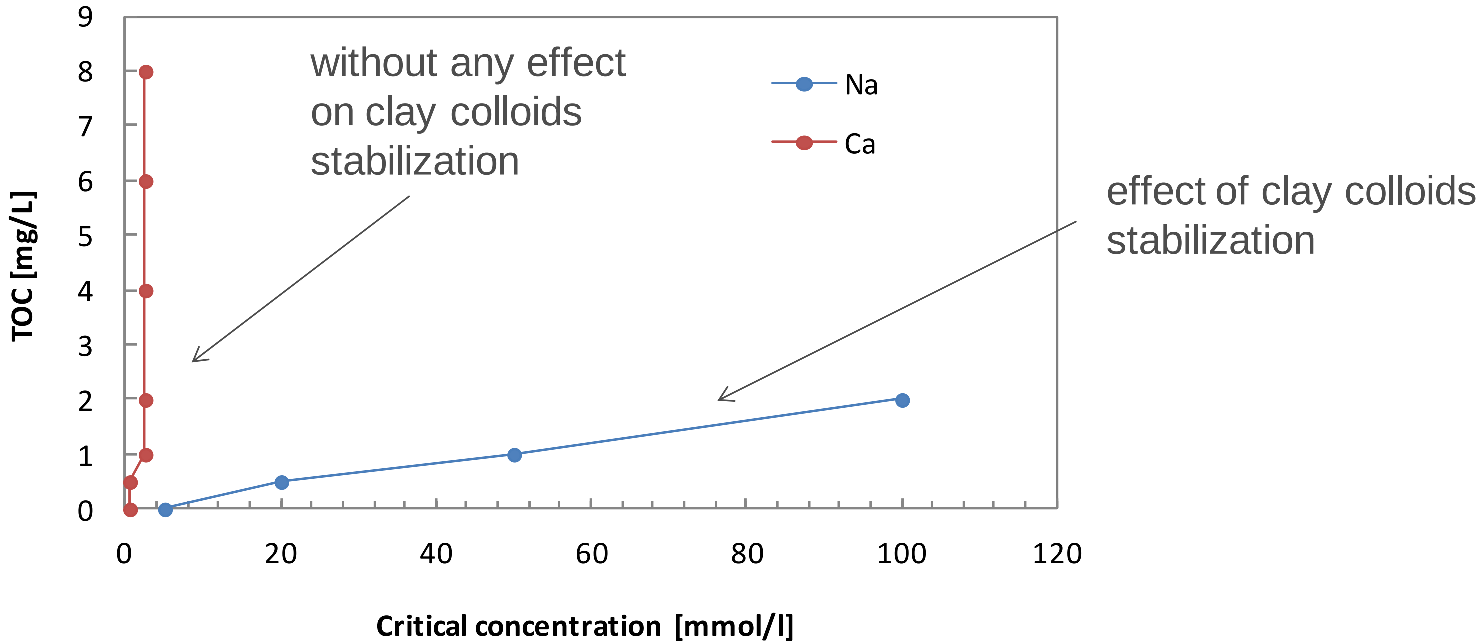
- The presence of organic substances in DGR is expected to be associated with host rock itself, microbial and anthropogenic activities and materials used in the construction.
- The interaction between the clay colloids and organic molecules greatly influences its stability.
- Studies were focused on humic and fulvic acids, which are natural organic substances often occurring in surface waters and near-surface groundwaters.



HA is adsorbed on the clay edge surfaces due to the surface complexation between clay aluminol and HA carboxyl groups.

WP4: Role of organic compounds

- Organic matter (like humic or fulvic acids) is able to stabilize clay colloids in NaCl electrolyte (experimental concentration up to 0.1 M NaCl). This means that in presence of organic matter more concentrated NaCl electrolyte is needed to coagulate clay dispersion (the CCC is higher). For example the CCC is four times higher in a suspension containing 0.5 mg/L TOC compared to the same suspension without humic acid, see D4.6 (Bouby et al., 2014).



Bouby M., Heyrich Y., Heck S., Schäfer T., Červinka R., Gondolli J. (2014): Status report on the influence of complexing agents on clay colloid stability. Deliverable D4.6. BELBaR.

WP4: Role of organic compounds

- In all the other electrolytes investigated ($CaCl_2$, $MgCl_2$) and at higher IS, the clay colloids undergo fast coagulation, independently of the presence of organic matter. This is true in various aqueous media containing different inorganic cations, showing that the IS remains the key parameter.
- Long term study tends to demonstrate that even under geochemical conditions where the colloids are expected to be stable, they may undergo a continuous slow agglomeration process.

WP4: The improvements of mechanistic model of bentonite swelling

- The theoretical basis for understanding of the effect of the Ca (divalent cation) on clay gel stability was summarised in D4.3 (Wang et al., 2013).
- A self-consistent weighted correlation approximation to density functional theory was developed (Wang et al., 2011a; Yang and Liu, 2015) to describe the structural and thermodynamic properties of counterion-only electrical double layers. The predictions agree well with the Monte Caro simulations and show that the Ca-bentonite would behave essentially as the Na-bentonite when the fraction of surface charge neutralized by Na^+ is more than 30 %. It is known from experiments, that this boundary lies between 20-30 %.

Wang Z., Liu L., Moreno L., Neretnieks I. (2013): Status report on the theoretical understanding of the effect of the Ca on clay gel stability. Deliverable D4.3. BELBaR.

Wang, Z., Liu, L. and Neretnieks, I. (2011a): The weighted correlation approach for density functional theory: a study on the structure of the electric double layer, J. Phys.: Condens. Matter, 23, 175002.

Yang, G. and Liu, L. (2015): A systematic comparison of different approaches of density functional theory for the study of electrical double layers, J. Chem. Phys., 142, 194110.

Oral presentation (Feb. 4): Interaction pressure between charged plate-like particles in electrolyte solutions: An application of density functional theory with the solvent primitive model - Longcheng Liu

WP4: List of deliverables (PU)

N°	Title	Responsible organisation	Nature	Dissemin. level	Delivery date
D4.1	~~State of the art report on experimental techniques used for investigations of clay colloid stability, including~~ an establishment of protocol for rheology and turbidity experiments	**ClayTech**, ~~CIEMAT, KIT-INE, NRI-Rez~~	R	RE	09/2012 (6 M)
D4.2	Progress Report on the effect of pH on clay colloid stability	**CIEMAT**, KIT-INE, NRI-Rez, ClayTech	R	PU	05/2013 (15 M)
D4.3*	Status report on the theoretical understanding of the effect of Ca on clay gel stability	**KTH**	R	RE	05/2013 (15 M)
D4.4	Status report on the reversibility of the coagulation process	**CIEMAT**	R	PU	06/2014 (27 M)
D4.5	Status Report on colloid stability and DOC effect	**KIT-INE**	R	PU	06/2014 (27 M)
D4.6	Status Report on influence of complexing agents on clay colloid stability	**NRI-Rez**, KIT-INE	R	PU	06/2014 (27 M)
D4.7	Status report on the effect of various anions	**ClayTech**, CIEMAT, KIT-INE, NRI-Rez	R	PU	06/2014 (27 M)
D4.8*	Status report on the effect of different bentonite types (Rokle, Mx-80, Febex, etc) on clay colloid stability	**CIEMAT**, KIT-INE, NRI-Rez, ClayTech	R	PU	06/2015 (39 M)
D4.9*	Rheology of attractive and repulsive montmorillonite/bentonite gels.	**ClayTech**	R	PU	06/2015 (39 M)
D4.10*	Effects of different mechanisms/factors on colloid stability of dispersions of calcium dominated bentonites in dilute solutions	**KTH**	R	PU	06/2015 (39 M)
D4.11	**WP4 partners final report on experimental results on clay colloid stability**	**NRI-Rez**, All	R	PU	11/2015 (44 M)

http://www.skb.se/belbar/public-deliverablesreports/

Publication plan

- **Deliverable 6.6 Development of a publication plan for the publication of peer reviewed project results in high-quality journals**
  - There is 46 planned or already published papers....

Acknowledgement

- To organizations for fruitful results and cooperation in WP4

- To SKB for project coordination

- The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

WP 5: Conceptual and mathematical models

Kari Koskinen, Posiva

Patrik Sellin, SKB

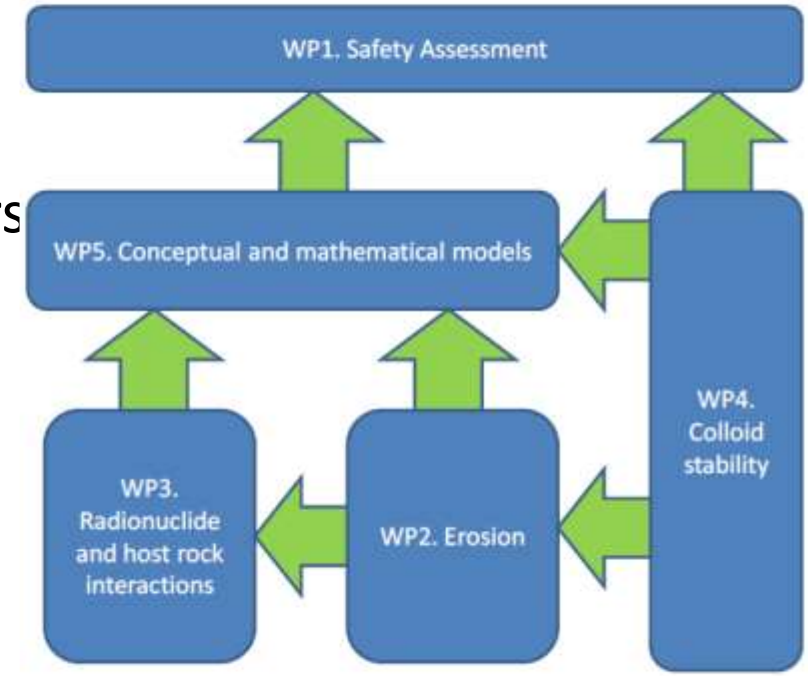
The course of events

2011	Objectives at the outset
2012	Review of models in the beginning
early 2013	Early advances
late 2013	Definition of benchmark
early 2015	Scaling from small-scale to full-scale
late 2015	The current uses in Safety Cases based on BELBaR-work

Objectives at the outset– 1/2

From DoW

- **Validate** and advance the **models** for predicting
  - mass loss of clay in dilute waters and clay colloids generation in special and
  - clay colloids facilitated radionuclide transport.
- **Formulate data needs** from other WP's
- **Use** the overall **understanding** in the safety assessment formulations **in WP1**



Objectives at the outset– 2/2

From DoW

- Conceptual modelling
  - reason dominant processes,
  - identify and reason relevant parameters and
  - articulate the data needed to implement new aspects.
- Mathematical and numerical modelling
  - validate models by predicting small-scale experiments (WP2-4)
    - reason scaling using conceptual understanding
  - implement new features arising from elaborated conceptual models

Review of models in the beginning

State of the art of models -report

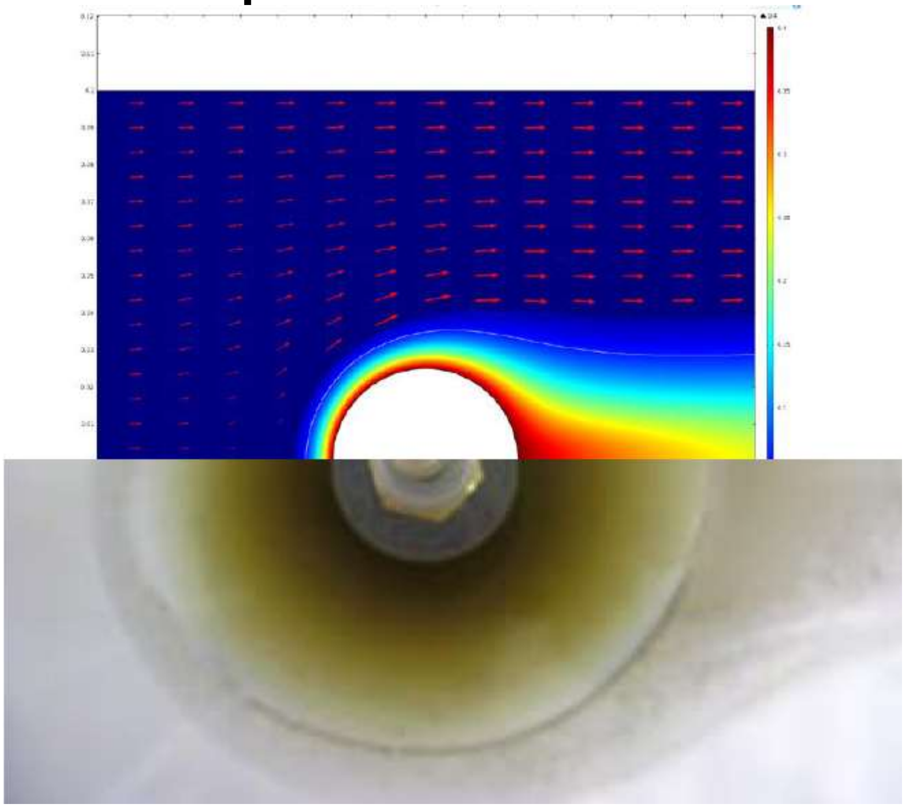
- Erosion of bentonite
  - baseline model by KTH
    - conceptual view
      - gel/sol behaviour and expansion
      - ion exchange and influence of divalent ions
      - friction in fractures
    - relevant parameters
      - viscosity of smectite gel/sol
      - forces on and between smectite particles
        - » gravity and buoyance
        - » changes in chemical potential
        - » attraction due to van der Waals
        - » repulsion due to electrical charges in and on smectite particles (DDL)
        - » friction
      - Debye length
    - numerical implementation
  - VTT modification of baseline model
    - simplification of some functional dependencies to enhance computational reproducibility
- Transport of bentonite colloids
  - Lagrangian implementation of particle migration
  - Colloid/nanoparticle interaction with stationary phase
  - heterogeneity of the domain – different assumptions tested with colloid breakthrough curves

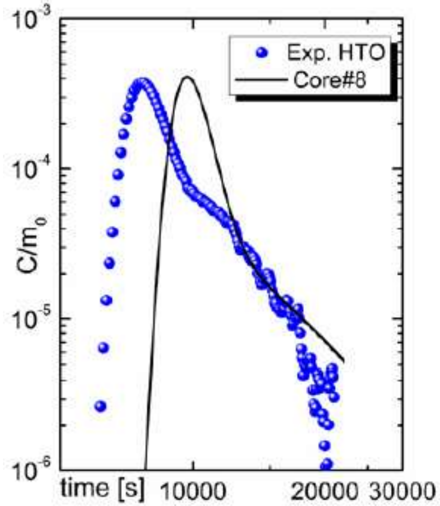
Early advances – 1/2

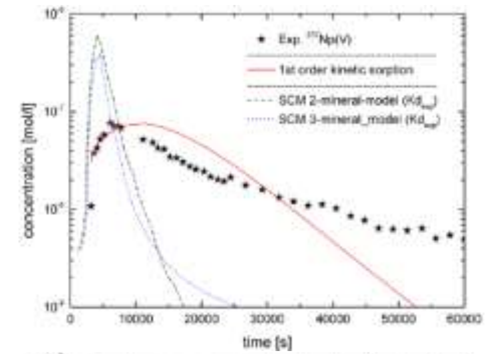
- Erosion of bentonite
  - simplifications sought for numerical model
  - mechanical model for SP presented (with stacking number as parameter)
  - development of alternative models for wetting and swelling at VTT
- Transport of bentonite colloids
  - systematic parameter studies need to be committed wrt transport of bentonite colloids

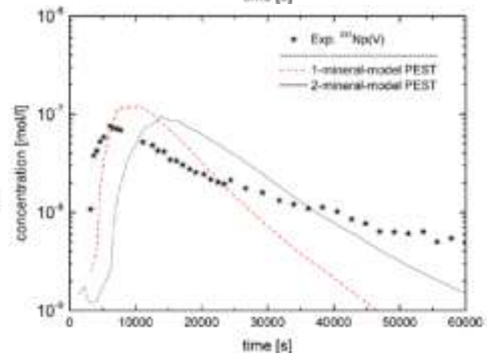
Early advances - 2/2

- Mismatch between computer simulations and experiments









Definition of benchmark – 1/3

- Justification of relevant processes and parameters accepted by participants missing

⇒BENCHMARK

- … in order to advance conceptual understanding AND
  - regarding which aspects?
  - make it more explicit

- … in order to validate numerical models
  - existing data?
  - new data?

Definition of benchmark – 2/3

- Aspects raised during and after the presentations

- Aspects selected for group discussions
  - central processes
  - accessory minerals
  - flocs
  - hysteresis
  - gravity

Definition of benchmark – 3/3

	PROCESSES	ACCESSORY MINERALS	FLOCS	HYSTERESIS	GRAVITY
GROUP 1	Swelling into fracture • measure details in the front • different apertures • in non-"sol forming" conditions • in "sol forming" conditions	Maybe not … just montmorillonite alone at this stage	Aren't they of part of buffer system?	Range of densities in which gel is table	Not doable

GROUP 2	• There are plenty of data available
	  • Rate of expansion
	  • Erosion rate
	• => FOCUS on swelling
	  • Maybe not in great details
		What is this actually about?
		• To include this we'd need to understand it better
			Not sufficiently well understood to be included into benchmarks	Data needed	Potentially important

GROUP 3	• Keep it limited • Expansion -> rate • (erosion -> rate) • 2bv~0.1 mm • NaMt • Tabletop • Low salinity 1 mM NaCl • No flow • -> Experiment -> upscaling the geometry • Expansion -> erosion -> geometry upscaling	Not to be considered in benchmarks	This is conceptual uncertainty - > This is question for modellers!	Not to be considered in benchmarks -> premature	We have too little data for benchmark -> premature

Scaling from small-scale to full-scale – 1/5

Ability to predict the experiments?

- two-region model developed
  - ”high resolution of rim only” -model
  - can be further simplified
  - impact of

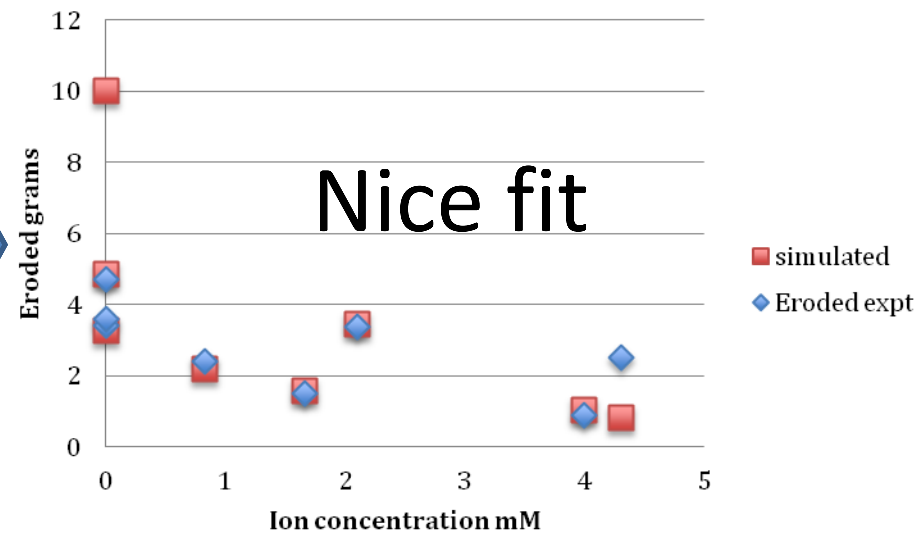
    ”old” full resolution model → simplified two-region model:

    mass loss ↓(factor of 1.5…5)

    $\Rightarrow r_{RIM}\uparrow$ (factor of 5…30))

- validation with 1:88 tests
  - far from satistactory

    $\Rightarrow$ assume:
    - flocs move with water
    - & $\phi_{@rim}$=const



Scaling from small-scale to full-scale – 2/5

Uncertain effects of factors

- longer rim
  - see next slides
- smectite → bentonite
- migration of flocs under gravity
  - boundary estimate: loss of clay as agglomerates at rim restrained by agglomerate migration
- others???

Scaling from small-scale to full-scale – 3/5

Simplified two-region model

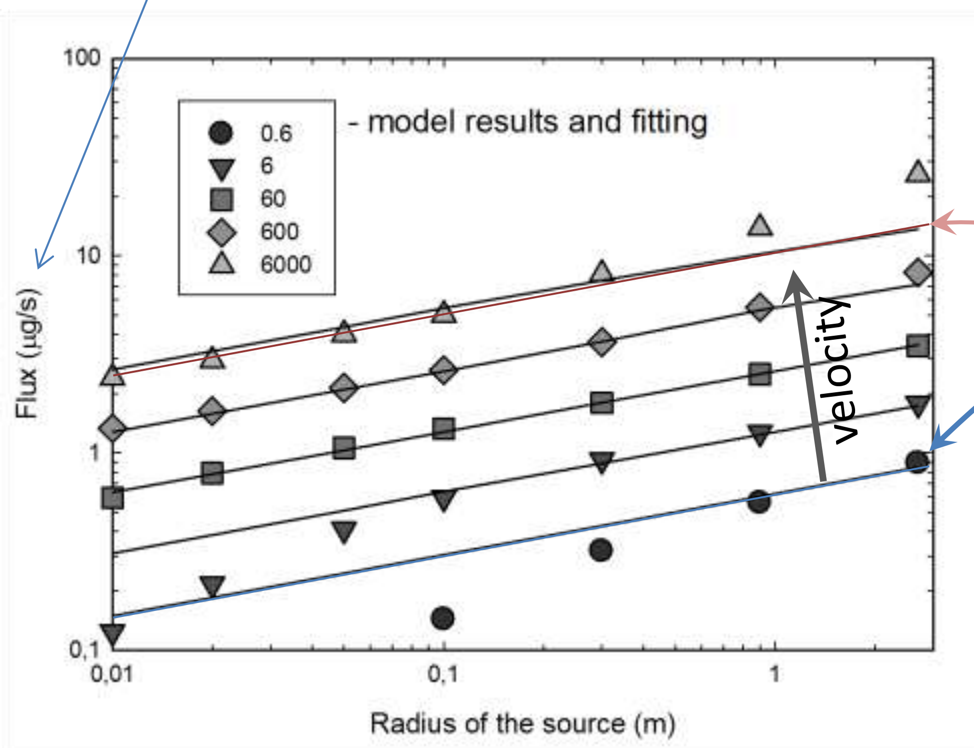
velocity [m/s]	**1E-07**	**1E-06**	**1E-05**
velocity [m/a]	*3*	*32*	*315*
Mass lost [kg]	140	148	172
Eroded mass [kg]	7,6	22	144
penetration depth [m]	34,2	32	14,7
time [a]	10000	10000	10000
mass loss [g/(m² a)]	**34**	**107**	**1 471**

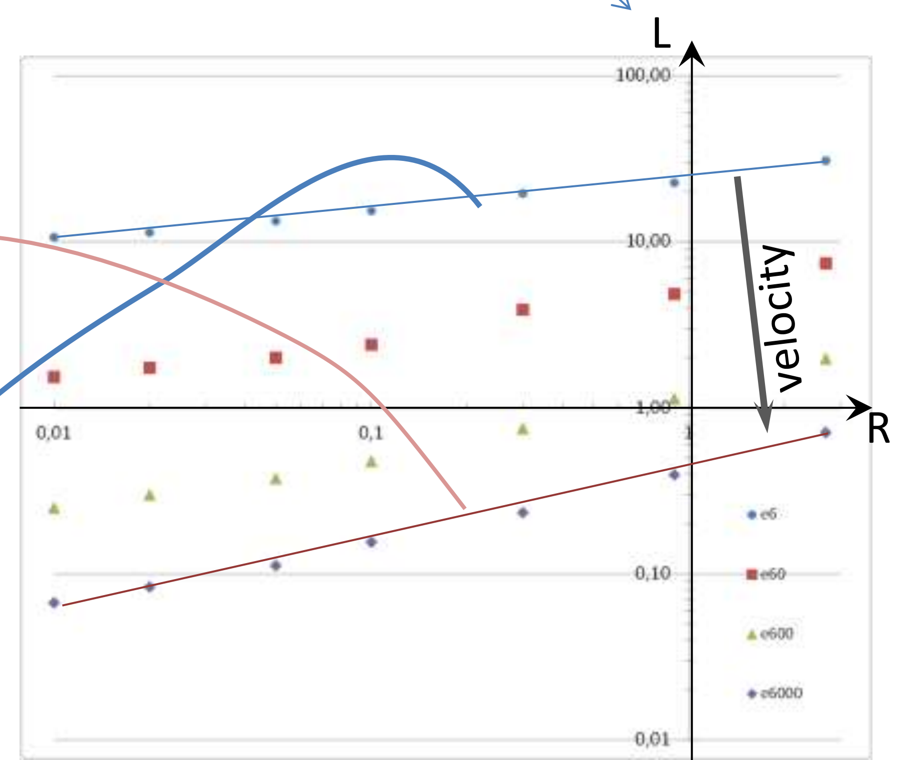
← depends on velocity (not evident in experiments)

Scaling from small-scale to full-scale – 4/5

”old” full resolution model → simplified two-region model in 1:88
“Detailed view” into intermediate scales

- giving higher estimates of mass loss
- giving lower estimates of rim location, L

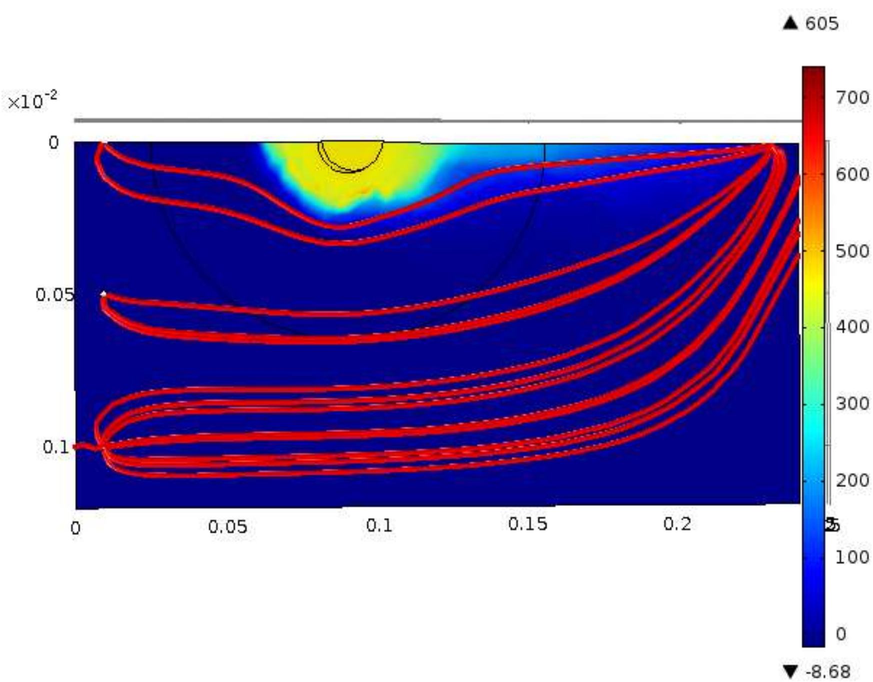


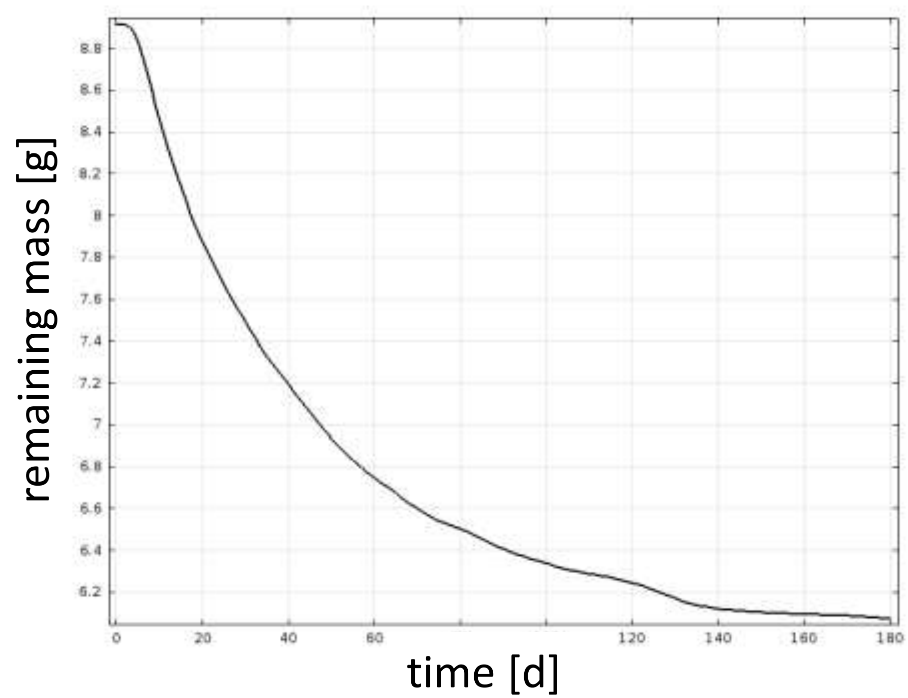


Scaling from small-scale to full-scale – 5/5

Alternative model development not finished …

- 3D!!!
- Water can flow through the colloid mass (Brinkman flow)
- Stokes-Brinkman equations: Stokes + effect of porosity





The current uses in Safety Cases based on BELBaR-work– 1/3

Against DoW

- **Validate** and advance the **models** for predicting?
  - mass loss of clay in dilute waters
    - nice match in 1:88-scale
    - bounding estimates in 1:1-scale
  - clay colloids facilitated radionuclide transport
    - dd
- **Formulate data needs** from other WP’s
    - data for penetration into fracture and erosion for NaMt
    - erosion dynamics for bentonite
    - strength of structure at rim
- **Use** the overall **understanding** in the safety assessment formulations **in WP1**
    - bounding estimates for mass loss of clay in dilute waters

The current uses in Safety Cases based on BELBaR-work– 2/3

Against DoW

- Conceptual modelling
  - reason dominant processes
    - swelling, flocs migration, gravity
  - identify and reason relevant parameters
    - initiated in benchmark but not agreed to finish
  - articulate the data needed to implement new aspects
    - see previous slide **Formulate data needs**
- Mathematical and numerical modelling
  - validate models by predicting small-scale experiments (WP2-4)
    - reason scaling using conceptual understanding
      - ability to perform bounding estimates
  - implement new features arising from elaborated conceptual models
    - Done

The current uses in Safety Cases based on BELBaR-work – 3/3

- Bounding estimates using numerical simulation methods developed in BELBaR
- These estimates to justify the assumptions used in Safety Cases

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Radioactive Waste Management

Treatment of Colloids in the Safety Case

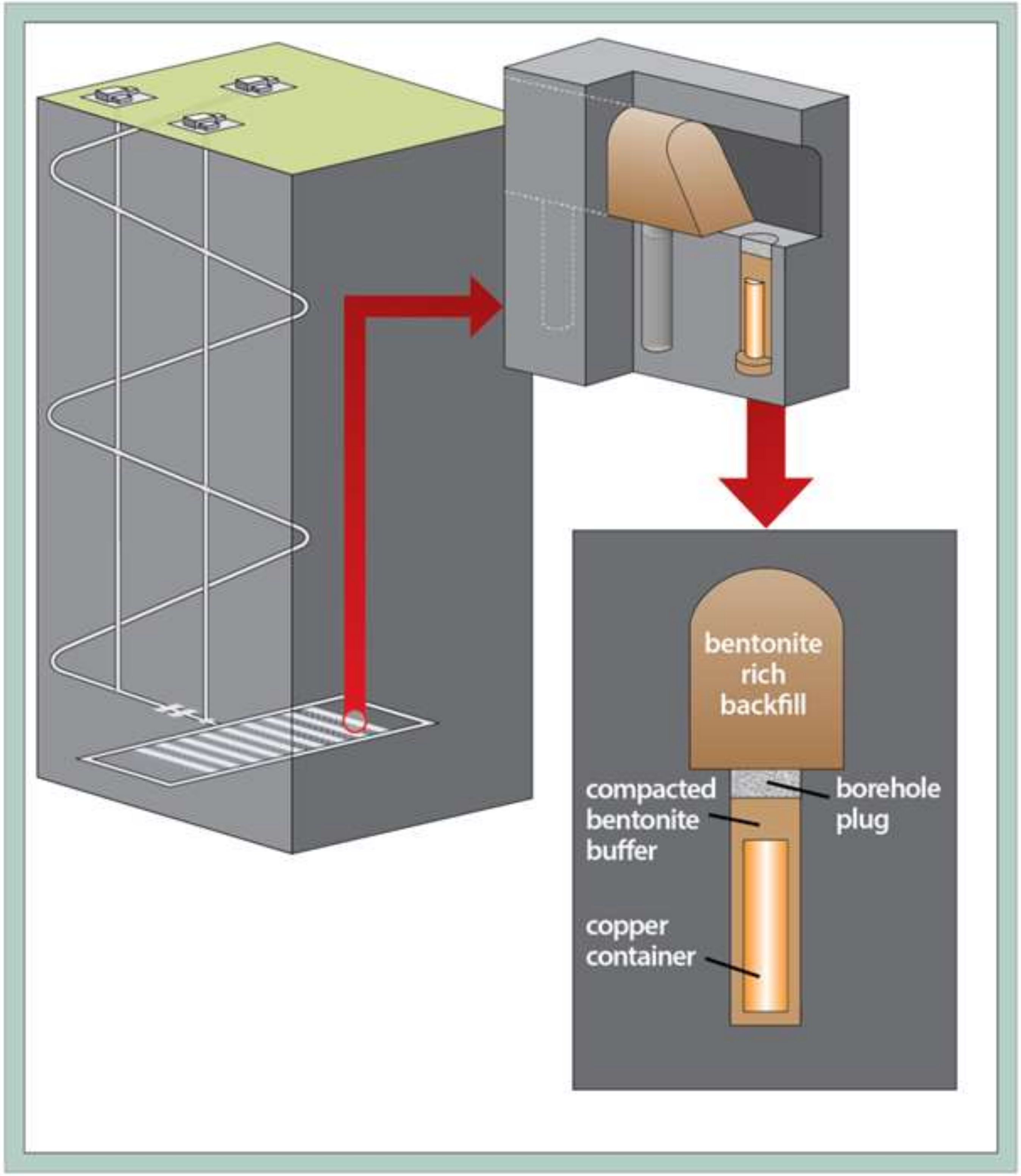
Clay Colloids in Aqueous Systems

3 – 4 February 2016, Berlin

Dr Amy Shelton,
Radioactive Waste Management (RWM)

Radioactive Waste Management

EURATOM



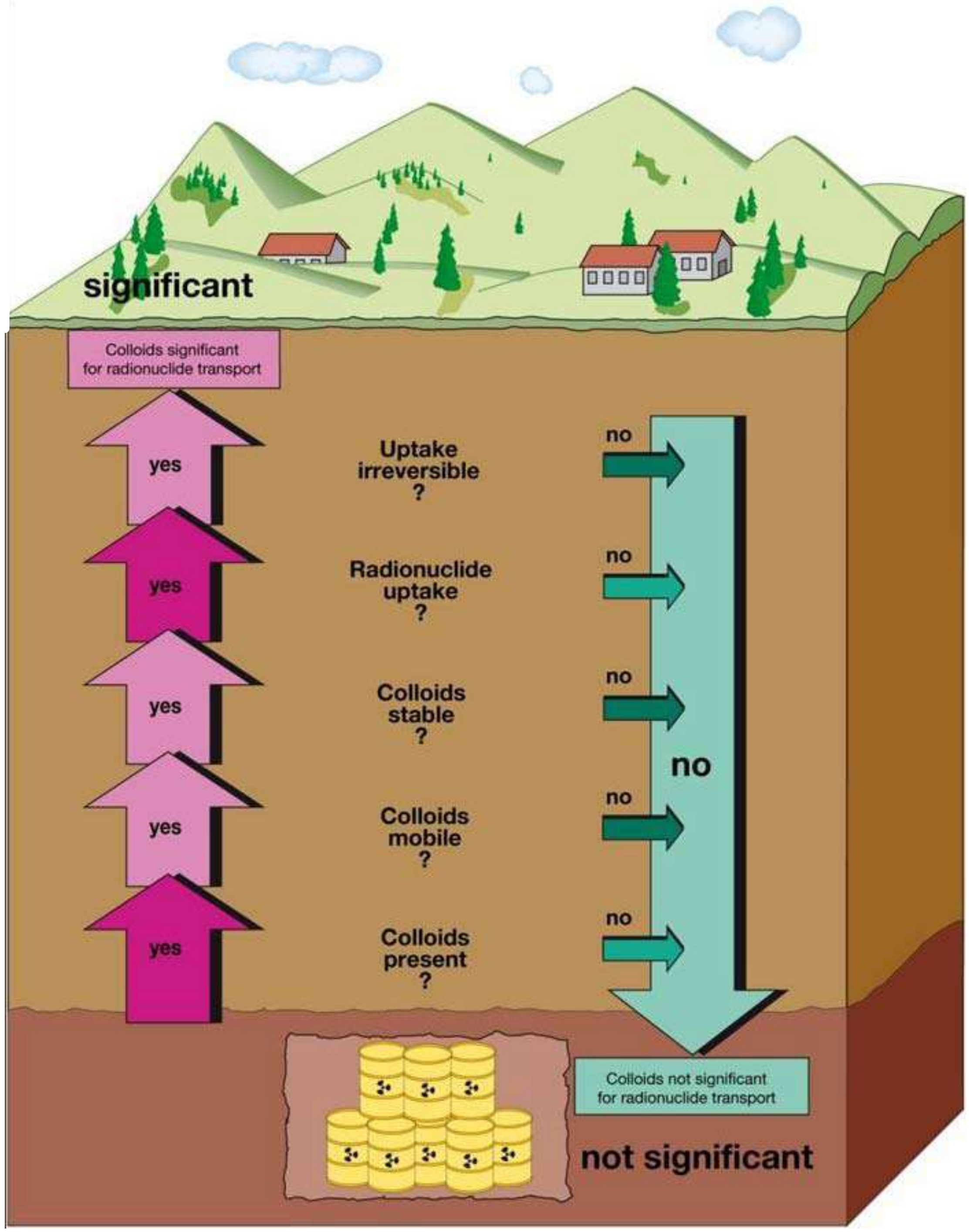
KBS-3 Concept

- Based on the multi- barrier principles of long term isolation and containment

- The components are:
  - Spent fuel
  - Copper canisters
  - Bentonite buffer
  - Bentonite tunnel backfill
  - Tunnel plugs
  - Geosphere

Radioactive Waste Management

Initial State-of-the-art report



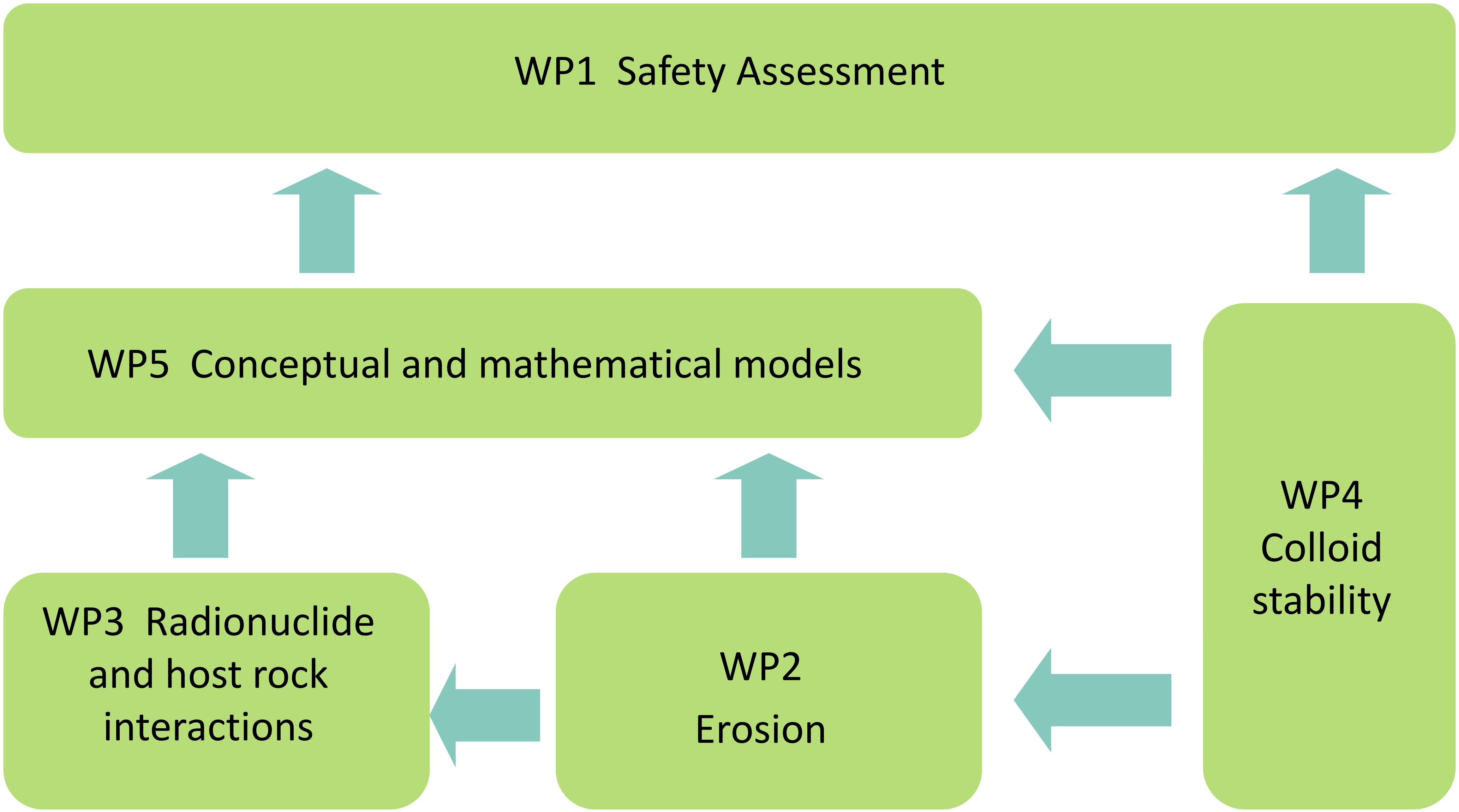
Radioactive Waste Management

WP 1 Safety Assessment

WP1 objectives:

- Formulate the issues that are important for the long-term safety assessment
- Identify the main uncertainties related to colloids in the safety assessment
- Provide the focus for the research work in BELBaR
- Produce State-of-the-Art Synthesis Report: Colloids and related issues in the long-term safety case

BELBaR Project WP Linkages: Information flow



Radioactive Waste Management

Synthesis of issues: Erosion

Mechanisms of erosion of clay particles from the bentonite surface

Safety case position at start of BELBaR	Outcomes of BELBaR
Erosion will cause a loss of bentonite buffer performance under some conditions. This may lead to corrosion failures of the canisters. Corrosion failure leads to the largest impact on risk, a less pessimistic approach may have significant impacts on the calculated risk.	In general, erosion/ colloid generation is rapid initially, but decreases with time and in some cases stops altogether. In static experiments – equilibrium is reached – maximum quantity of colloids generated depends on initial conditions – but erosion will not be continuous. Chemical forces driving dispersion processes are considered to be more important than mechanical forces even in the dynamic system Potential connection between flow rate and erosion when ionic strength of GW is below the CCC

Radioactive Waste Management

Synthesis of issues: Erosion

Characteristics of Bentonite Clay

Safety case position at start of BELBaR	Outcomes of BELBaR
Divalent cations have not been studied that systematically. Should the existence and quantitative effect of divalent cations be argued, the importance of this outstanding uncertainty would reduce.	Compaction density of bentonite clay – with higher compaction, the quantity of particles produced is observed to be higher. Higher erosion observed in Na- exchanged bentonites. Low (and sometimes no) erosion observed in Ca- exchanged bentonites – even in low ionic strength conditions. A small proportion of Na in bentonite (25%) is enough to promote significant dispersivity of the clay. Link between maximum eroded mass and the smectite content of the clay

Synthesis of issues: Erosion

Groundwater Chemistry

Safety case position at start of BELBaR	Outcomes of BELBaR
The key factor for colloid stability is the ionic strength and the content of divalent cations. pH should have an effect, but the pH-range considered in the safety case is rather limited.	Ionic strength of GW is an important factor with respect to erosion. In general it has been observed that increasing ionic strength, decreases colloid generation. Divalent cations (Ca^{2+}) are more effective as coagulants than monovalent cations (Na^{+}). Presence of Ca^{2+} in solution inhibits the formation of colloids. Erosion is only observed at very dilute conditions. Question of conservatism with respect to consideration of the deionised GW scenarios – but consideration needs to be given to composition of glacial melt waters

Radioactive Waste Management

Synthesis of issues: Erosion

Clay- Groundwater interactions

Safety case position at start of BELBaR	Outcomes of BELBaR
Changes in bentonite porewater solute concentrations can be modelled. The related rates assumed to be limited by the availability of different porewater solutes. Mass loss rate assumed to have hydrodynamic contribution. The buffer and the groundwater never reach a true equilibrium.	Groundwater evolution in the long term will affect the chemistry of the clay/ groundwater system. Unlikely that mechanical shear is the key mechanism to perturb gel phase. Hysteresis effect could enable clay to be stable to erosion. Calcium incorporation in an open/ dynamic system could reduce/ eliminate the production of colloids.

Synthesis of issues: Erosion

Groundwater velocity

Safety case position at start of BELBaR	Outcomes of BELBaR
Groundwater velocity has been considered as a variable. The loss of bentonite will be affected by the groundwater velocity and it is important to verify this dependence for erosion rates.	Understanding the effect of the presence of a hydraulically active fracture – does water flow at the bentonite surface or gel- front increase colloid generation. In tests where erosion was observed erosion is well correlated to GW velocity. Tests conducted in less dilute conditions saw less mass loss, therefore potentially the use of maximum erosion rates to estimate mass loss could lead to overly conservative erosion predictions. Observed that system chemistry is more relevant than flow velocity in terms of driving erosion processes.

Synthesis of issues: Erosion

Clay extrusion paths

Safety case position at start of BELBaR	Outcomes of BELBaR
Fractures have been assumed to be planar with a constant aperture. Extrusion of clay into a fracture is an integral part of the current model and will have a strong impact on the mass loss. Piping may occur before full saturation of the buffer under certain circumstances.	Horizontal and sloped fractures display a different mechanism of mass loss. Where all other test conditions are identical – increased slope angle leads to increased mass loss. However, effect of slope is more dramatic at lower angles (0˚ – 25˚) compared to 45˚-90˚. Irrespective of slope at a cation charge greater than or equal to 8.6 mEq – rate of erosion is effectively zero.

Radioactive Waste Management

Synthesis of issues: Colloid, RN & host rock interaction

Retention processes

Safety case position at start of BELBaR	Outcomes of BELBaR
Retardation of colloid transport in the far field, will delay the arrival of radionuclides in the biosphere. The extent of this isn't currently taken into account.	Retention of colloids has been observed under conditions which would have been through to be unfavourable. Rock matrix diffusion is cited in terms of an interpretation of previous observations for the behaviour of colloids in flow paths. In terms of colloid diffusion coefficients – the main differences observed are attributed to size variation.

Radioactive Waste Management

Synthesis of issues: Colloid, RN & host rock interaction

Radionuclide sorption

Safety case position at start of BELBaR	Outcomes of BELBaR
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 3. colloid-free matrix pore space (conservative assumption, but also realistic for the small pore sizes of granitic rock). Reversible, linear sorption of radionuclides onto colloids has been assumed.	Sorption reversibility of irreversibility in terms of the migration of radionuclides can potentially be limiting or supporting. Its been observed that the affinity of radionuclides towards the rock was in general greater than the affinity towards the colloids, indicating reversible sorption. Colloid mediated transport of radionuclides is dependant on the composition of the liquid phase – link to colloid stability and competition for sorption sites between ions and radionuclides can speed up transport. Full reversibility of sorption cannot be guaranteed, reversibility kinetics depend on geochemical parameters.

Radioactive Waste Management

Synthesis of issues: Colloid stability

Colloid stability controlling processes

Safety case position at start of BELBaR	Outcomes of BELBaR
Stability of compacted bentonite in dilute porewater conditions has been evaluated by laboratory measurements. The controlling process is hydration of exchangable cations limited by the availability of cation free water. Currently the uncertainties in geochemical conditions are greater than in uncertainties in the stability limit. Colloid stability studies have found that model colloids that possess a significant net negative charge at neutral pH, i.e. silica and illite clay, show the greatest stability under neutral pH conditions.	Provided that the ionic strength of groundwater is above the CCC, highly compacted clays in engineered barriers will act as a swelling repulsive paste and expand. Colloid stability is influenced by the differing mineralogy of different bentonites Apparent hysteresis effect where aged gels are observed to be stronger.

Radioactive Waste Management

Synthesis of issues: Colloid stability

Influence of other factors on colloid stability

Safety case position at start of BELBaR	Outcomes of BELBaR
Accessory minerals seem to enrich near the bentonite-groundwater interface. Filtration has been discussed as a possible mean to reduce erosion. Colloid size, solution ionic strength and water flow rate are factors which strongly influence colloid migration. Association of inorganic particles with natural organic compounds is an important mechanism for colloid stabilisation. This mechanism could potentially operate to stabilise and enhance colloid populations in the near-field porewater, this remains an area of uncertainty.	Na and K (M^+) and Mg and Ca (M^{2+}) act in a similar way during coagulation process Interaction of smectite with a mineral such as kaolinite or Al2O3 produces aggregation of particles. Organic matter is able to stabilise colloids in NaCl electrolyte. In $MgCl_2$ and $CaCl_2$, clay colloids undergo fast coagulation independently of the presence of organic matter.

Radioactive Waste Management

Synthesis of issues: Conceptual and mathematical models

Erosion of the bentonite buffer and radionuclide transport mediated by bentonite colloids

Safety case position at start of BELBaR	Outcomes of BELBaR
The factors considered are; 1. groundwater velocity 2. fracture aperture 3. transport resistance of bentonite gel in terms of diffusivity 4. gel cohesivity in terms of viscosity Pessimistic assumption neglecting safety promoting aspects have been used. At the colloid concentrations likely in the far field, a significant increase in risk could arise if a proportion of the radionuclides associated with colloids are irreversibly sorbed. In that case the risk will depend on the mobility and particle lifetimes.	Based on the experimental evidence observed, review our conceptual and mathematical models of the influence of colloids on the erosion of the bentonite buffer

Radioactive Waste Management

WP1 Final State of the Art Report

- Integrate information produced by other WPs, considering implications for current state of the art, i.e. answers to the issues identified on previous slides
- Examine extent to which other WP findings provide satisfactory answers to the needs identified at the project outset
- Define scenarios for colloid issues, discuss uncertainties in these scenarios and identify model and data needs for their treatment
- Updated State-of-Art report to include justified recommendations for improved and updated treatment of colloids and related issues in relation to long-term safety assessments, based on integrated project findings

Summary

The key issues to be addressed in the final State-of-the-art report from each WP:

- Bentonite erosion and production of colloids (WP2) – understanding of the main mechanisms of erosion of clay particles from the bentonite surface and quantification of the (maximum) extent of the possible bentonite erosion under different physio-chemical conditions.
- Colloid, radionuclide and host rock interactions (WP3) –determined the sorption reversibility of radionuclides to the colloids and whether the current assumption of reversible sorption can be justified.
- Clay colloid stability (WP4) – better understanding and representation of the stability and mobility of clay colloids under repository site conditions.
- Improvements to models (WP5) –obtained improved, validated models of colloid influence on the erosion of the bentonite buffer and colloid-mediated radionuclide transport.

Overall, moving towards a justification for a review of current pessimistic assumptions in the safety case regarding colloid behaviour, to present a more realistic and confident safety case.

Radioactive Waste Management

BELBaR

This work has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement no. 295487 (BELBaR Project).

EURATOM

Radioactive Waste Management

Clay Colloids in Aqueous Systems

3-4 February 2016, Berlin, Germany

Venue: Seminaris CampusHotel Berlin

Flow of clays

Jon Otto Fossum

Department of Physics

Norwegian University of Science and Technology - NTNU

Trondheim, Norway


NORWAY
Nordkapp
Vardø
Hammerfest
Norwegian Sea
Kirkenes
Alta
Tromsø
Kautokeino
Lofoten Islands
Narvik
Å
Arctic Circle
Bodø
NTNU
Mo i Rana
SWEDEN
FINLAND
0 400 km
0 200 miles
Trondheim
Ålesund
Åndalsnes
Bottenhavet
Central Norway
Jotunheimen National Park
Finse
Geilo
Lillehammer
Helsinki
ATLANTIC OCEAN
Bergen
Oslo
Stockholm
Tallinn
Fredrikstad
ESTONIA
Stavanger
Risør
Baltic Sea
Kristiansand


Laboratory for Soft and Complex Matter Studies at
NTNU, Trondheim, Norway:

NTNU

Department of Physics

http://folk.ntnu.no/fossumj/lab

<u>Soft condensed matter</u> are complex materials which are easily deformable by external stresses, electric or magnetic fields, or by thermal fluctuations.

Examples:
Foods, cosmetics, personal care products, household products, plastics at vatious stages of processing, salves, paints, crude oils, clays.............., i.e. complex materials built from nano-, micro- particles/structures.

NTNU

Department of Physics

http://folk.ntnu.no/fossumj/lab

Our main motivation for studying <u>clays</u> is that clays may be viewed as good representative model systems for soft condensed matter and complex materials, with ”near” applications.

Questions to ask:

How does nano-scale physics (fex. clay nanostructures) translate into macroscopic (fex. clay flow) behaviors?

What is universal? What is specific?

We are curiosity driven:

NTNU

«HEY, SÀM, THE BIG ROUND YELLOW THING CAME UP AGAIN»

Clay avalanches

NGI

Norwegian Geotechnical Institute

Clay avalanche: Rissa Norway 1978

Observation:
Extreme mechanical instability of certain clayey soils, under given humidity conditions

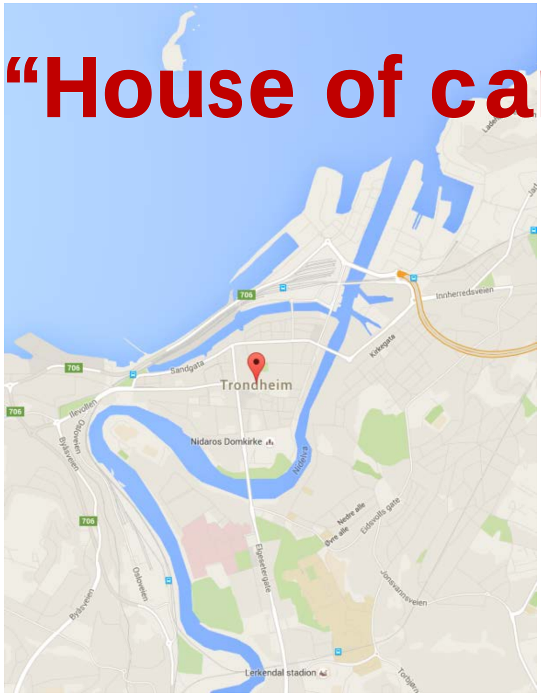
Example:
The Rissa landslide (1978, near Trondheim, Norway)

- Triggered by the excavation of 1000 m3 prior to building a barn
- Duration: 6 min
- 7 to 8 millions m^3 of soil were displaced
- 40 persons were taken, 1 died
- 7 farms were rammed
- 33 ha of lands were touched
- A linear length of 80 m of coast ended up in the fjord
- **The slope was very moderate**

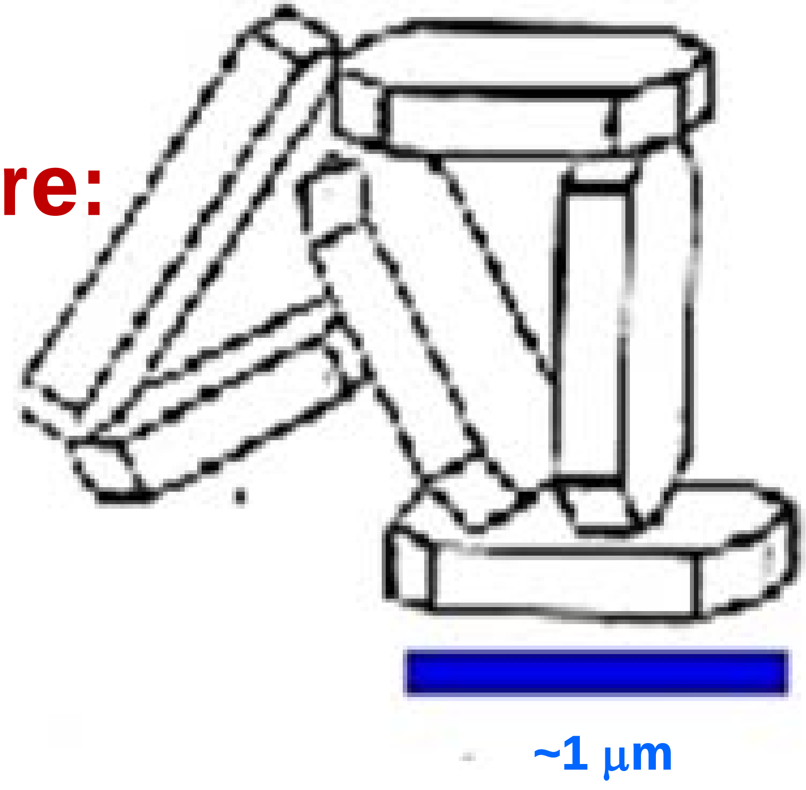
Natural clays are found as sediments.

The <u>natural quick clays</u> were sedimented at the en of the last ice age, for example at river mouths in saline water.

The specificity of the natural quick clays is that the salt during time has been washed away by water, which has weakened the cohesion of the material.



“House of card” structure:




Laboratory for Soft and Complex Matter Studies at
NTNU, Trondheim, Norway:

Simple analog landslide experiments

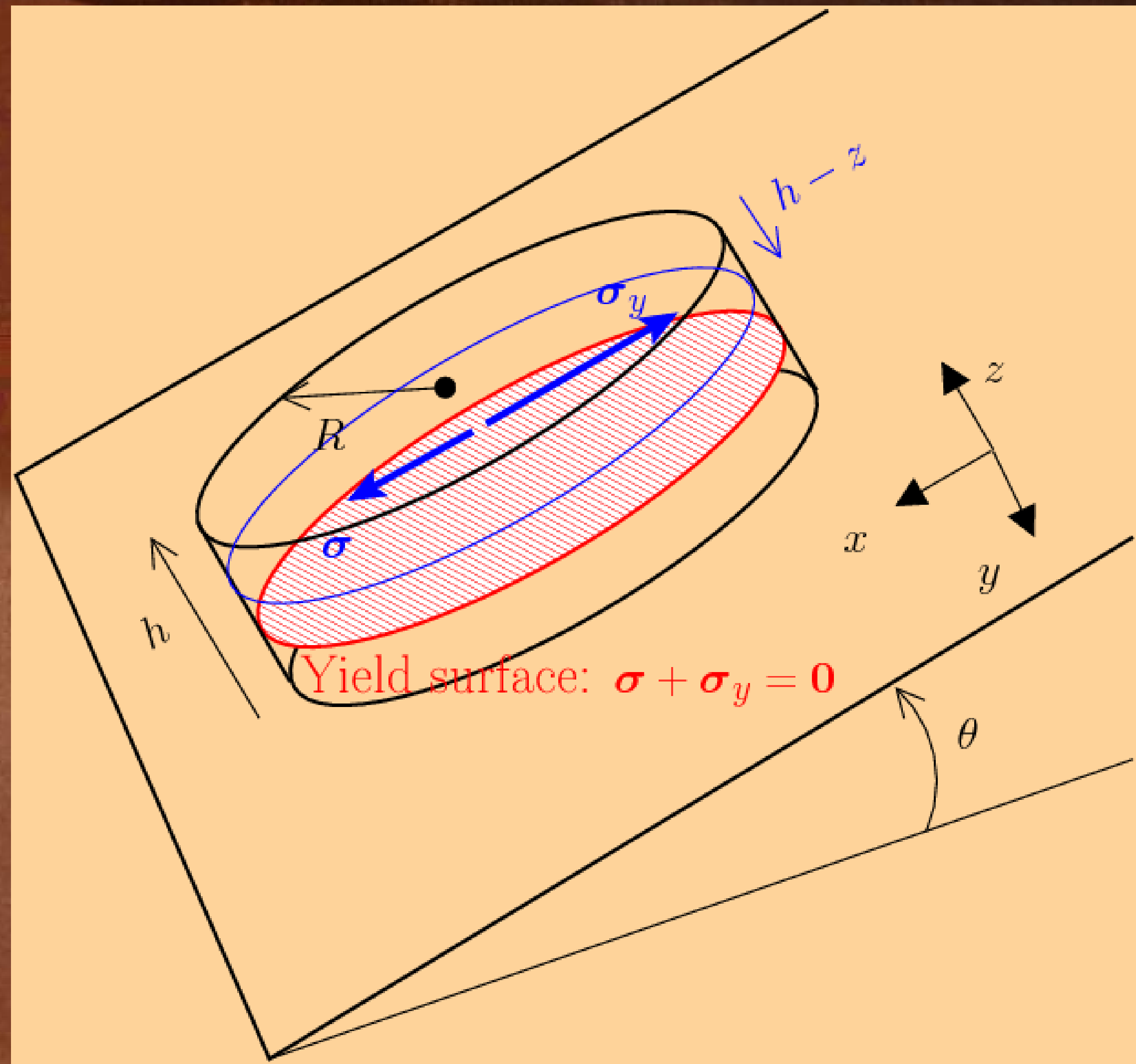
Quickclay and Landslides of Clayey Soils,
A.Khaldoun, P.Moller, A. Fall, G.Wegdam,B. De Leeuw, Y. Meheust, J.O. Fossum, D. Bonn,
Géosciences Rennes 1, University of Amsterdam, ENS-Paris, NTNU-Trondheim
Physical Review Letters 103, 188301 (2009)

Shear stress imposed by gravity:

$$\sigma(z) = \rho\, g\, (h - z)\, \sin\theta$$

(null at the free surface)

All material below the yield surface is expected to flow



NTNU – Trondheim
Norwegian University of
Science and Technology

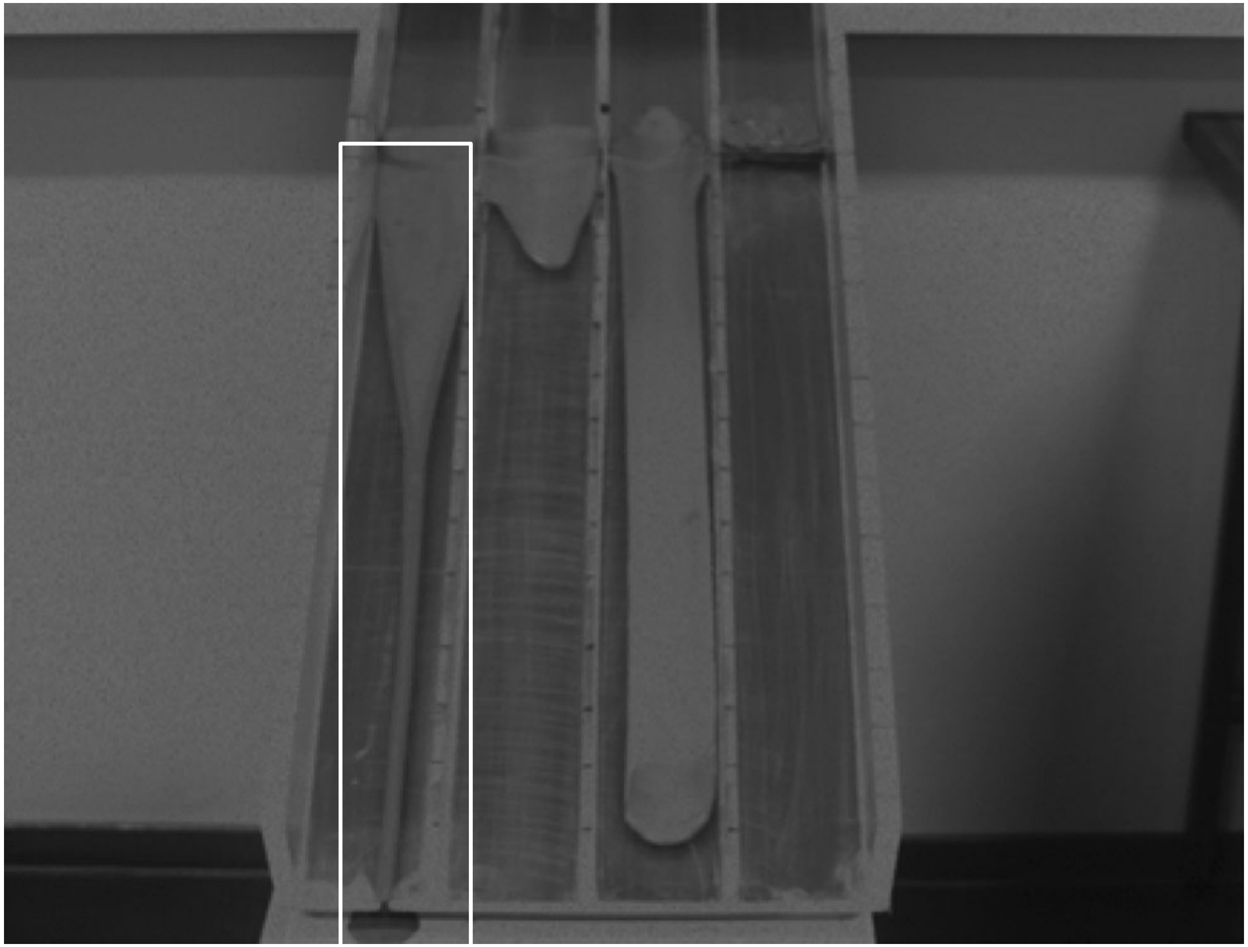
Our samples:

The marine clay from the Trondheim area is a quick clay consisting of:
70% non-swelling clays [kaolinite 1:1, illite 2:1, chlorite 2:1]
1% swelling clays [vermiculite, montmorillonite]
The rest is primary minerals (quartz, …)

Our samples were made from the natural clay, with controlled amount of water.
The samples at rest are colloidal gels with a **Yield stress!**

Analog laboratory landslide experiments

NTNU

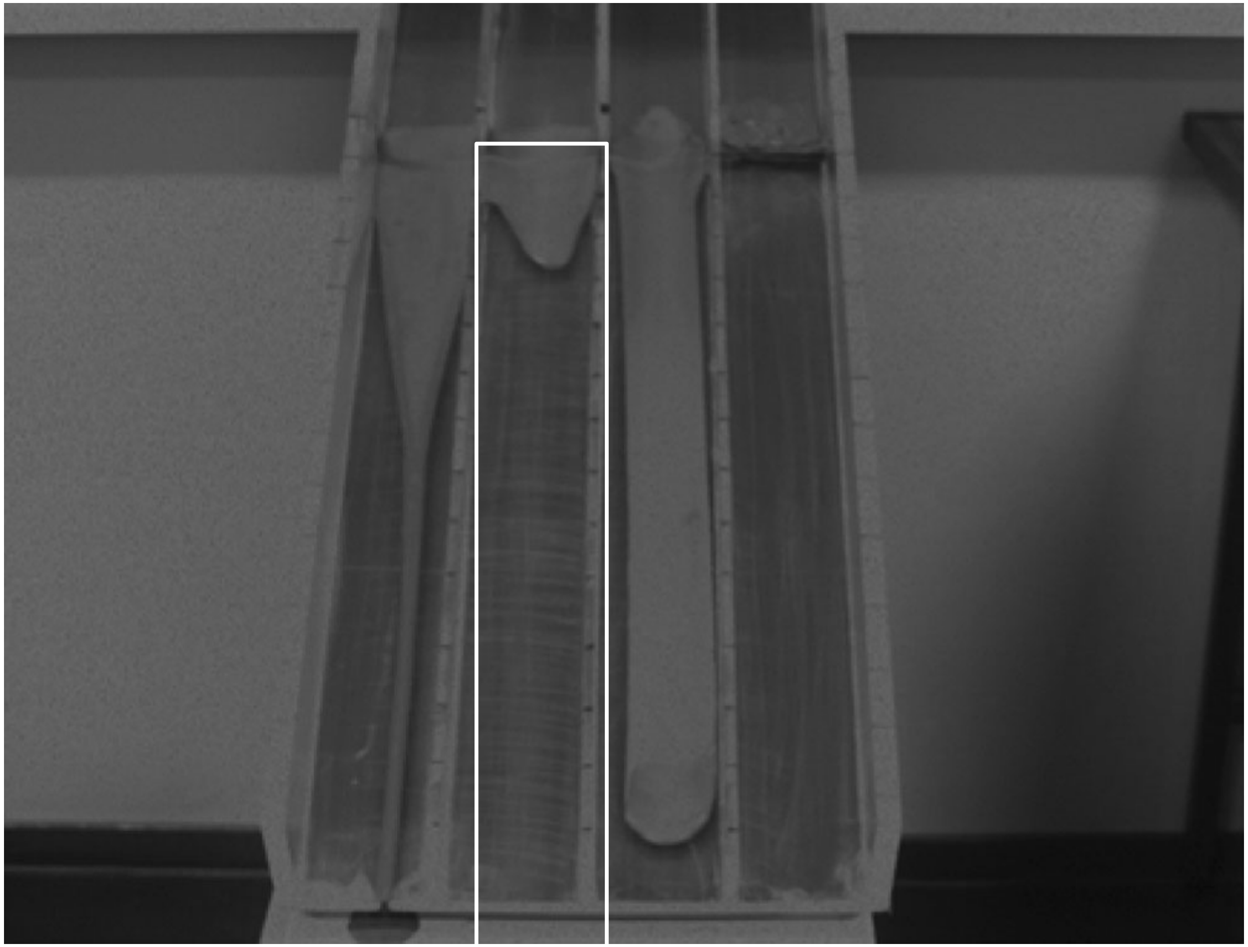


56% 58% 61% 63%

Weight% clay

Quasi-newtonian flow

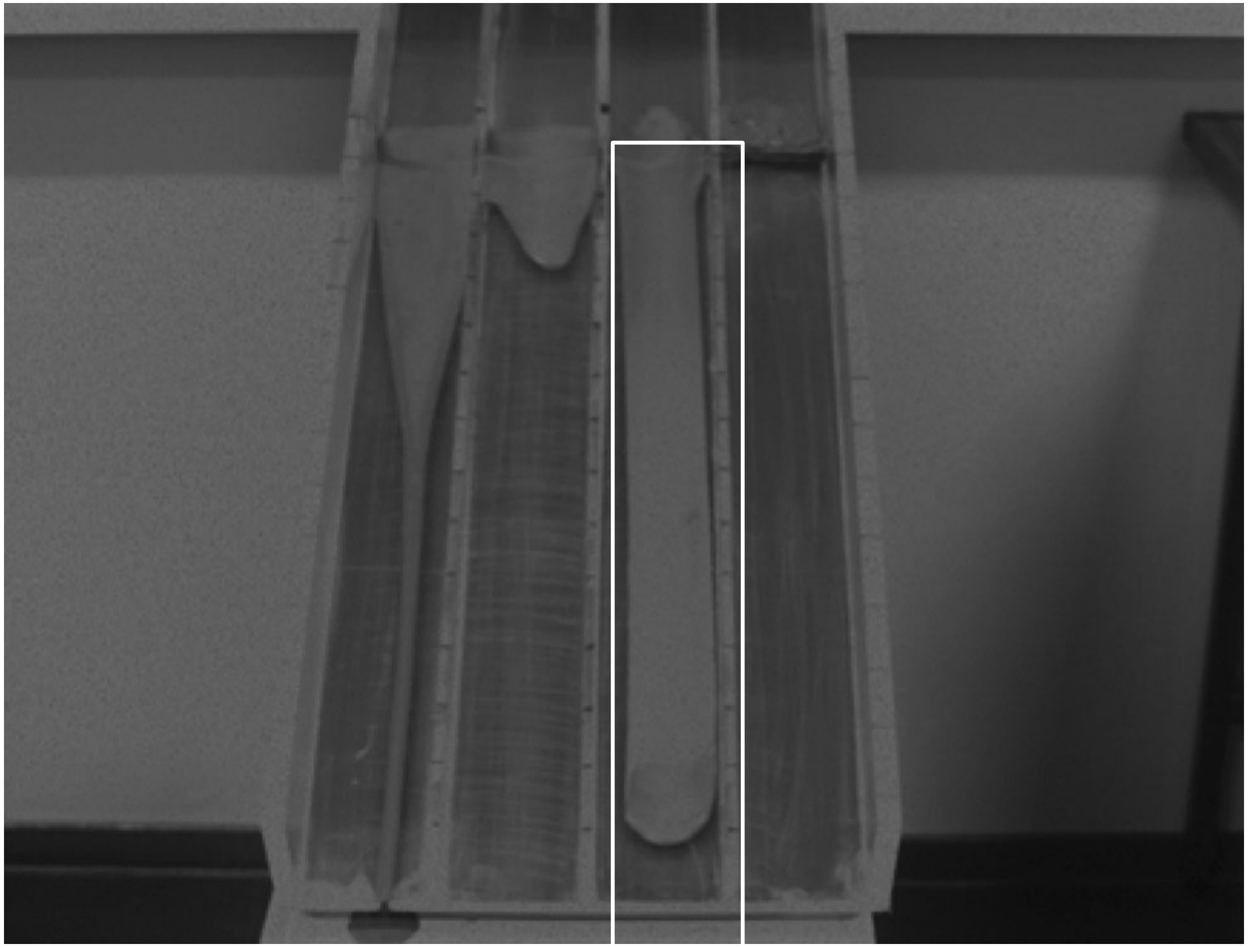
Analog laboratory landslide experiments (3)



56%   58%   61%   63%   Weight% clay

Yield stress fluid flow

Analog laboratory landslide experiments



56% 58% 61% 63%

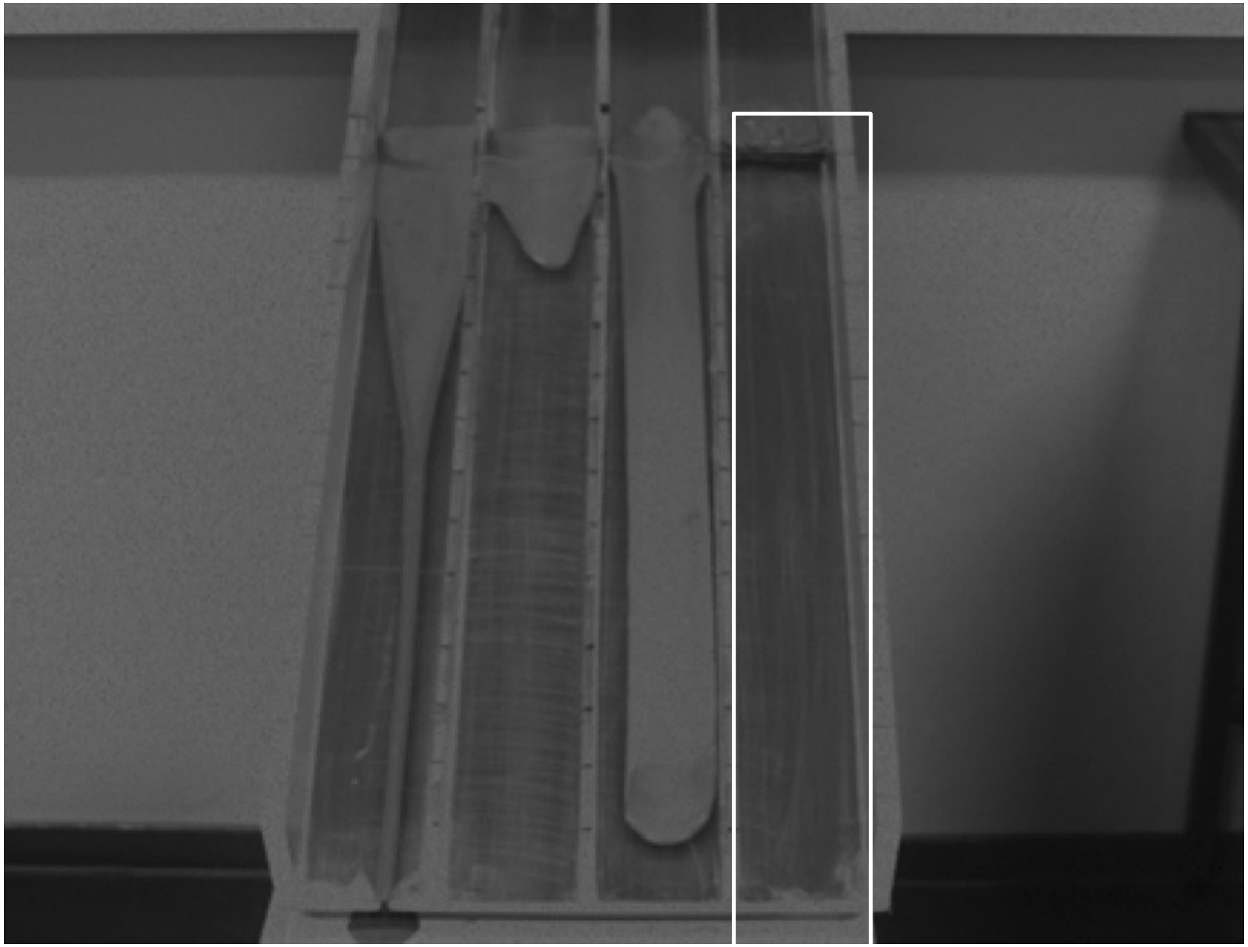
Weight% clay

Landslide regime = flow on a **thin lubrication layer**

⇒ This is why the Rissa farm buildings remained upright

Analog laboratory landslide experiments

NTNU



56% 58% 61% 63%

Weight% clay

(steric hindrance of particle alignment ?)

Laboratory land slide experiments:

Model includes:

Slide length and velocity

Runoff length as a function of yield stress

Initial settling of the heap on the horizontal plane

Critical yield stress that separates two regimes:

Depending on a heap's initial aspect ratio, which is controlled by its yield stress, the flow regime will be controlled either by friction at the base of the heap, or by inner cohesion.

In addition: Preparation of a synthetic quick clay

- Composition: illite + bentonite + salt
- Protocol: Illite is washed to remove any salt
  3% of washed bentonite (swelling clay)
  Controlled addition of salt and measure of the elastic modulus as a function of the salt concentration

Our conclusions (so far) on quick clay avalanches:

→ A material containing more water is not necessarily more unstable

→ For a limited range of water contents, the slide occurs on a very thin lubrication layer (lubrication layer/threadmill effect)

→This occurs when the material's yield stress is larger than a critical value that can be related to a simple theoretical model including the volume of the sample

→ It is possible to prepare in the laboratory a synthetic material that has the same mechanical properties as the natural quick clay: A small amount of swelling (smectite) clay is essential for the behavior observed

What can trigger a slide under natural conditions?

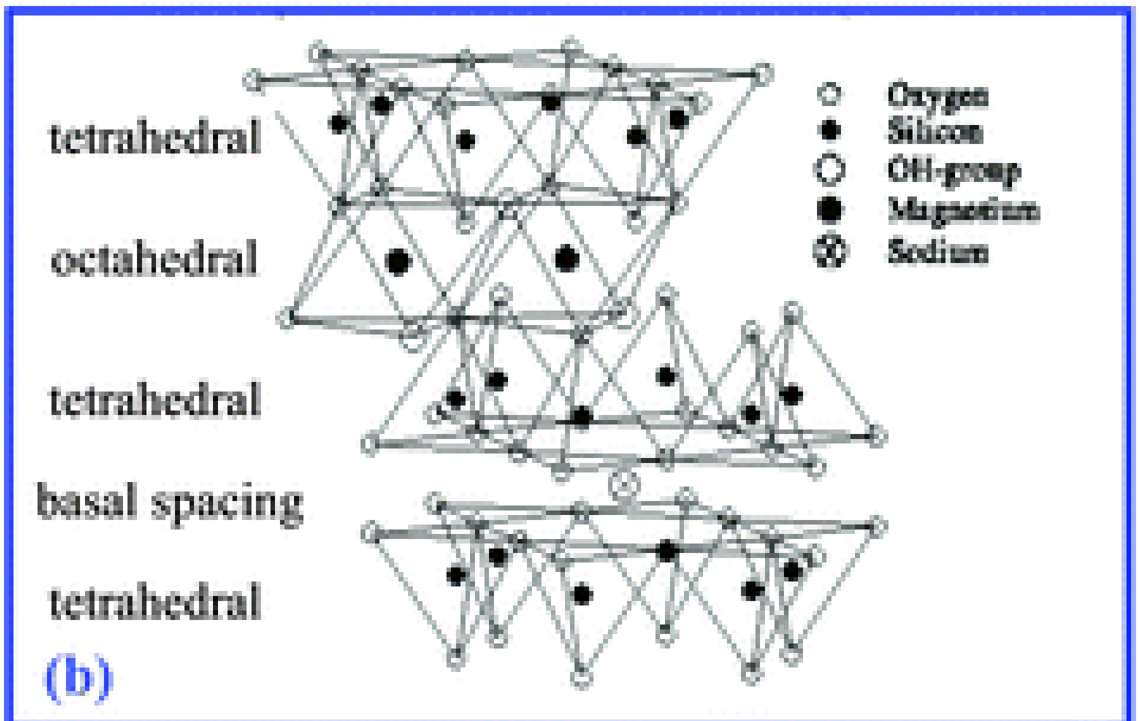
- Mechanical perturbation: Fex. an earthquake
  The Rissa landslide was triggered by excavation work
- Other triggering factor: Rain prior to the mechanical pertubation:
  A 1% concentration change can be enough!

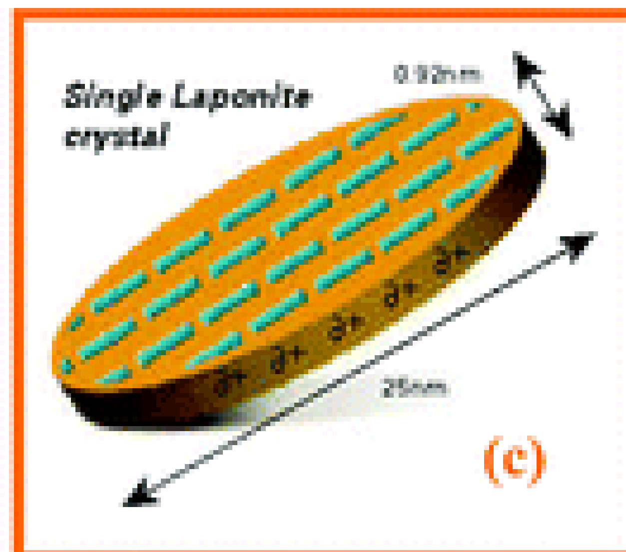
Phys.Rev.Lett. 103, 188301 (2009)

Appropriate question: Did we really study the “native” quick clay?

The most common and most used synthetic clay: Laponite (the only monodosperse colloidal clay)

(a) $Na^{+}_{0.7}[(Si_{8}Mg_{5.5}Li_{0.3})O_{20}(OH)_{4}]^{-0.7}$





Clay Minerals (1971) **9**, 231.

THE RHEOLOGICAL PROPERTIES OF DISPERSIONS OF LAPONITE, A SYNTHETIC HECTORITE-LIKE CLAY, IN ELECTROLYTE SOLUTIONS

B. S. NEUMANN AND K. G. SANSOM

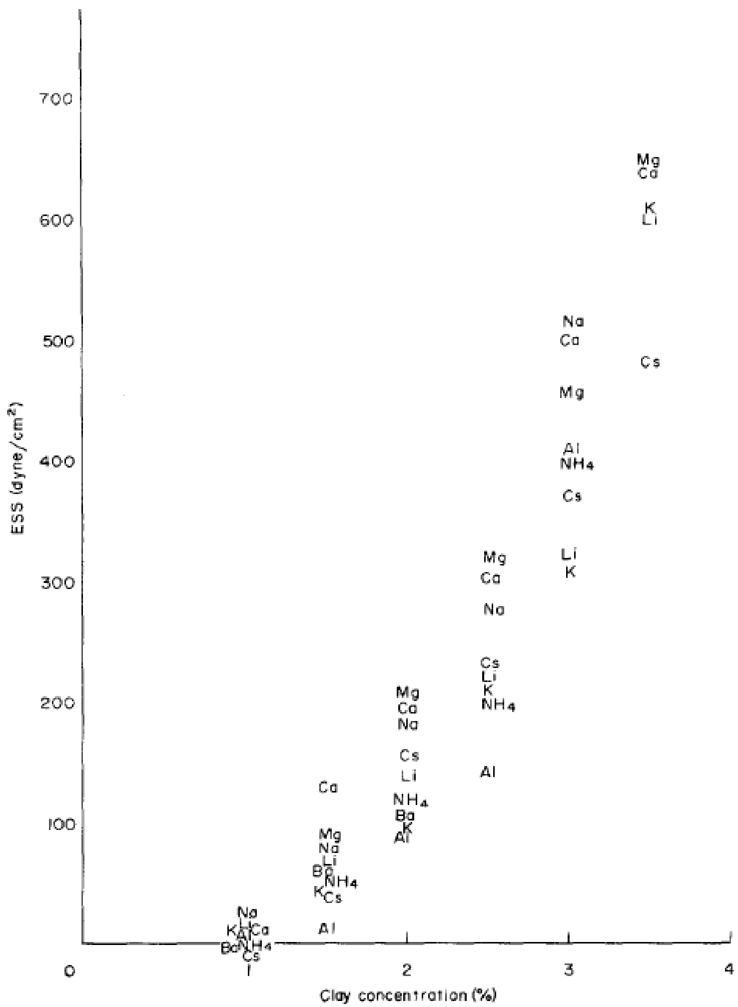


FIG. 5. Effect of clay concentration on yield value.

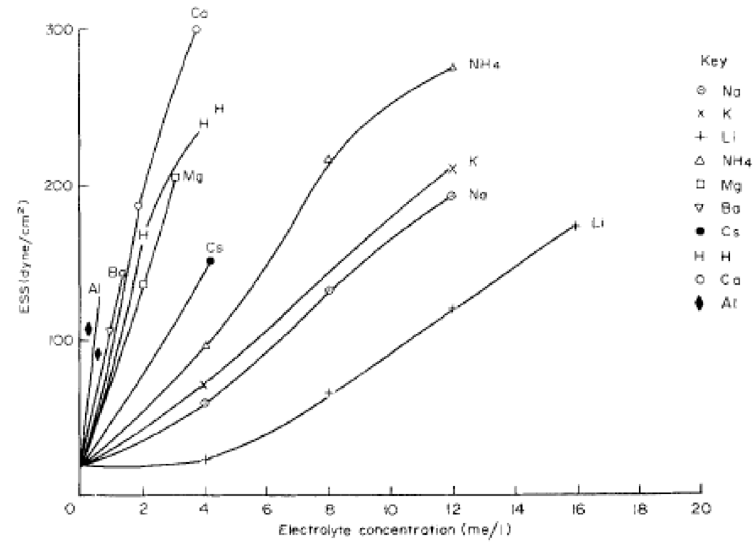


FIG. 2. Effect of electrolyte on Yield Value at 2% clay concentration.

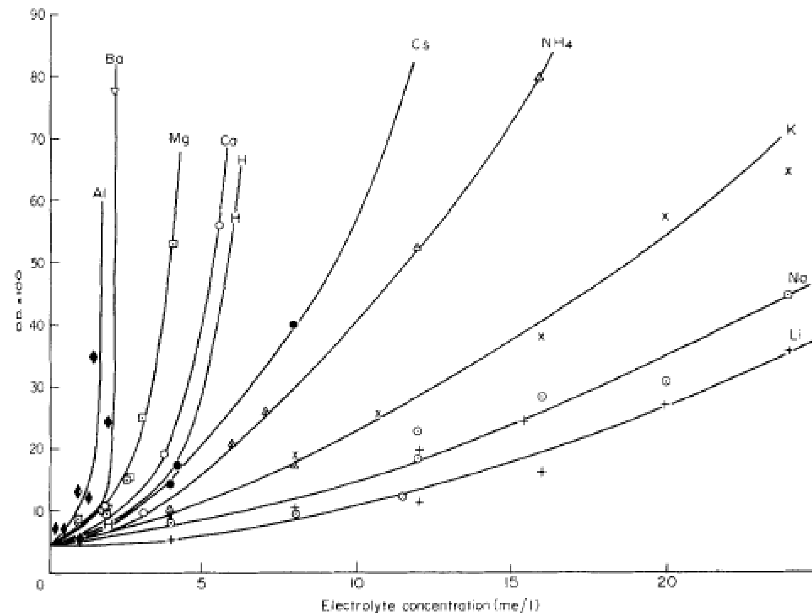
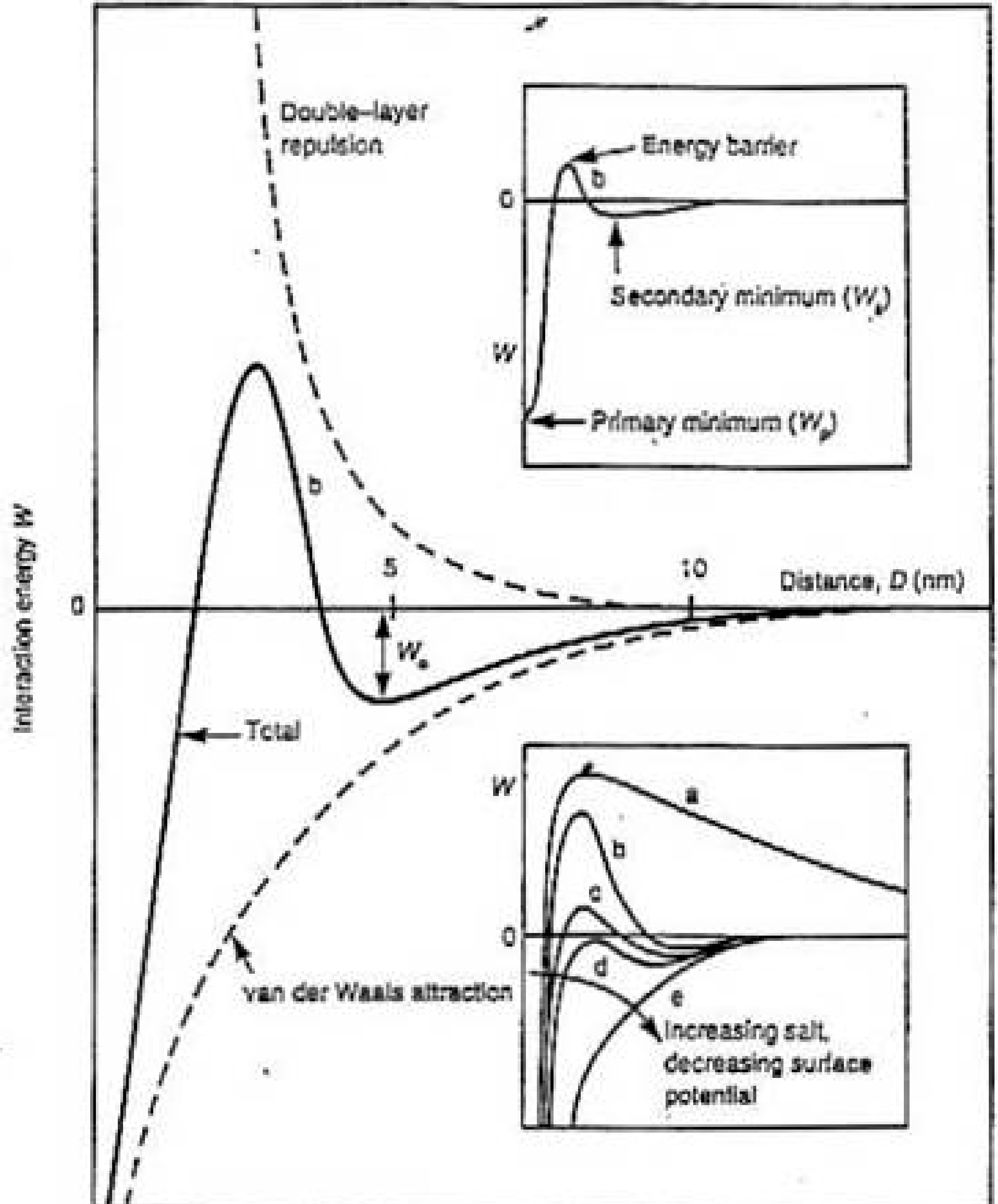


FIG. 3. Effect of electrolyte on optical density at 2% clay concentration.

DLVO Theory:
vdW
+ Screened Electrostatic Rep.



J. Israelachvili

PHYSICAL REVIEW E **69**, 031404 (2004)

NTNU

Nonergodic states of charged colloidal suspensions: Repulsive and attractive glasses and gels

Hajime Tanaka,[1] Jacques Meunier,[2] and Daniel Bonn[2,3]

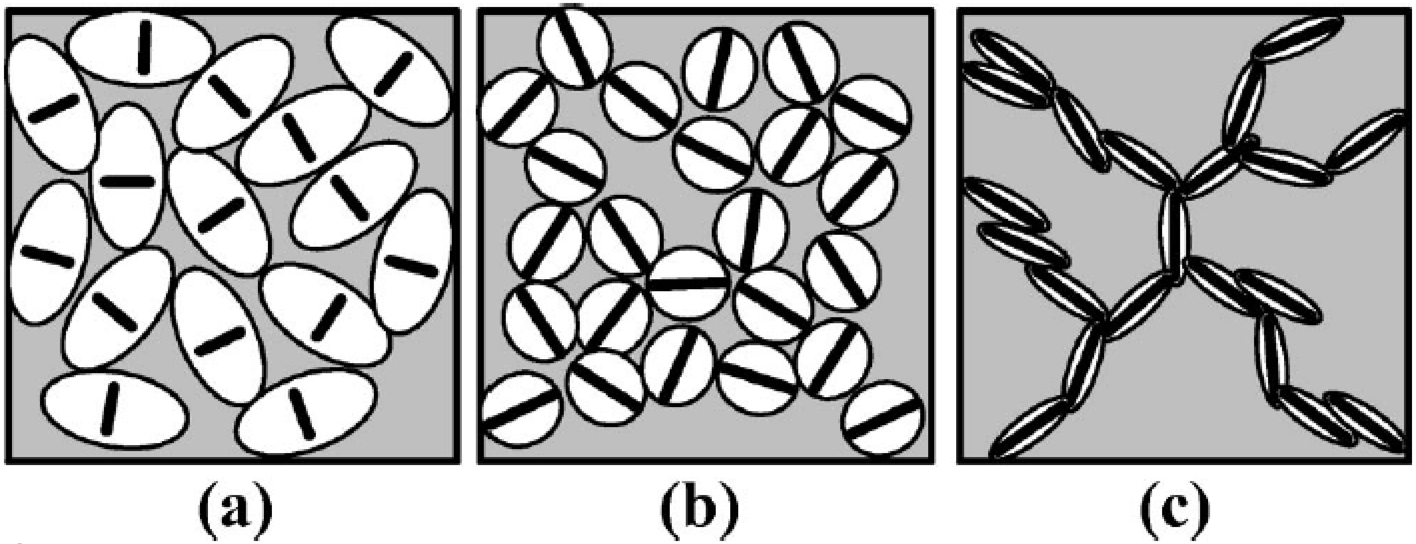


FIG. 1.
Schematic figures representing repulsive ‘‘Wigner’’ colloidal glass (a), attractive glass (b), and gel (c). Each thick line represents a Laponite disk, while a white ellipsoid represents the range of electrostatic repulsions:

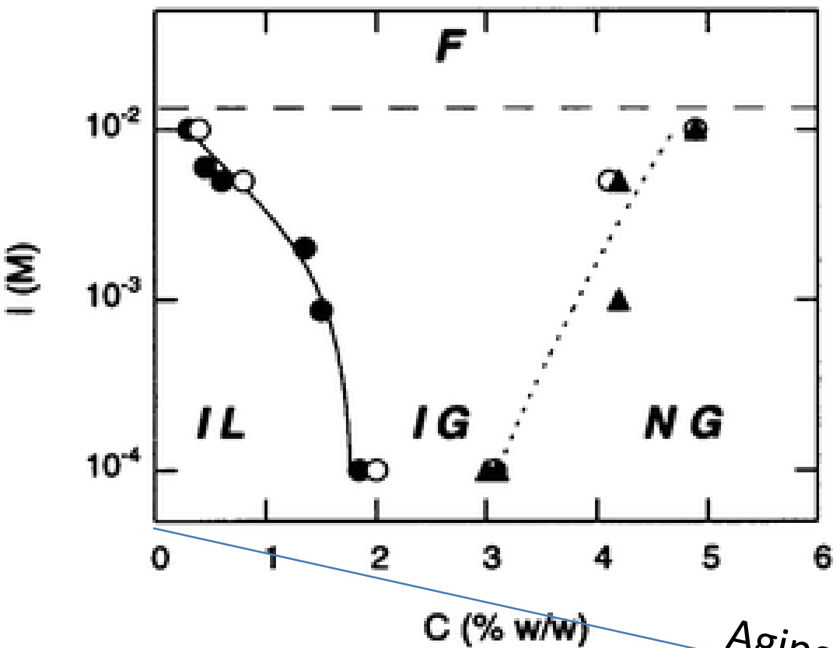
(a), long-range electrostatic repulsions dominate.
(b), attractive interactions affect the spatial distribution but repulsive interactions still play the predominant role in the slow dynamics of the system.
(c), attractive interactions play a dominant role; a percolated network forms, which gives the system its elasticity and higher yield stress.

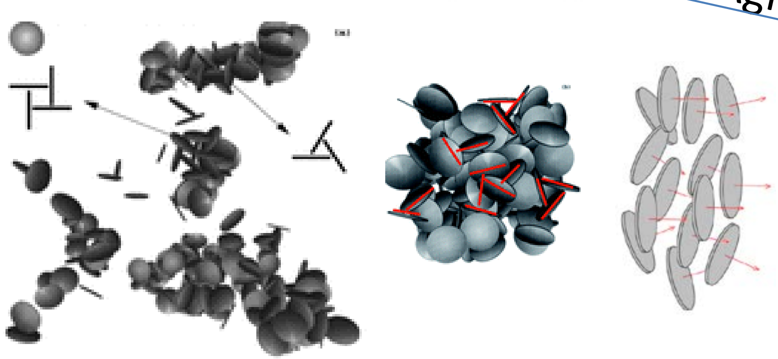
Langmuir **1998**, *14*, 4718–4723

NTNU

On Viscoelastic, Birefringent, and Swelling Properties of Laponite Clay Suspensions: Revisited Phase Diagram

A. Mourchid,* E. Lécolier, H. Van Damme, and P. Levitz*





Aging time

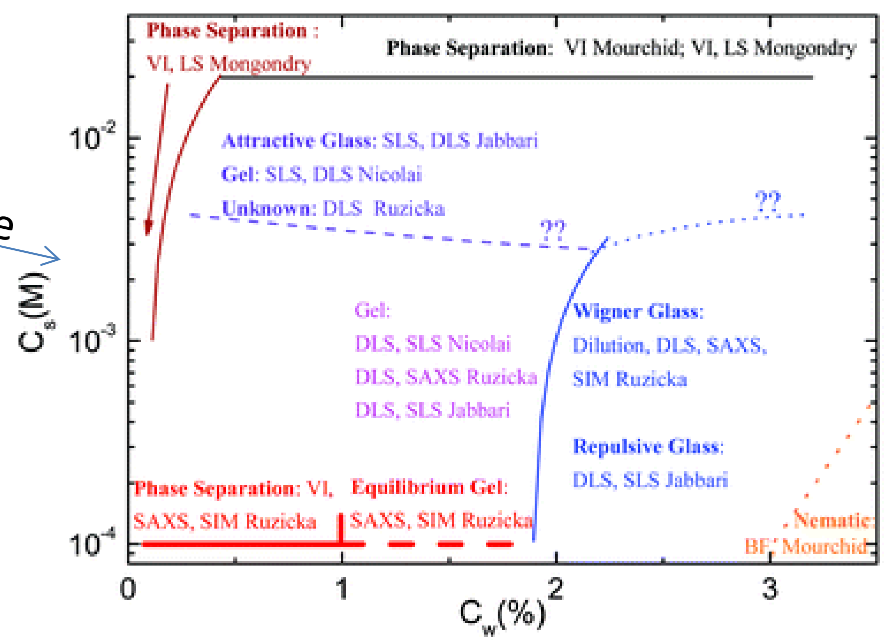
Soft Matter

Cite this: *Soft Matter*, 2011, **7**, 1268

www.rsc.org/softmatter

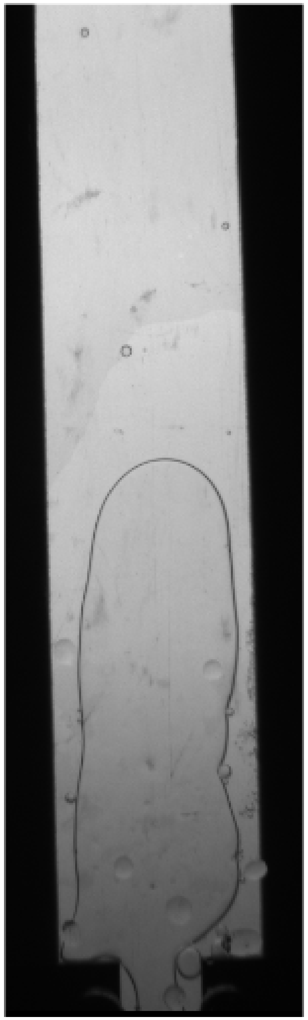
A fresh look at the Laponite phase diagram

Barbara Ruzicka*[a] and Emanuela Zaccarelli*[b]

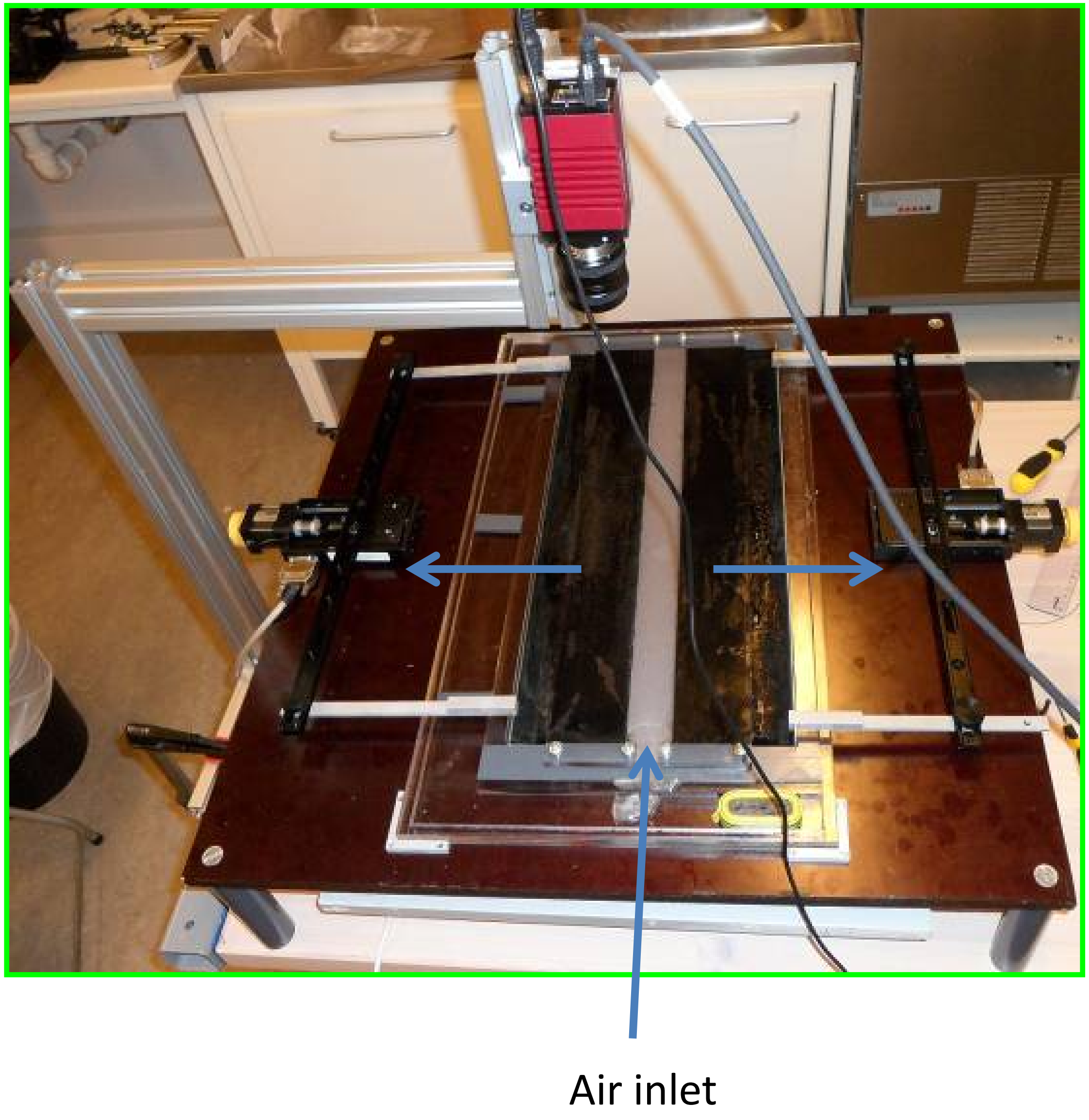


Ongoing experiments ESPCI-ParisTech/NTNU:
Fingering to fracturing transition at sol-gel transitions: Transparent clay gel

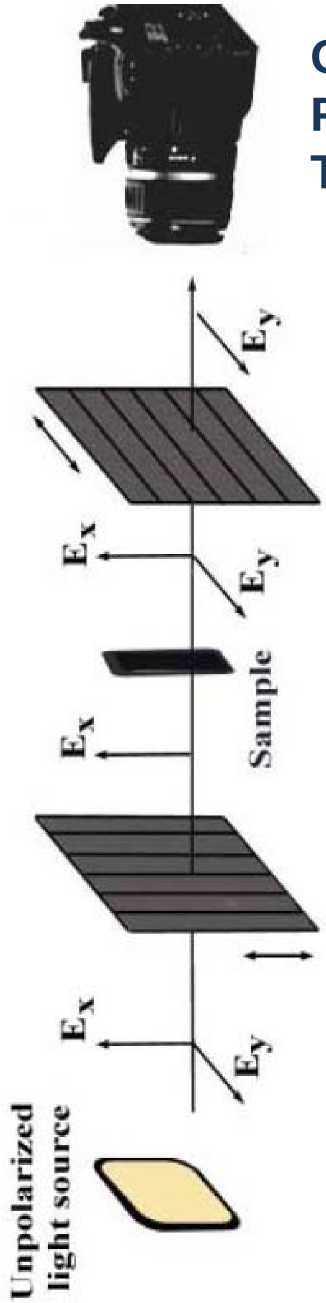
3 wt%, 2.5 hours, 2 mm/s

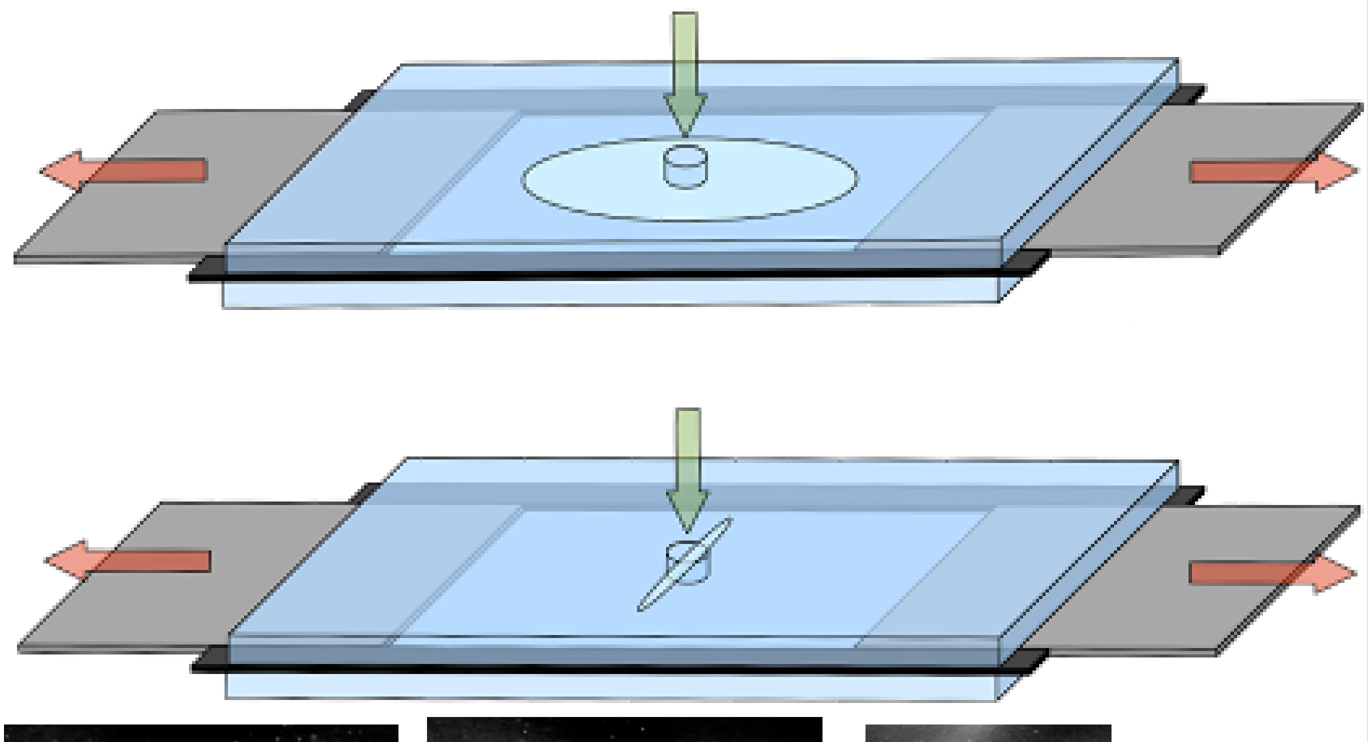


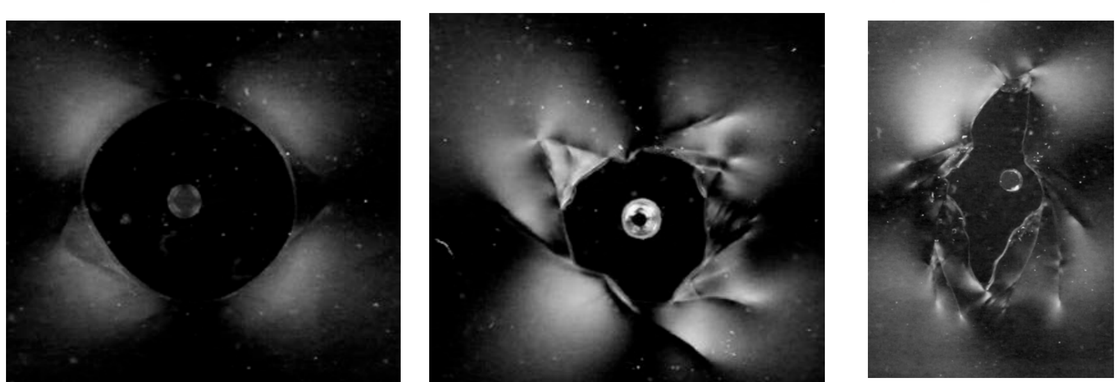
3 wt%,17 hours, 2 mm/s



Ongoing experiments ESPCI-ParisTech/NTNU:
Fingering to fracturing transition at sol-gel transitions:
Transparent Laponite clay gel



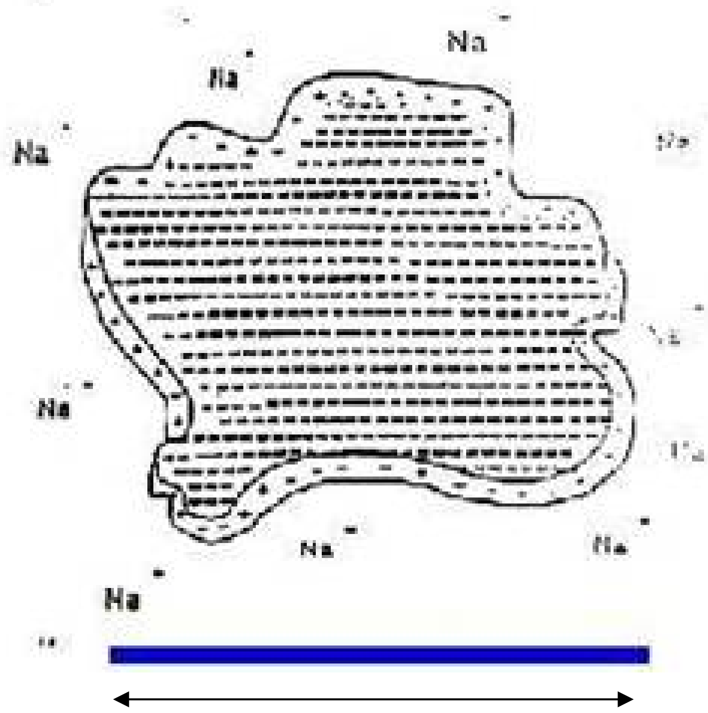




Clays are nano-/micro-particles:

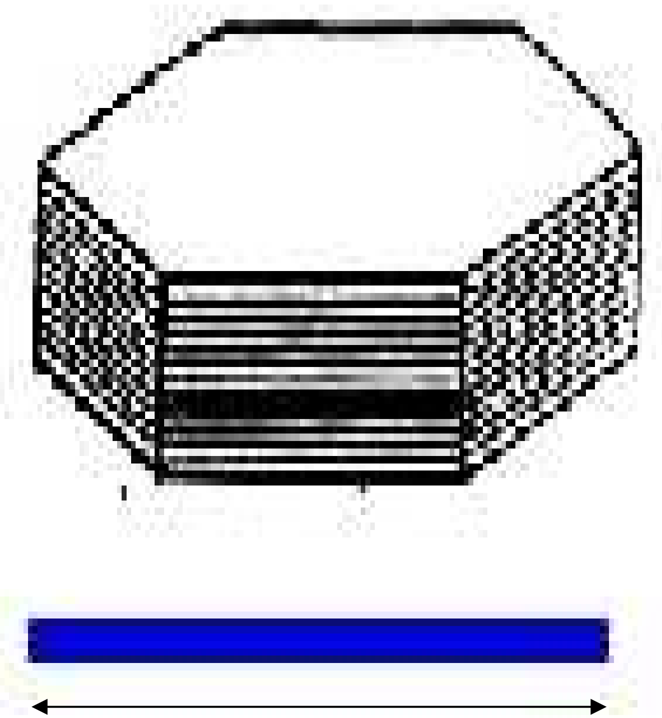
Two basic forms at nano-/micro-scale:

1 nm thick ”nanocards”
(«Osmotic Bentonite»/Laponite)



~ µm

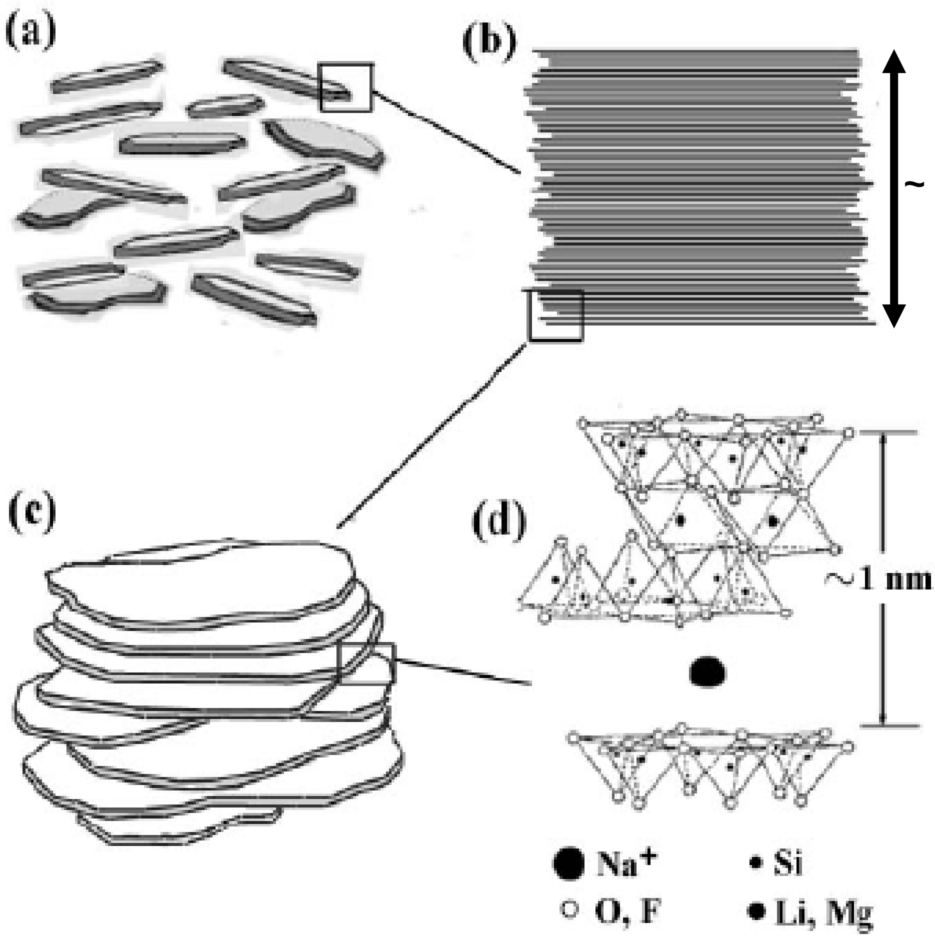
~100 nm thick nanolayered particles
”decks of nanocards”
(Kaolinite/ «Crystaline bentinite»)



~ µm

Our clay experimental model system:

Q-fluorohectorite synthetic clay: Q_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+, Li^+, Ni^{2+}, Fe^{3+}, etc)



Sources of fluorohectorite:

Corning Inc.
x ≈ 0.6 ± 0.05
Lateral ~ 0.5-10 μm
(incl. 20% known impurities)

Inorg. Chem.
Univ. Bayreuth, Germany
Prof. Josef Breu
x = (0.2 <->0.6) ± 0.005
Lateral > 100 μm
(pure)

One of our experiments:

Orientational order in gravity dispersed clay colloids: A synchrotron x-ray scattering study of Na-fluorohectorite suspensions. E. DiMasi, J.O. Fossum, T. Gog, and C. Venkataraman. **Phys.Rev. E 64, 061704 (2001)**

Clay (Fluorohectorite)
powder
About 3 % in weight

Pure Water

NaCl

About 10^{-3} M

Basic clay particle

~100nm

~µm

Liquid

Isotropic gel or glass?

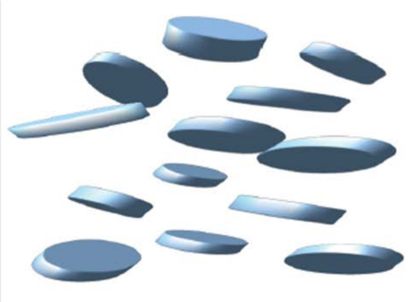
Nematic like gel or glass?

Sediment

4 "Phases" in same Sample Tube

Self-assembly is essential in materials science:

Making a macroscopic sample (i.e. about 10^{20} nanoparticles) by physically picking up and moving nanoparticles into place, one by one, would take about 300 million years, even if the time for moving individual particles could be made as short as 1 millisecond.

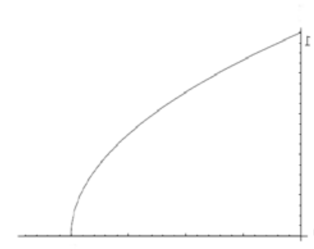


NTNU

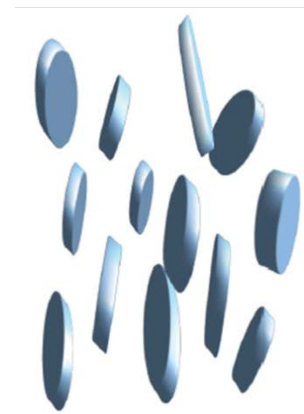
Liquid Crystalline Phases Characterization

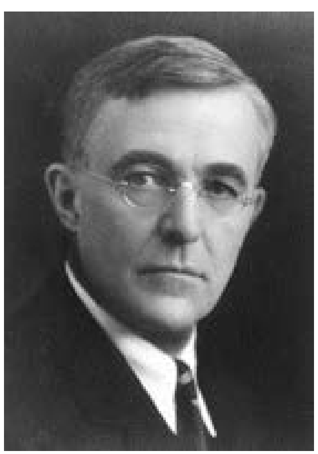
Order Parameter = O.P.
= Angular distribution function
$= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1 \rangle$

Isotropic Phase (O.P. = 0)



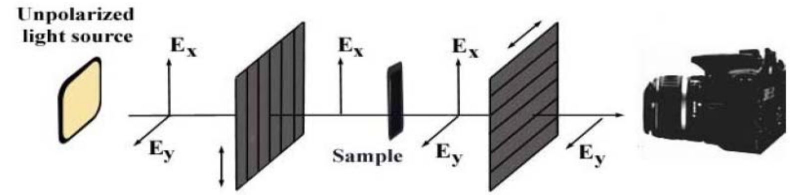
Nematic Phase (O.P. ≠ 0)



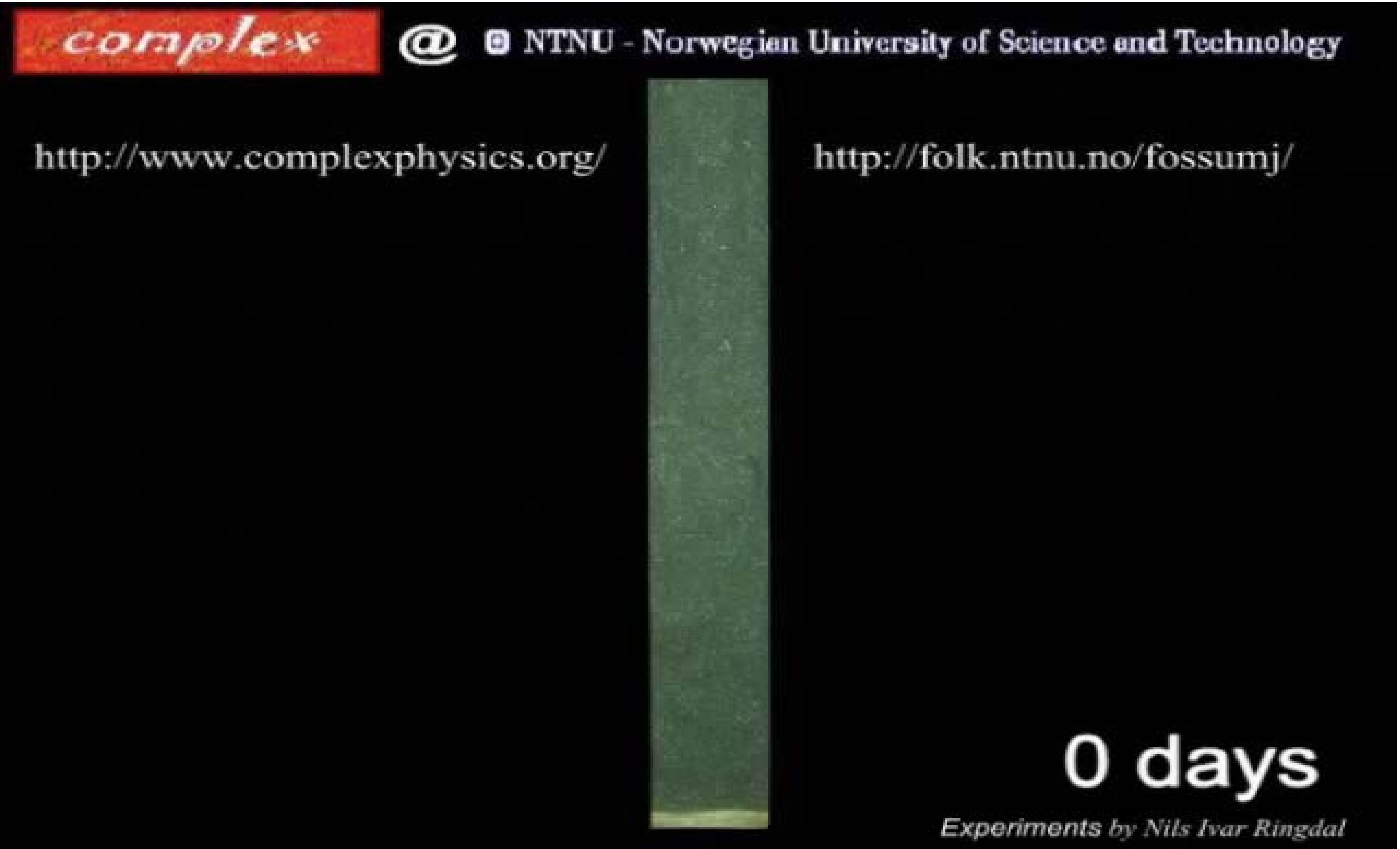


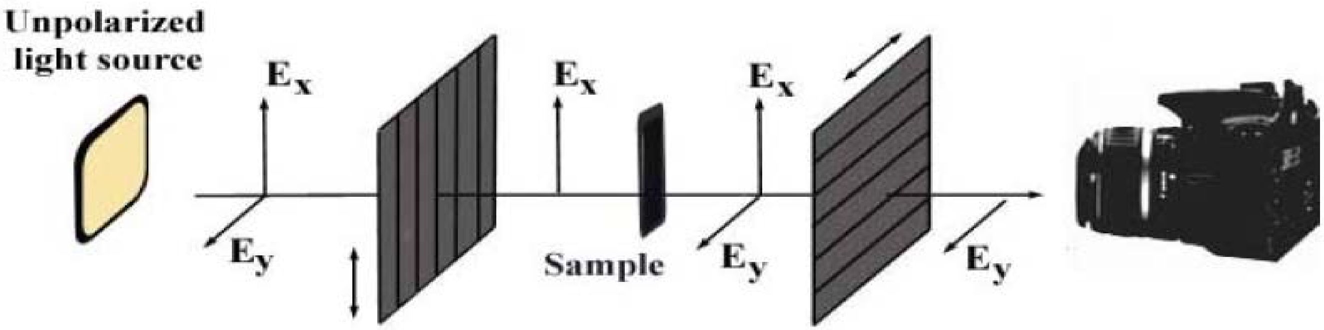
Irving Langmuir (Nobel Prize in Chemistry 1932): 1st experimental work in 1938 on liquid crystal structures in a clay suspension.

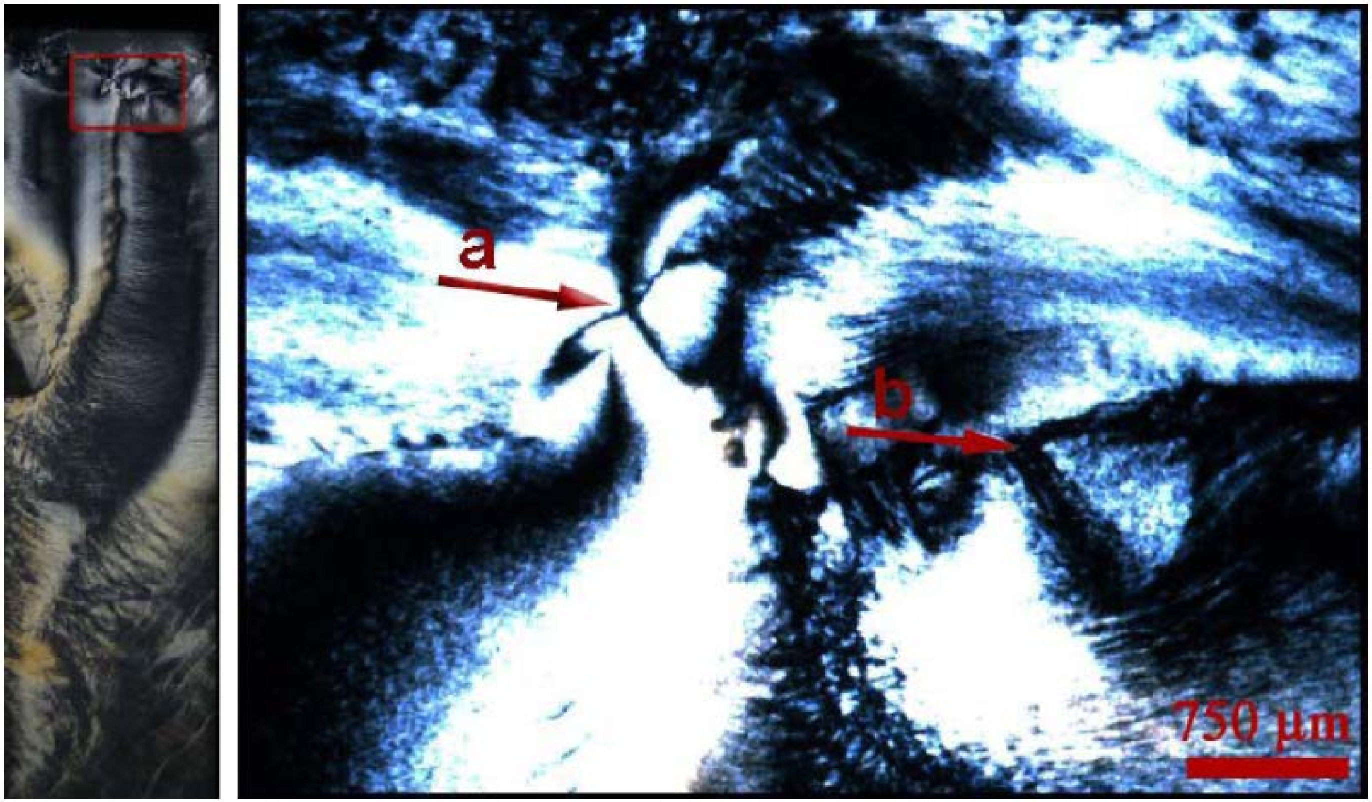
J. Chem Phys. 6, 873 (1938)



Self-organization by sedimentation clay particles in H_2O:



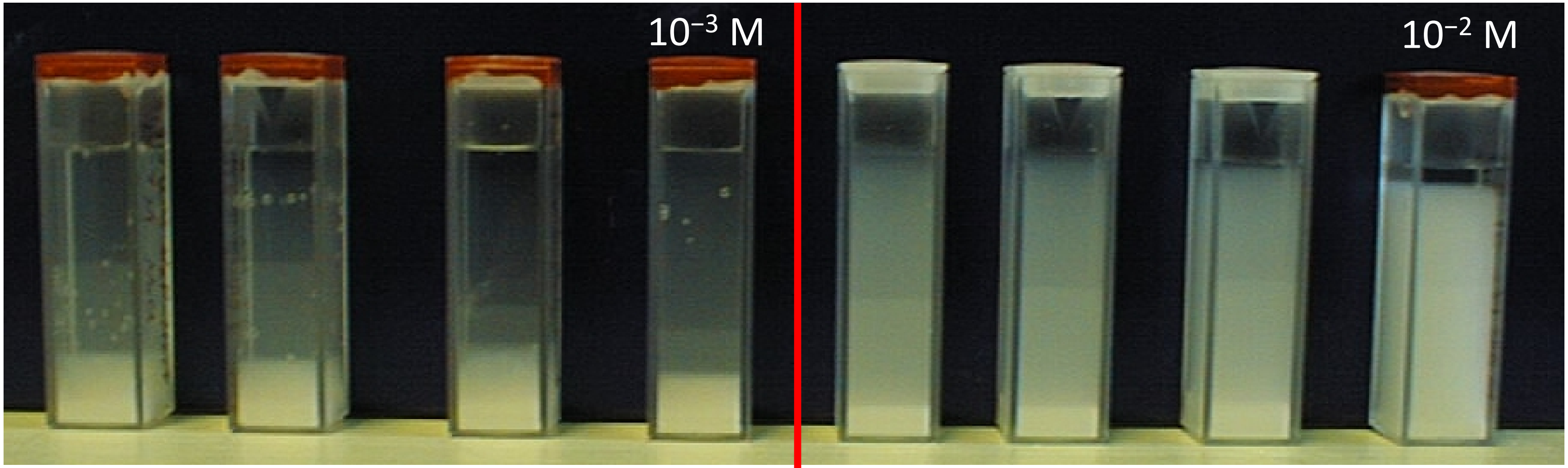




a and **b**
are ”typical” nematic defect signatures:
Disclinations ("discontinuity" in the "inclination" of the director)

Nematic textures in colloidal dispersions of Na-fluorohectorite synthetic clay. N.I. Ringdal, D.M. Fonseca, E.L. Hansen, H. Hemmen, and J.O. Fossum. **Phys.Rev. E 81, 041702 (2010)**

Increasing NaCl salt:



”Repulsive nematic”
”Wigner glass”

Particles push each other out towards container walls,
→ nematic
at high enough concentration
→ «large» domains

”Attractive nematic”
”Gel”

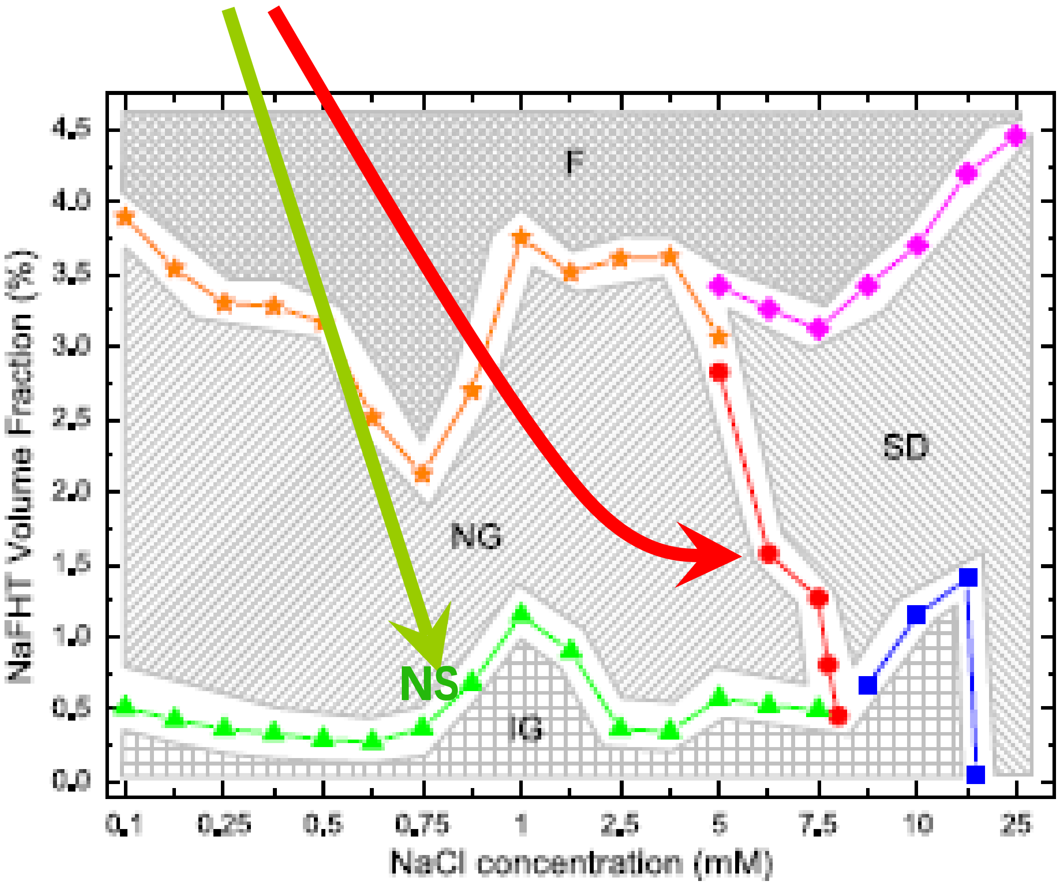
Particles ”catch each other” in DLVO local minima
→ «small» domains

The phase diagram of polydisperse Na-Fluorohectorite–water suspensions: ***A synchrotron SAXS study***

D. M. Fonseca, Y. Meheust, J. O. Fossum, K. D. Knudsen, and K. P. S. Parmar, **Phys.Rev. E 79, 021402 (2009)**

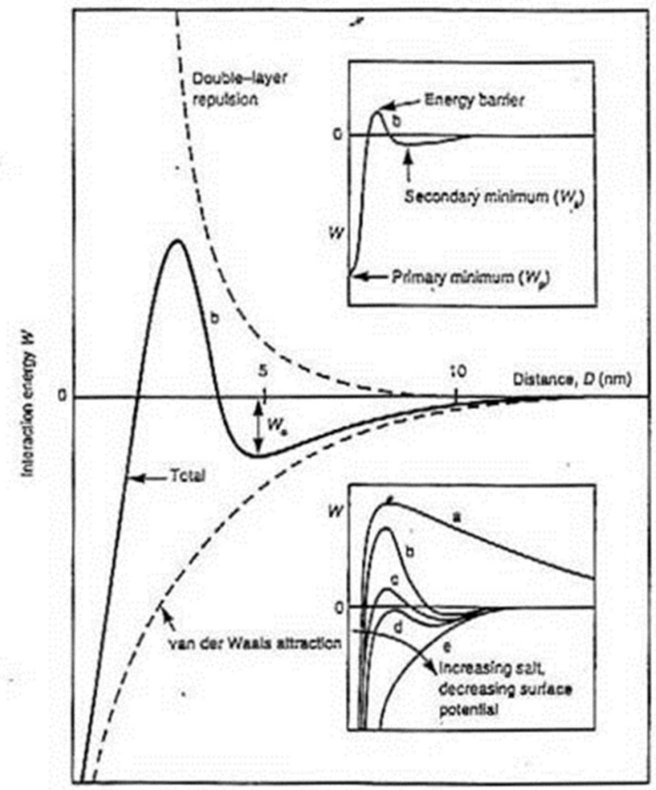
NTNU

Transitions of interest



Obtained by combining:

- Eccentricity of SAXS scattering
- Angle of tilt of SAXS scattering
- X-ray transmission



DLVO theory: vdW + Screened electrostatic rep.
(i.e The clay particles are effectively soft)

Clay avalanches

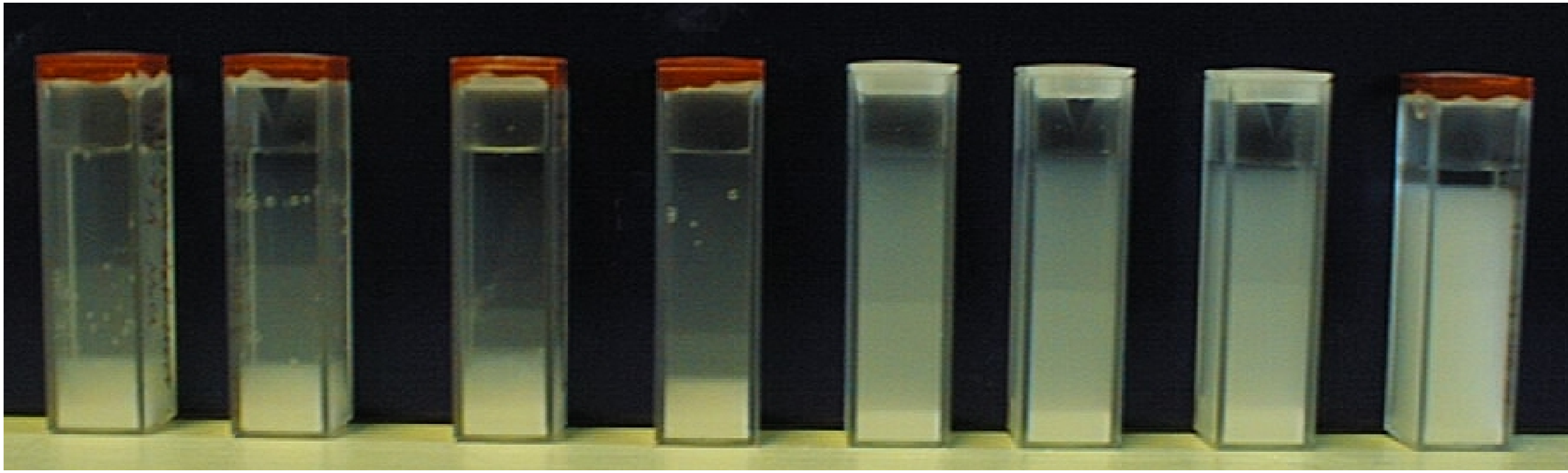
NGI

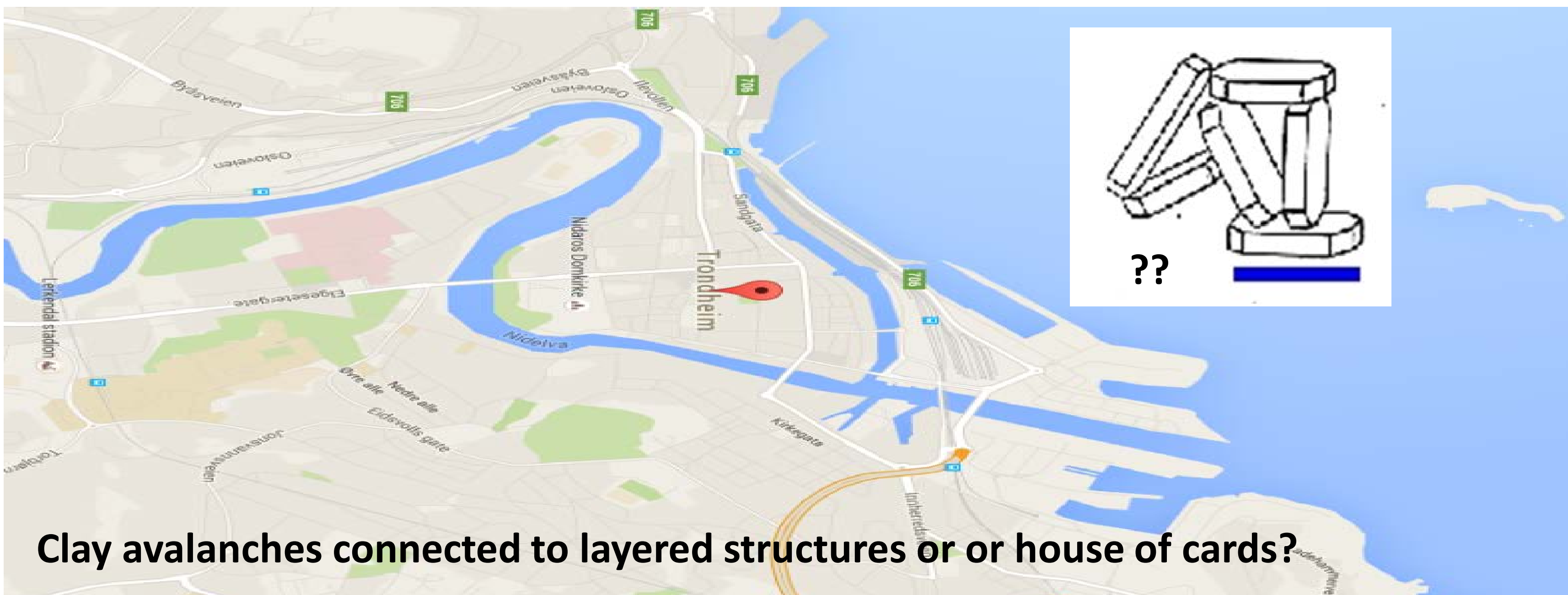
Norwegian Geotechnical Institute

Clay avalanche: Rissa Norway 1978

Increasing salt:

NTNU



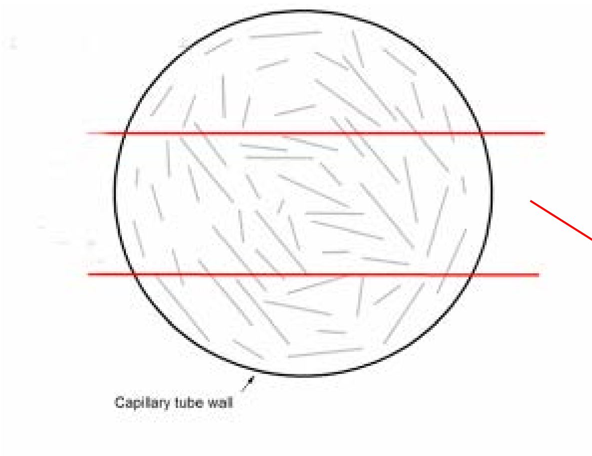


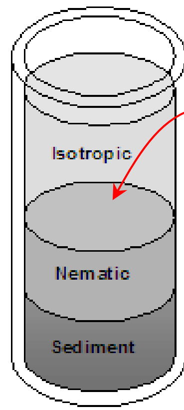
Clay avalanches connected to layered structures or or house of cards?

Snow avalanches and weak layers:
All snow exists as layers. Some layers are relatively more cohesive (stronger layers) and others are relatively less cohesive (weaker layers).

When the snowpack is stressed by rapid changes (e.g. wind-drifted snow, new snow, or rain) this stress can cause the weak layer to fracture.

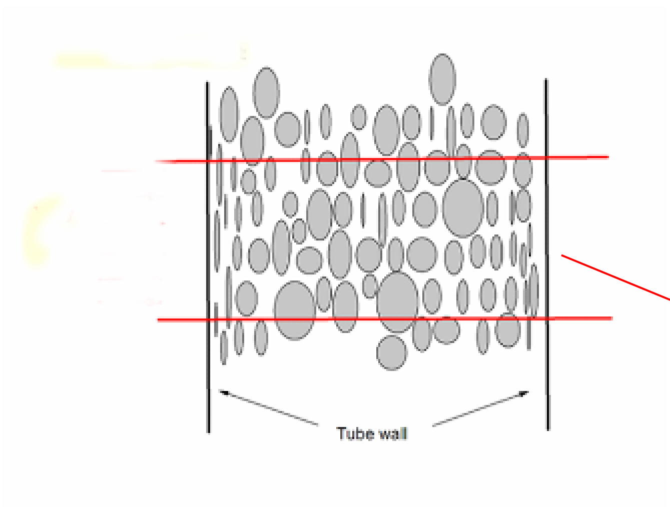
Cartoon of nematic phase of clay platelets seen from above:

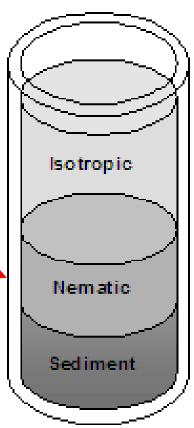




Wall anchoring

Cartoon of nematic phase of clay platelets, side-view:



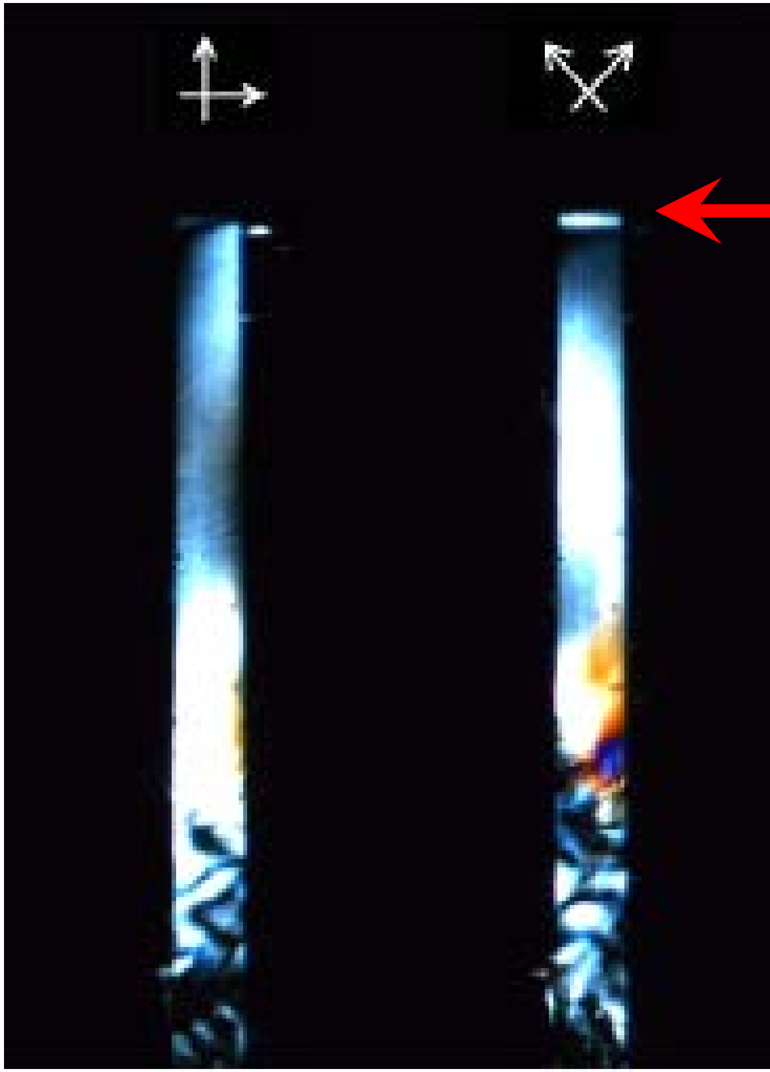


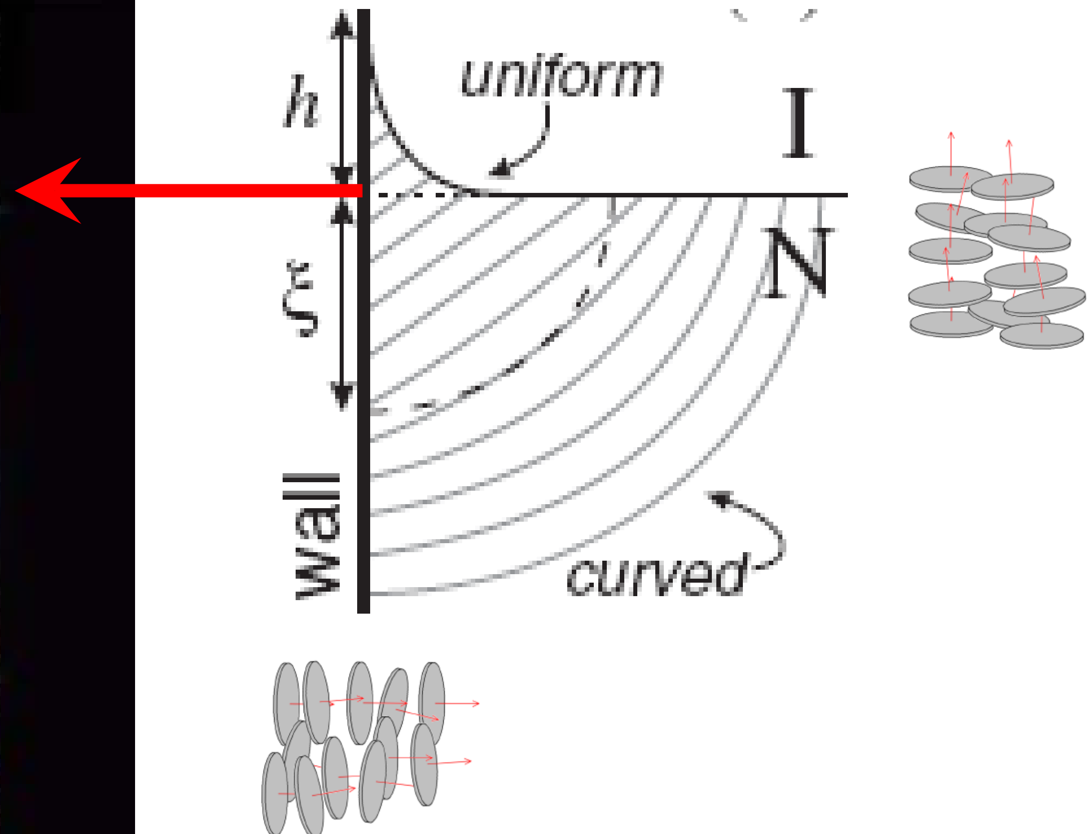
Order Parameter = O.P.

= Angular distribution function

$= S_2 = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$

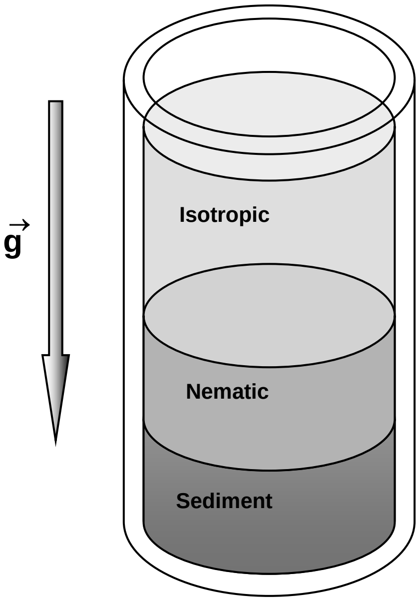
Anchoring to Nematic-Isotropic Interface:





The Isotropic-Nematic Interface in Suspensions of Na-Fluorohectorite Synthetic Clay. H. Hemmen, N. I. Ringdal, E. N. De Azevedo, M. Engelsberg, E. L. Hansen, Y. Meheust, J. O. Fossum and K. D. Knudsen. **Langmuir 25, 12507–12515 (2009)**

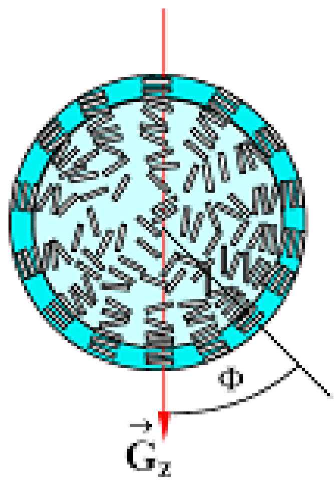
Response to magnetic field: Magnetic field guided self-organization:



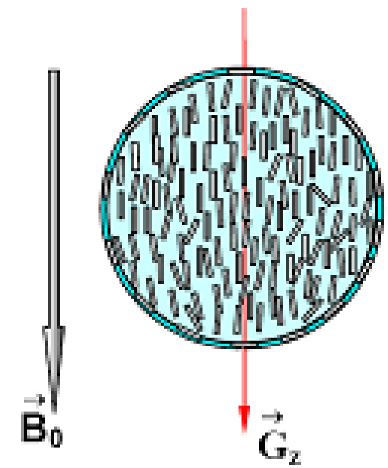
Glass wall anchoring confirmed by spatially resolved MRI measurements of anisotropic self-diffusion coefficient of water in the nematic phase.

Magnetic field induced ordering, due to diamagnetic anisotropy of the platelets at fields <u>above about 1 Tesla</u>.

$S_2 \sim -0.3$

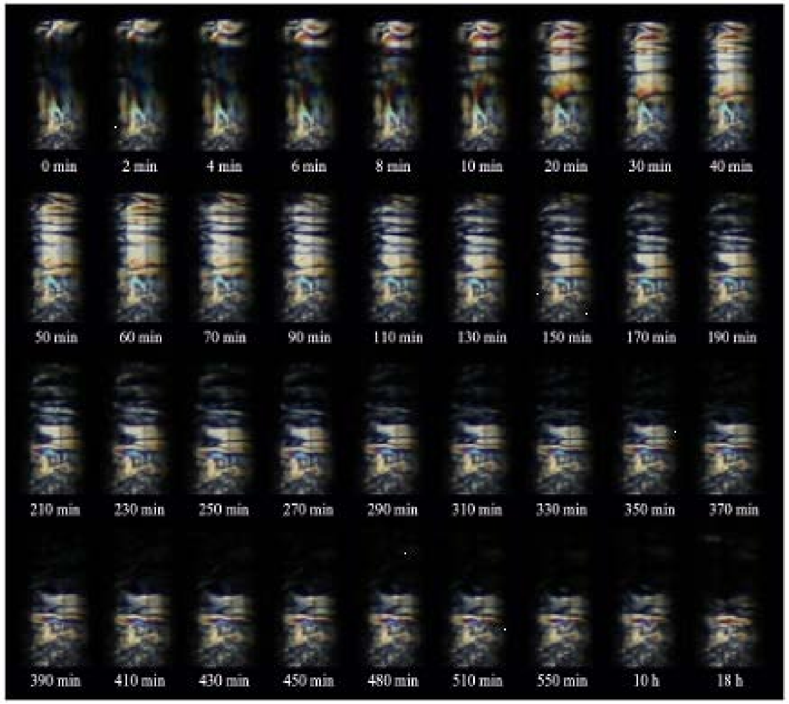


$S_2 \sim +0,5$

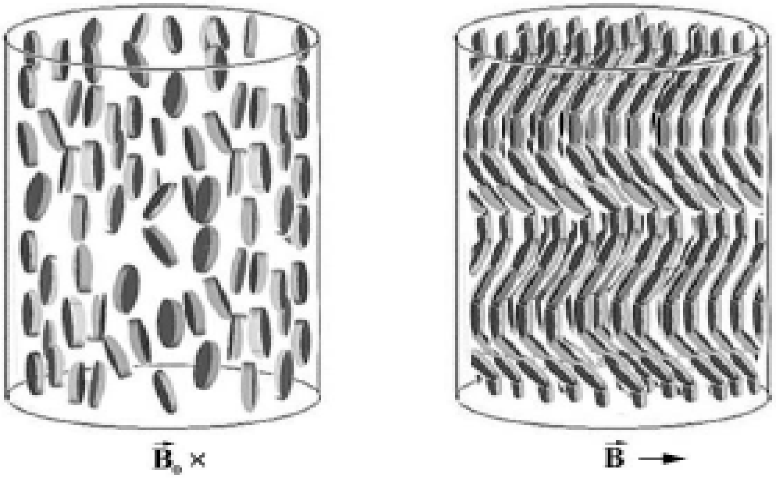


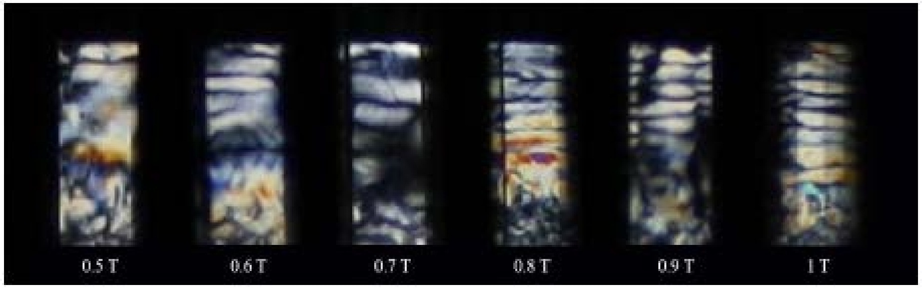
Anisotropic water diffusion in nematic self assemblies of clay nano-platelets suspended in water. E. N. de Azevedo, M. Engelsberg, J. O. Fossum and R. E. de Souza, **Langmuir 23, 5100 (2007)**

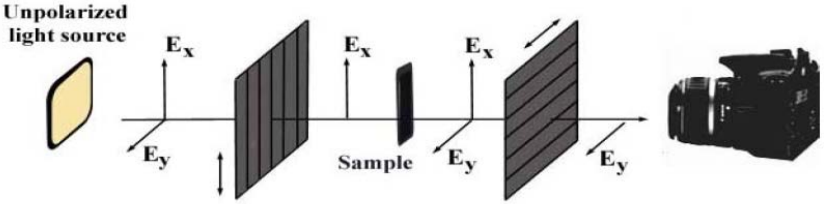
Color control of clay nematics between crossed polarizers



The Frederiks transition in an aqueous clay dispersion, H. Hemmen, E.L. Hansen, N.I. Ringdal and J.O. Fossum,
Revista Cubana de Fisica, vol. 29-1E, 59-61 (2012)

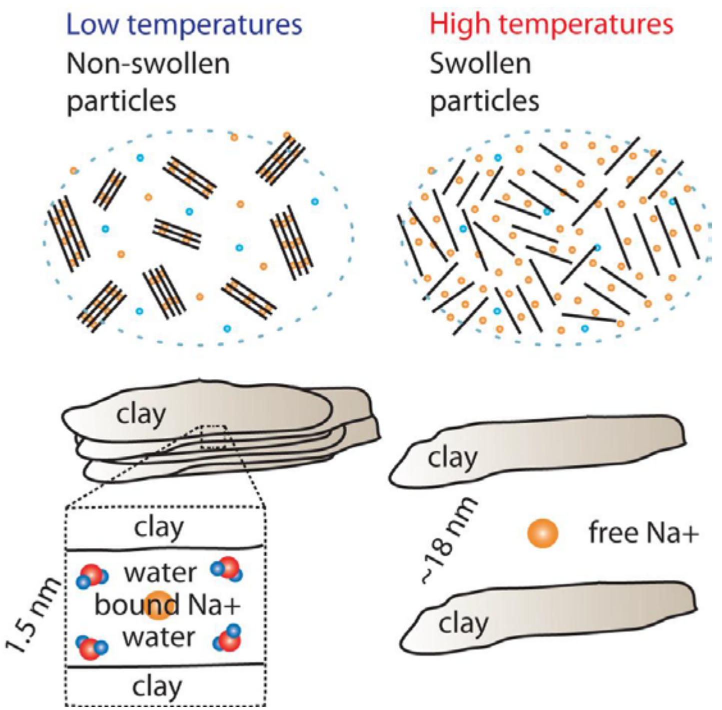




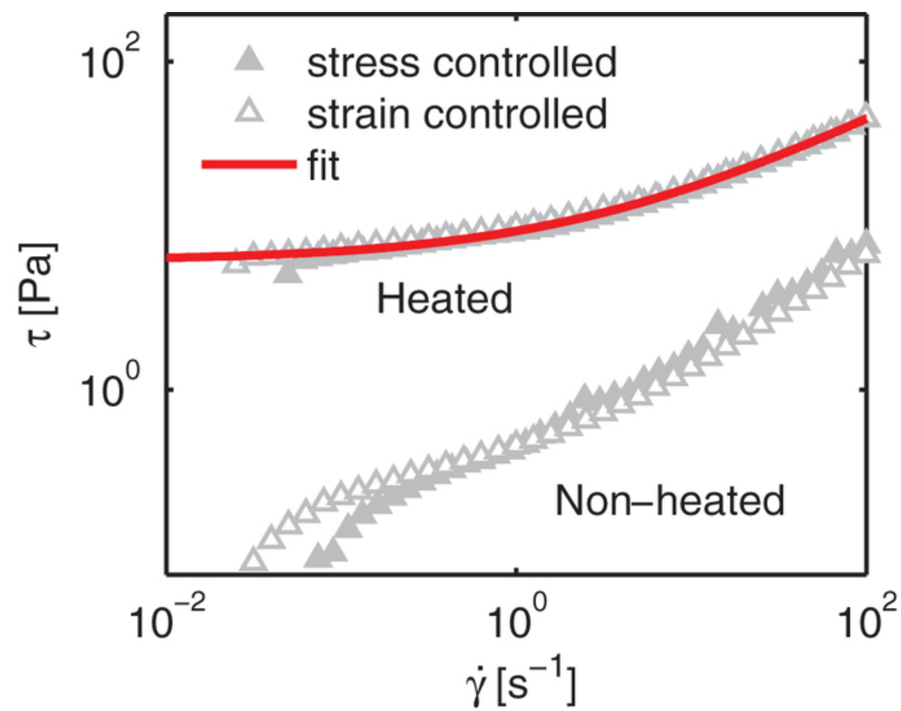


Swelling transition of a clay induced by heating, E. L. Hansen, H. Hemmen, D. M. Fonseca, C. Coutant, K. D. Knudsen, T. S. Plivelic, D. Bonn & J. O. Fossum, Scientific Reports by Nature 2, 618 (2012):

Crystalline → Osmotic → (Reversible only through drying) → Crystalline



Measured by synchrotron X-ray scatttering

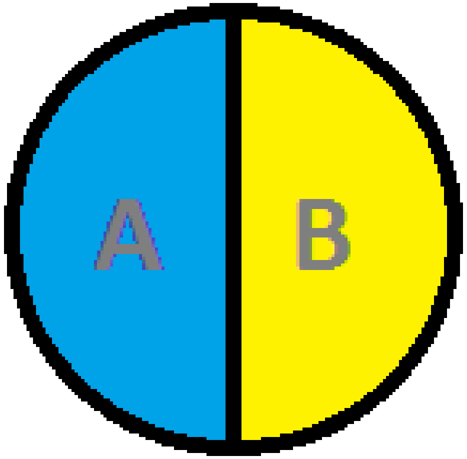


Measured by rheometry

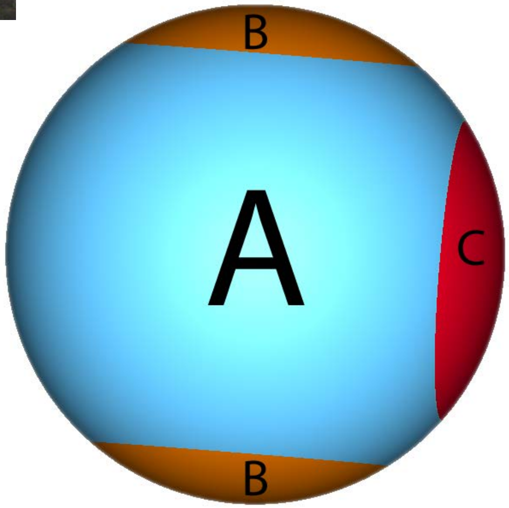
Current trends in soft matter physics: Active matter; Patchy particles

In ancient Roman religion and myth, Janus is the god of beginnings and transitions, thence also of gates, doors, passages, endings and time.

Usually depicted with **two faces**, looking to the future and to the past



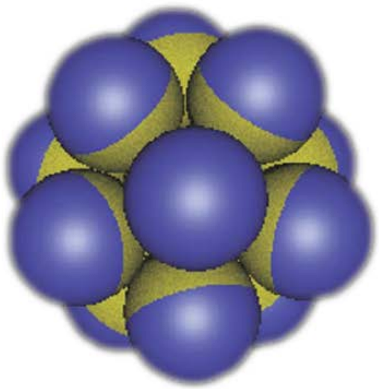
Janus particles

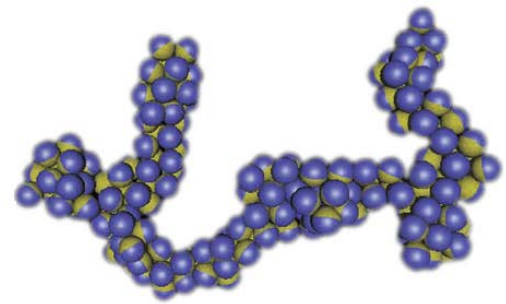


Patchy particles: Colloids with a valence

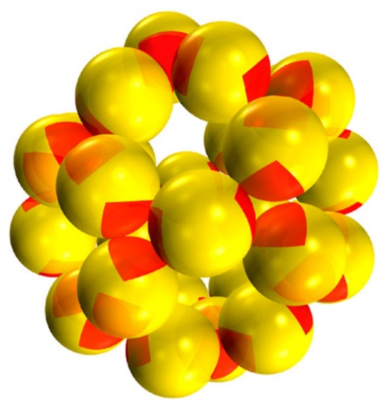
Applications Janus or patchy units: Self-assembly into (ordered) structures «Colloids with valence»

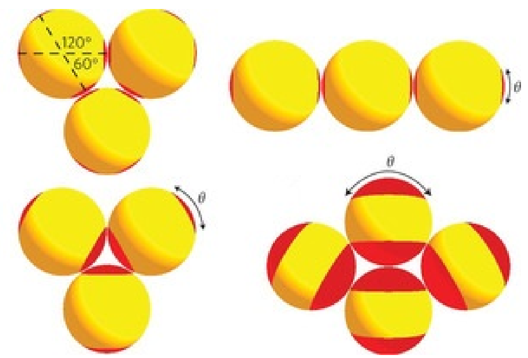
Janus



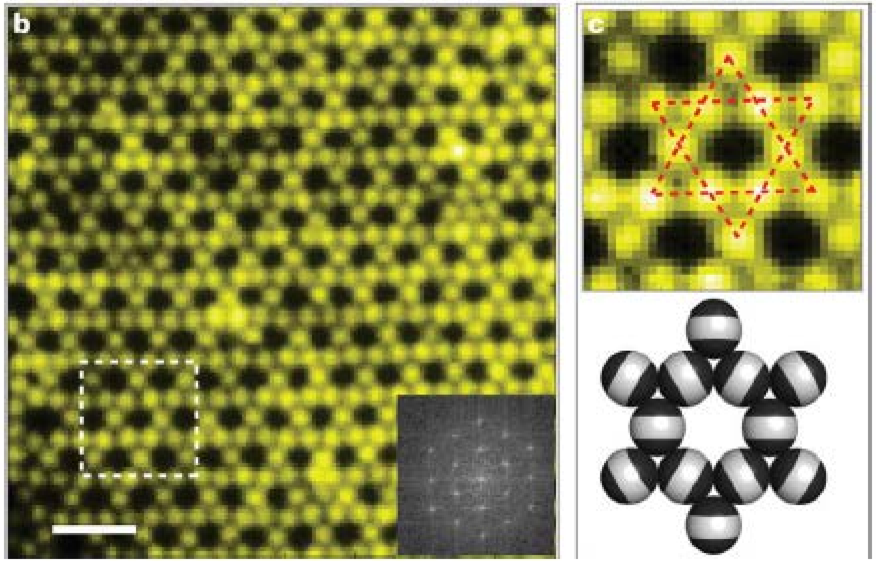


Patchy



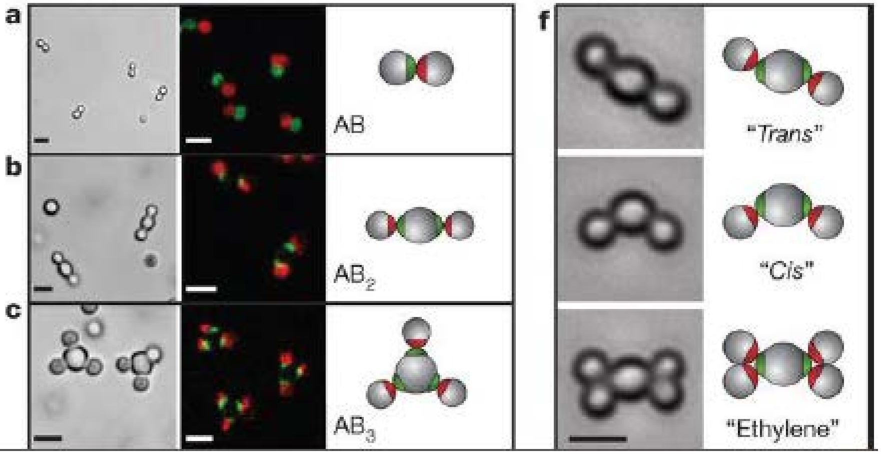


S. Granick & S. Jiang & Q. Chen, **“Janus particles”**, Physics Today, **68** (2009)
F. Romano & F. Sciortino, **“Patterning symmetry in the rational design of colloidal crystals”,** Nature Commun. **3**, 975 (2012)



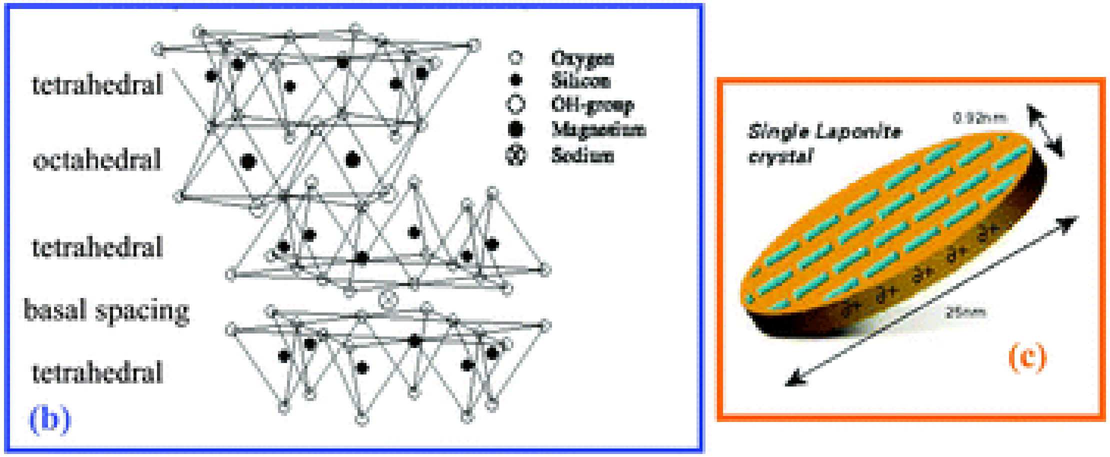
Patchy colloidal “molecules”
David Pine Group, Nature 2013

“Kagome lattice”
Q. Chen, S. C. Bae & S. Granick,
Nature 2012



Self-assembly into (ordered) structures

(a) $Na^{+}_{0.7}[(Si_{8}Mg_{5.5}Li_{0.3})O_{20}(OH)_{4}]^{-0.7}$



Laponite
(synthetic clay particles)

Figure 2: Behaviour of the patchy-particle model for Laponite discs.

From

Observation of empty liquids and equilibrium gels in a colloidal clay

Barbara Ruzicka, Emanuela Zaccarelli, Laura Zulian, Roberta Angelini, Michael Sztucki, Abdellatif Moussaïd, Theyencheri Narayanan & Francesco Sciortino

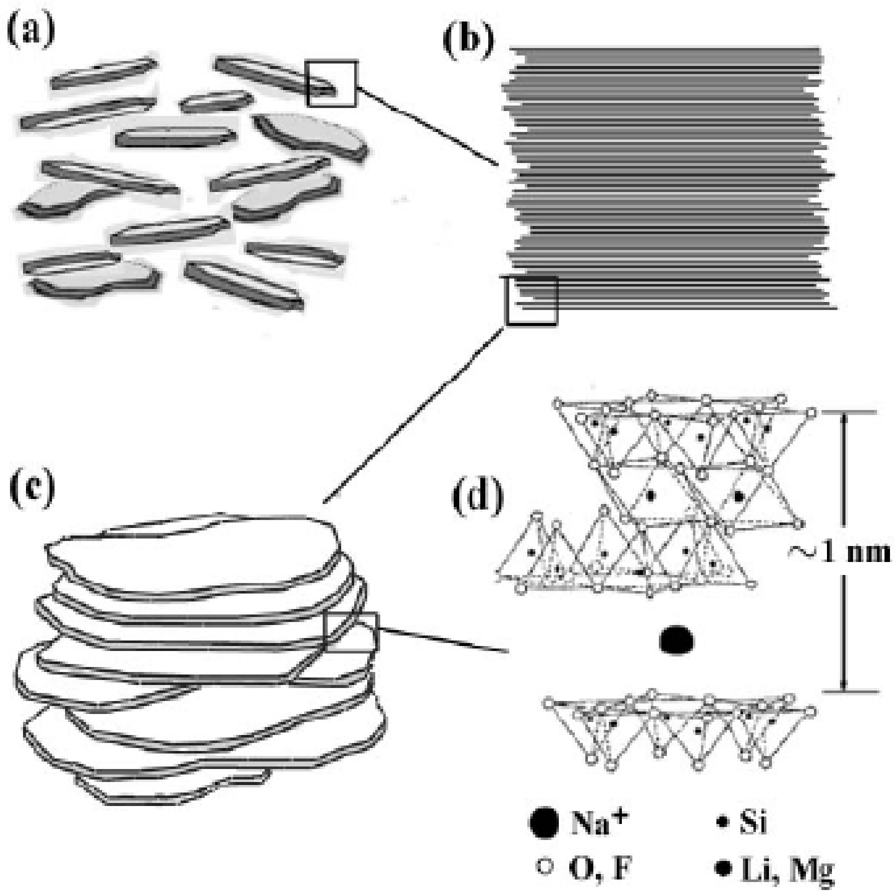
Nature Materials **10**, 56–60 (2011) | doi:10.1038/nmat2921

Received 30 April 2010 | Accepted 09 November 2010 | Published online 12 December 2010

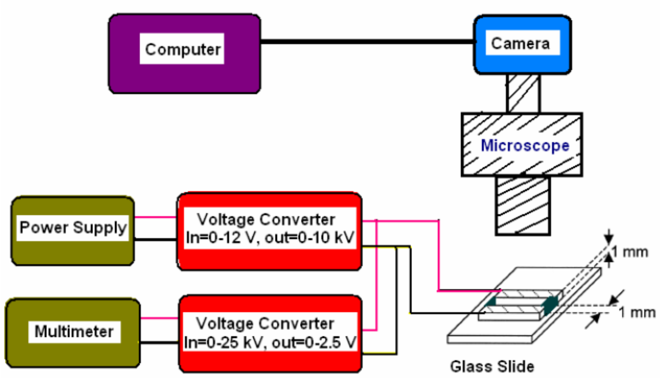
Example of «natural patchy nano-particles»

NTNU

Q-fluorohectorite: Q_x-$(Mg_{3-x}Li_x)Si_4O_{10}F_2$,
Q is the exchangeable cation (Q = Na^+, Ni^{2+}, Fe^{3+}, etc)

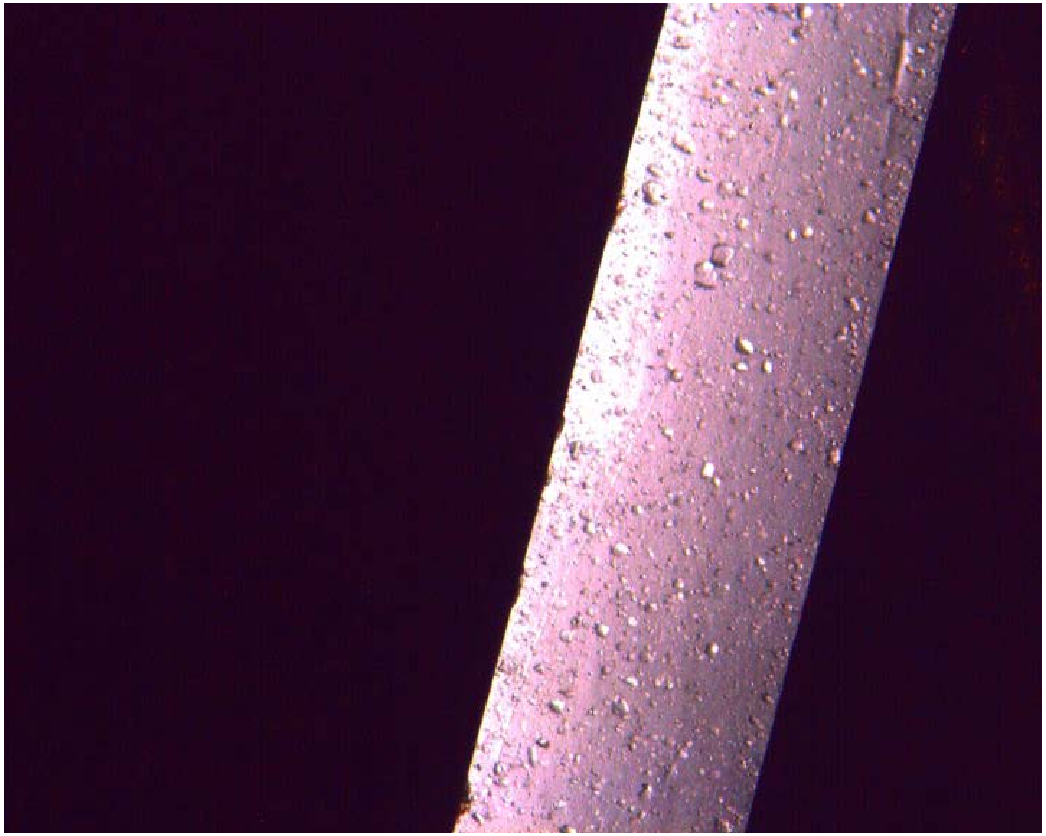


Clay particles suspended in oil:

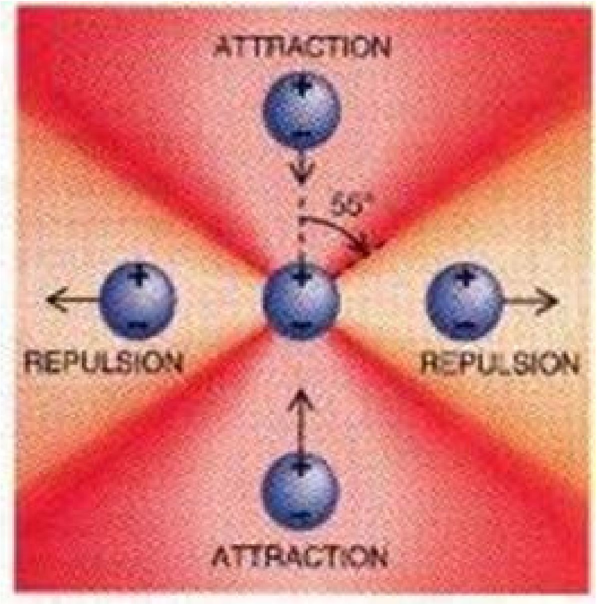


Video microscopy (real time):

- ~500 V -



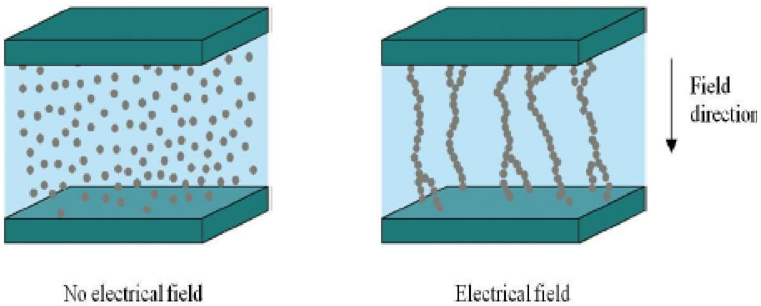
- 1 mm -



Electrorheology: Smart Materials

Electro-rheological fluids

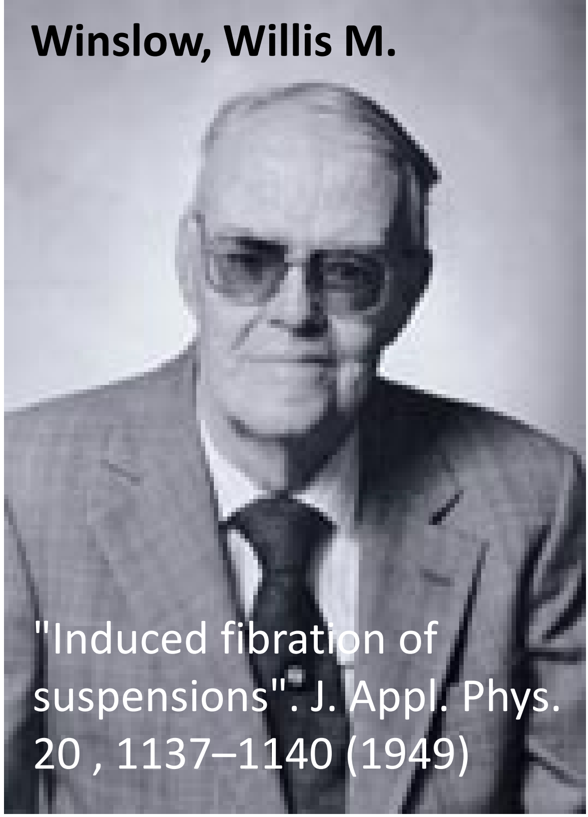
<u>Winslow effect:</u>



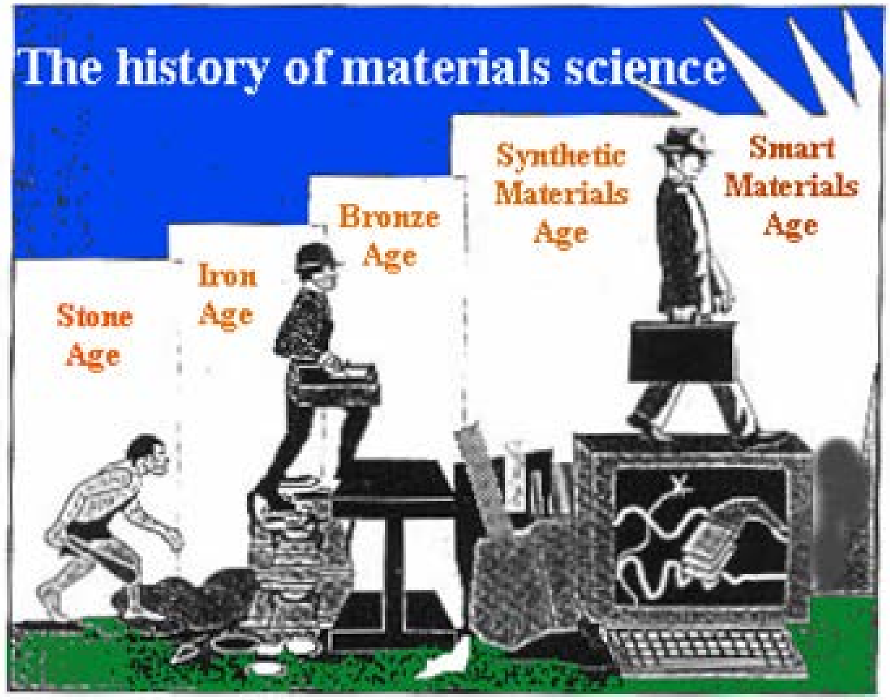
Viscosity can increase by a factor 100 000 in response to an electric field!

- Electric fields induce dipole attraction and chain formation
- Rapid and reversible: valves, clutches, breaks, flexible electronics, microfluidics
  http://en.wikipedia.org/wiki/Electrorheological_fluid

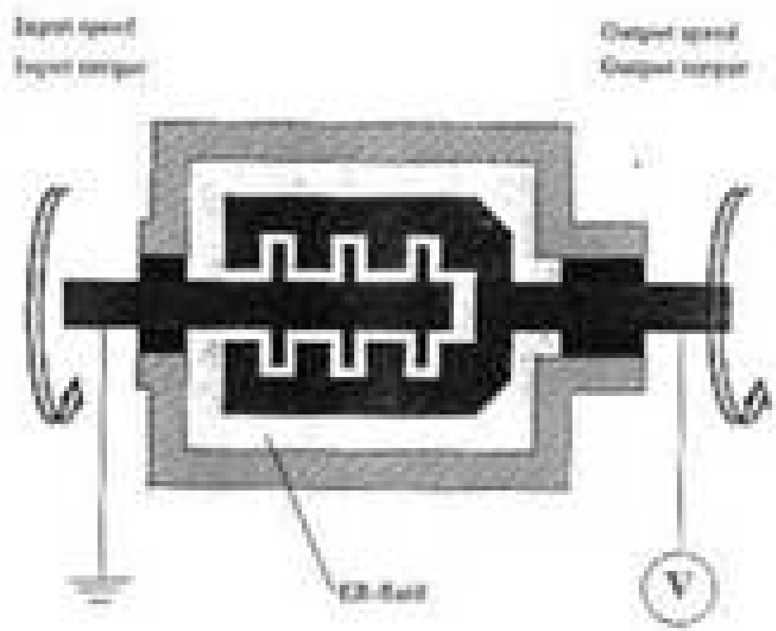
Large yield stress -> 200 kPa or more 100 times viscosity increase (up to 100000 times according to wiki)



U.S. Patent 2,417,850: Winslow, W. M.: 'Method and means for translating electrical impulses into mechanical force', 25 March 1947



The history of materials science
Stone Age
Iron Age
Bronze Age
Synthetic Materials Age
Smart Materials Age

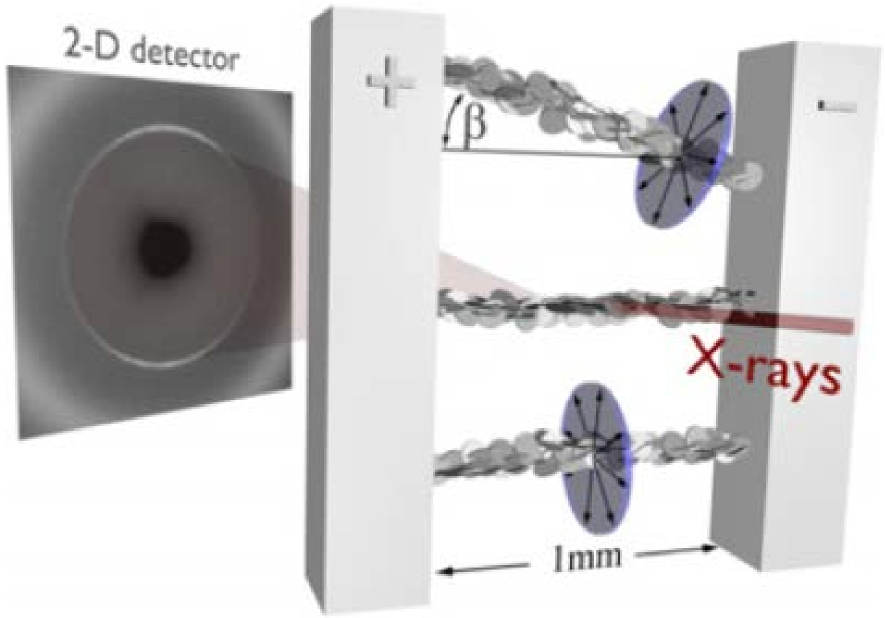


V

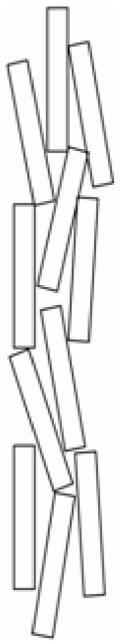
Swiss Norwegian Beam Line SNBL at ESRF Grenoble:

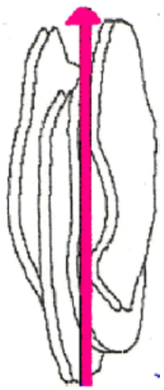
ESRF = European Synchrotron Radiation Facility

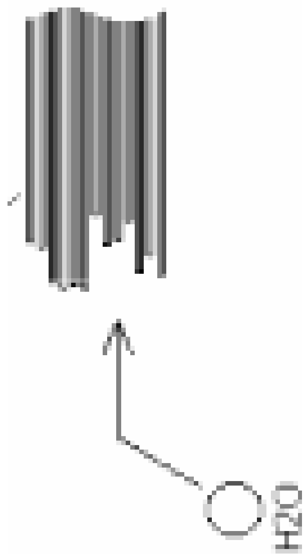
WAXS:

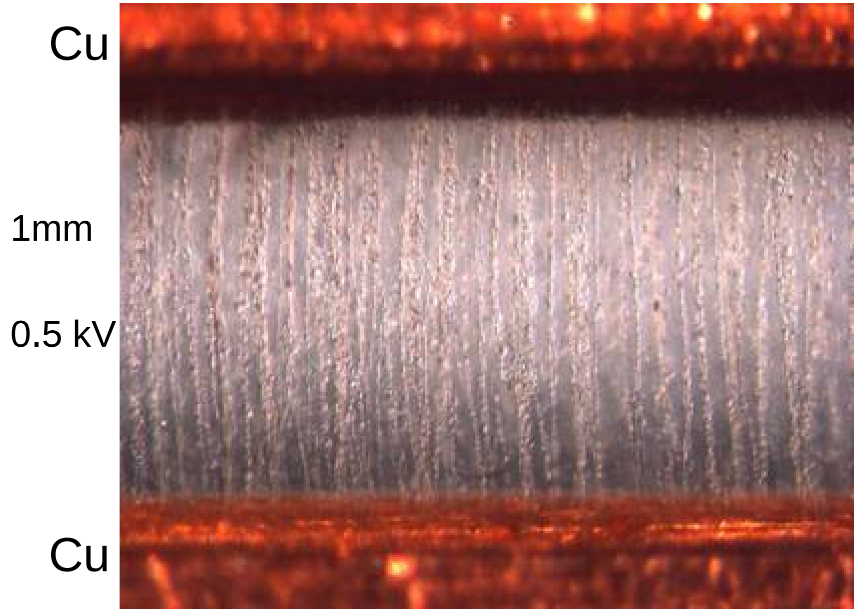


Experiments at SNBL/ESRF:

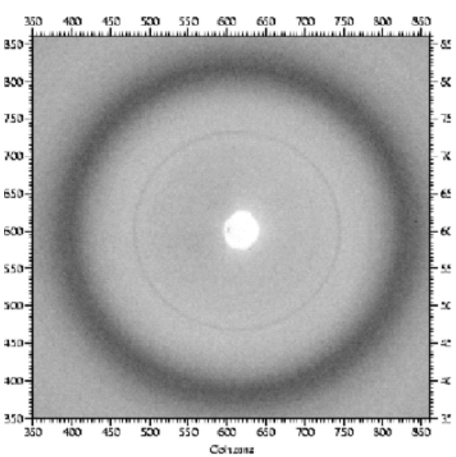




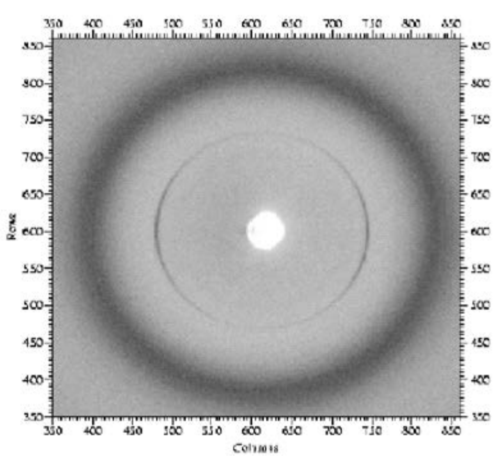


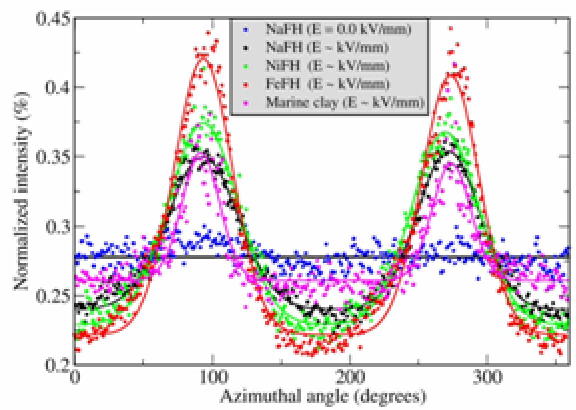


Before: 0 V/mm

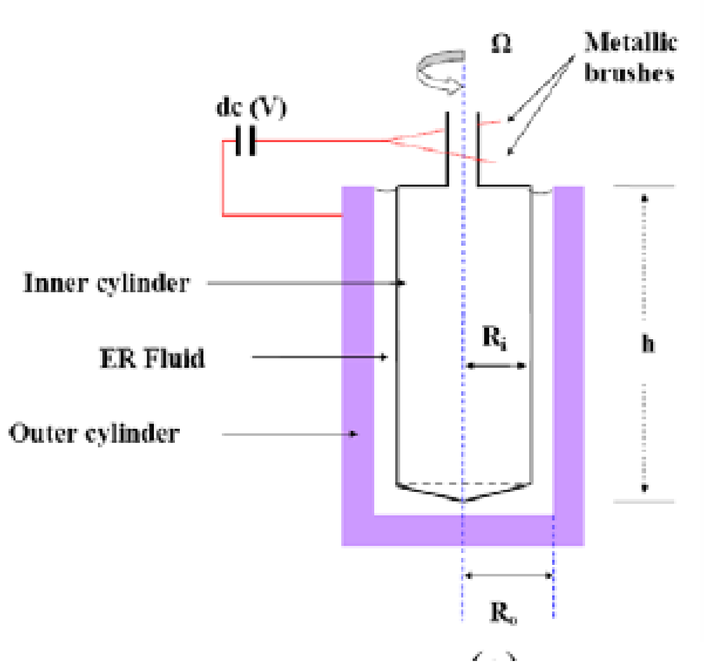


After: 500 V/mm





Our Physica MCR 300 Rheometer inl electrorheol. cell:



Langmuir 24, 1814 (2008)

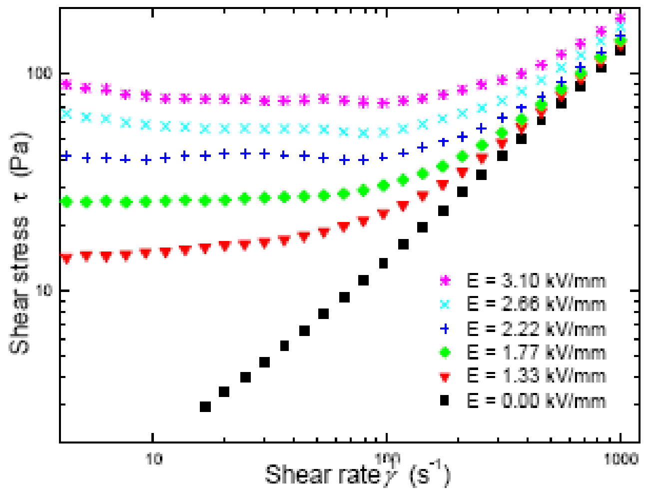
J. Phys.: Condens. Matter 22, 324104 (2010)

J. Rheol. 55, 2011 (2010)

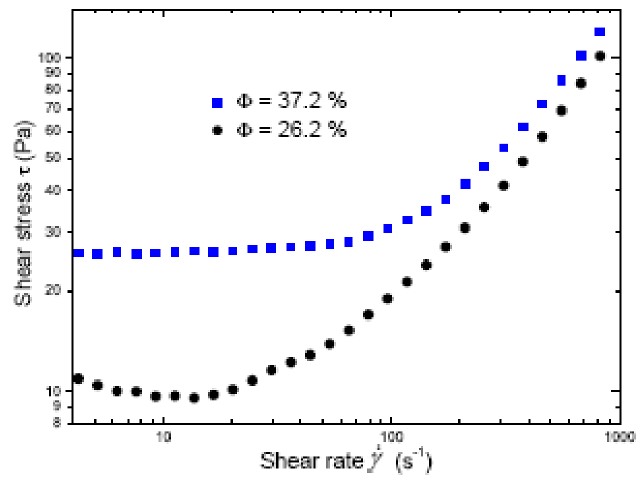
Flow-curves for fluorohectorite in silicone oil:

NTNU

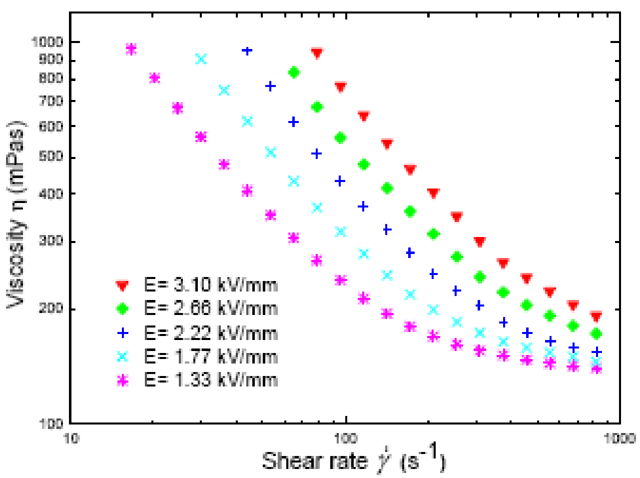
Dynamic yield stress:
Yield stress for a completely broken down (i.e., subjected to continuous shearing) ER fluid.
CSR Tests: **Steady-State Shearing.**
Typically measured by extrapolating the shear stress versus shear rate curve back to the shear stress intercept at zero shear rate.



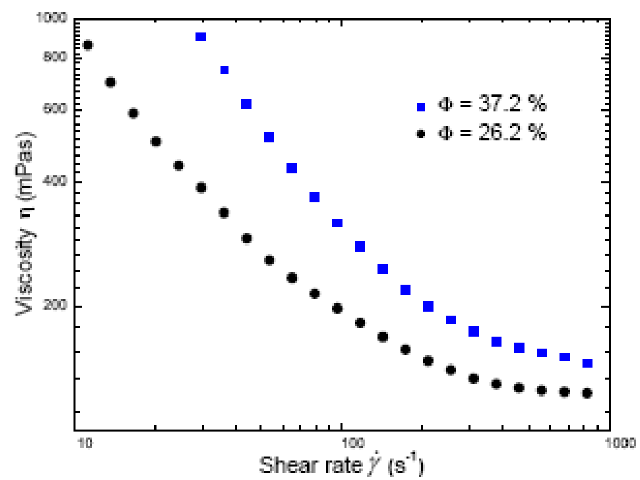
(a)



(a)



(b)



(b)

$$\tau = \eta \, d\gamma/dt$$

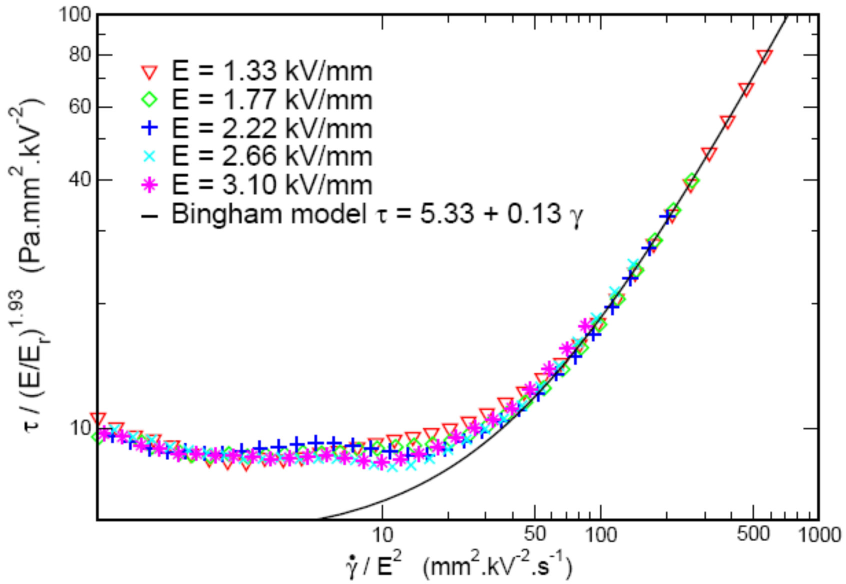
Scaling (data collapse) of flow curves:

•Dipole-dipole interaction is proportional to the square E^2 and to $(1/\text{distance})^2 = (1/\Phi)^{2/3}$

•Shear strength acting on a particle within an ER chain is proportional to the shear rate $d\gamma/dt$

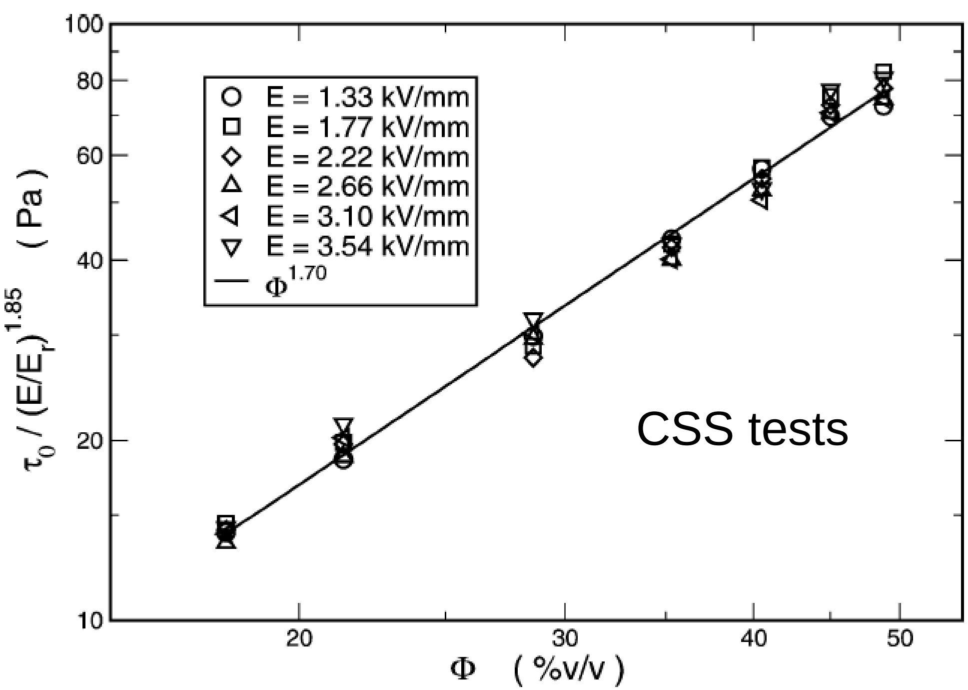
•Normalized shear representing relative impact of the shearing process on the cohesive ER structures, is $(d\gamma/dt)/(\Phi^{2/3}E^2)$

$$\tau(\Phi, E) = \Phi^{\beta} E^{\alpha} f\left(\frac{\dot{\gamma}}{\Phi^{2/3} E^2}\right)$$



Yield stress:

Theories predict: $$\tau \propto E^{\alpha}\,\Phi^{\beta}$$



Static yield stress:
Yield stress for an undisrupted ER fluid.

Log-log plot of the static yield stress, normalized by $E^{1.86}$, vs. the volume fraction at different strengths of the applied electric field. A power law $\beta \approx 1.70$ fits to the whole dataset..

ER Suspensions of Laponite in Oil *Langmuir, Vol. 24, No. 5, 2008* 1821

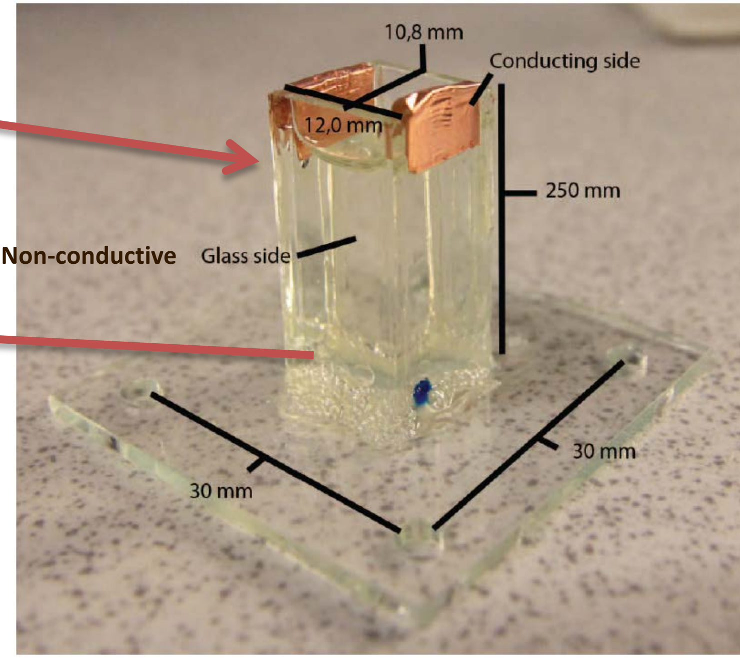
Table 1. Comparison of Static Yield Stress Values for Various ER Fluids Including That Addressed in the Present Paper, under an Applied Electric Field of About 1.0 kV/mm

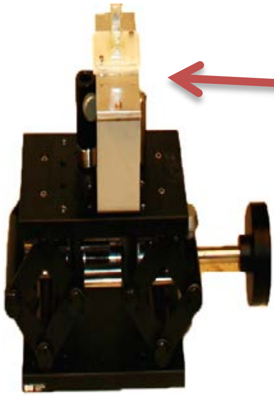
ER fluids →	our sample	mica[18]	hematite[43]	saponite[44]	zeolite[45]	GER[46]
Φ →	1.9% (v/v)	15% (v/v)	15% (v/v)	0.11 g/mL	30% (v/v)	30% (v/v)
τ_0 (Pa) →	~20	~100	~85	~50	~3000	~15000

Sample cell

2x ITO transparent electrodes

2x glass walls





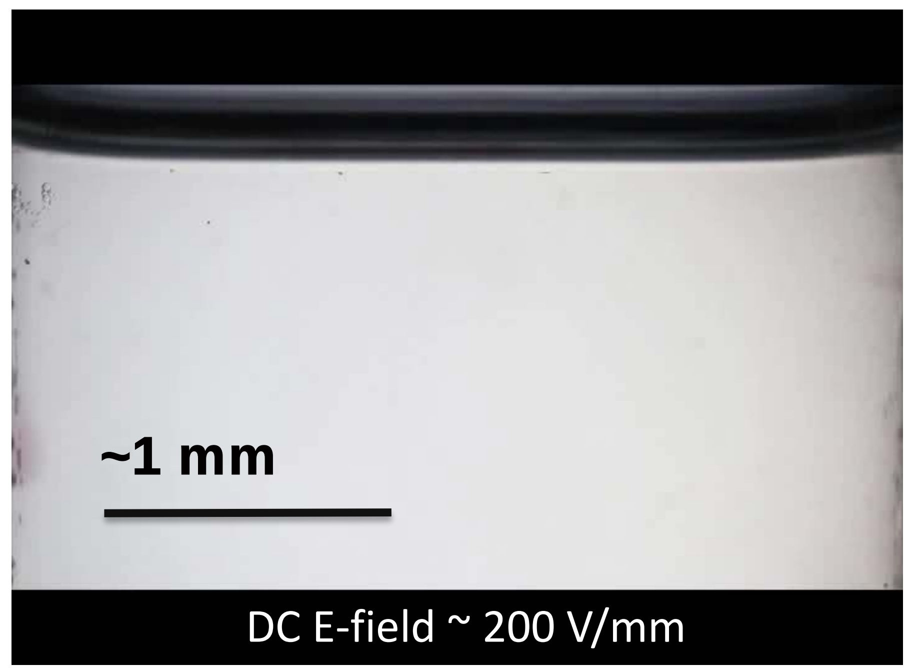
Translation stages

Clay in silicone oil dispersion

(~ 1 mm diameter drop)

Castor oil

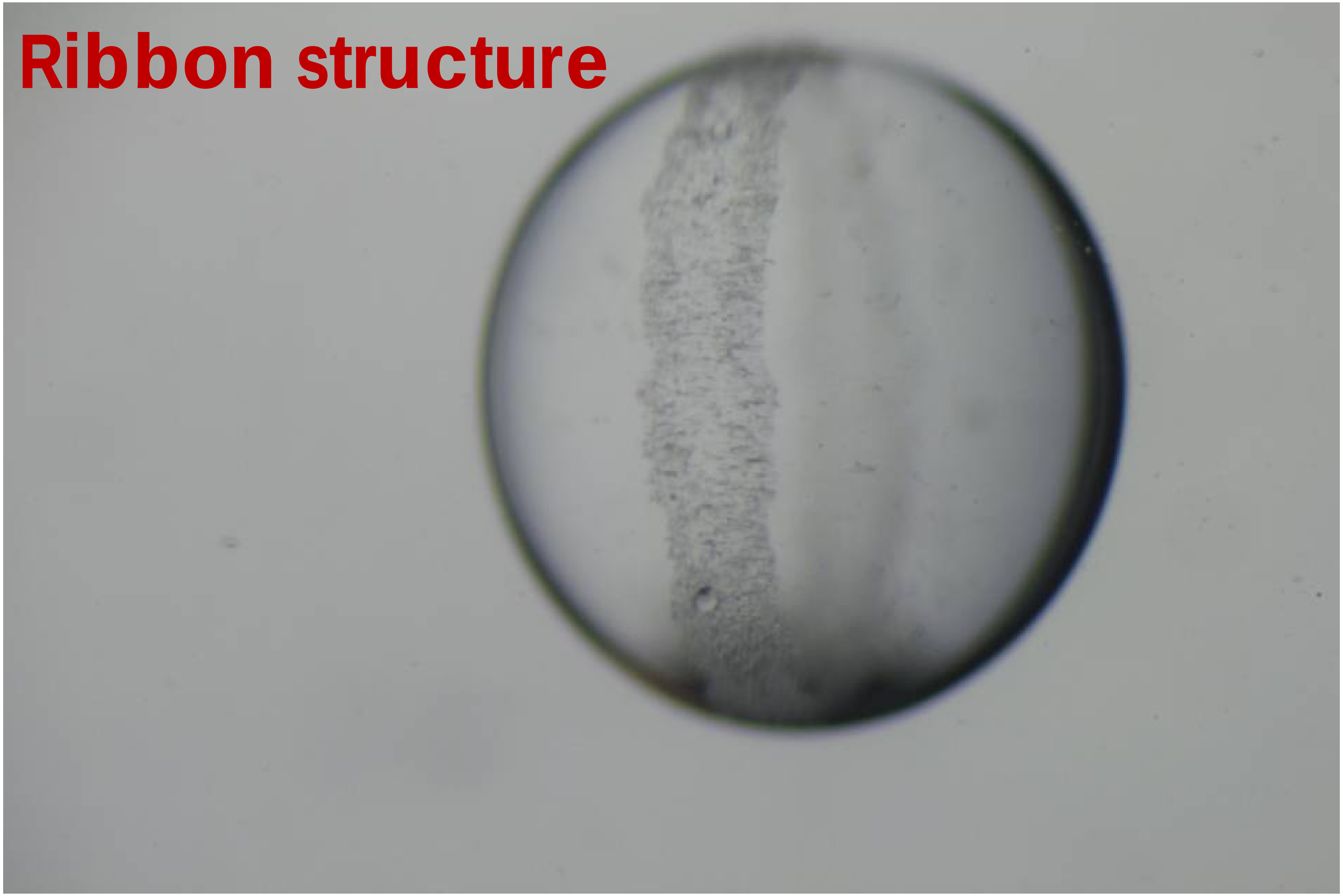
(continuous phase)



Speeded up x10

E-field induces flows of liquids

Ribbon structure



Our Condition 1: Two leaky dielectric liquids

Our Condition 2: $\sigma_{drop} < \sigma_{surrounding}$

When DC E-field applied:

Free charge accumulation

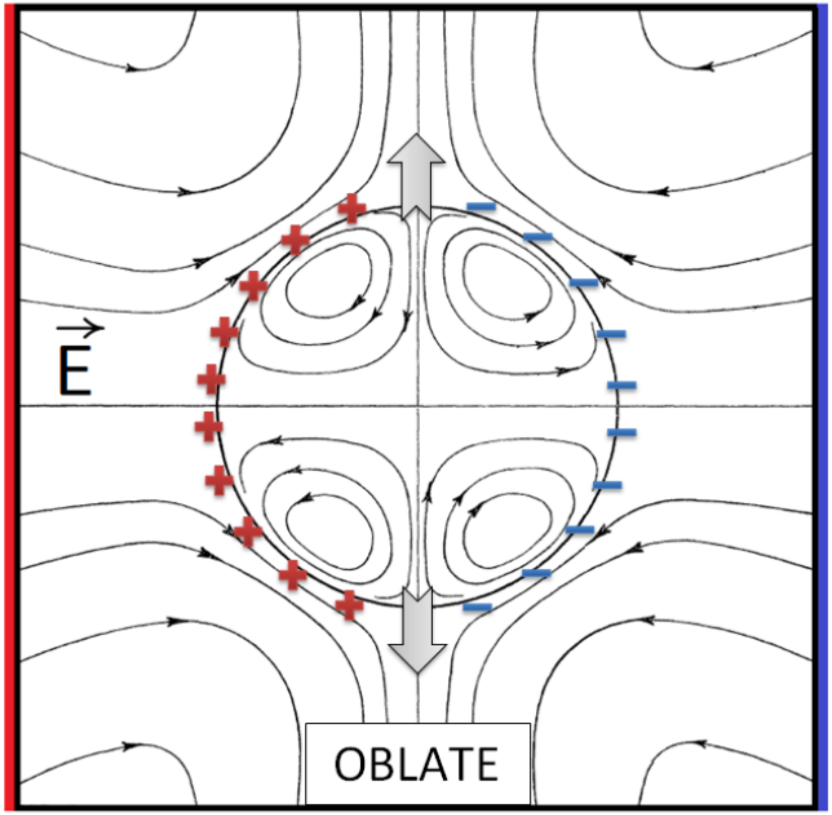
↓

Maxwell electric stress

↓

Liquid circulation flows

Oblate deformation



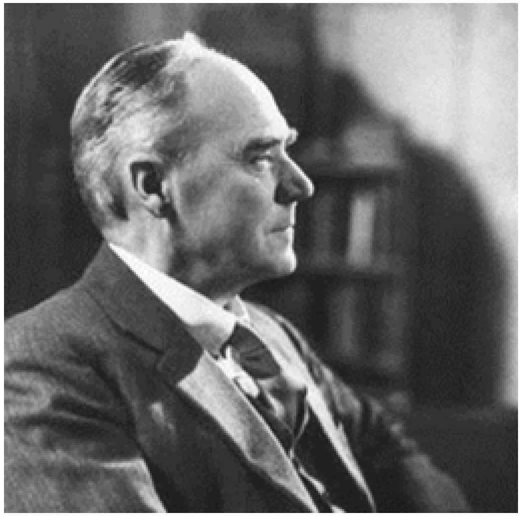
Adopted from [Taylor 1965]

Electro-hydrodynamic flow

NTNU

Discard the notion that the suspending fluids can be treated as insulators:

- Conductors: water, mercury
- Dielectrics: benzene
- **"Leaky dielectrics":** castor oil, corn oil, mineral oils, etc



Studies in electrohydrodynamics

I. The circulation produced in a drop by an electric field

By Sir Geoffrey Taylor, F.R.S.

(*Received* 22 *July* 1965)

With an addendum by A. D. McEwan and L. N. J. de Jong

(*Received* 21 *December* 1965)

Proc. R. Soc. Lond. A 291,159-166 (1966)

Our Condition 1: Two leaky dielectric liquids

Our Condition 2: $\sigma_{drop} < \sigma_{surrounding}$

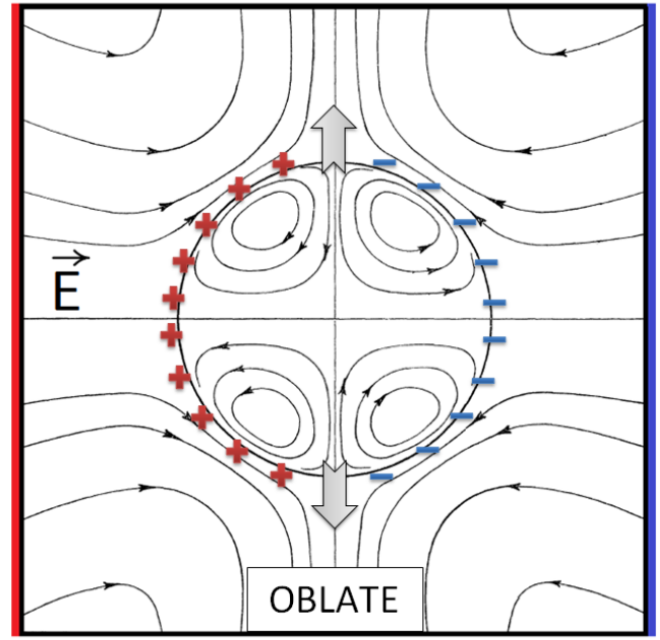
When DC E-field applied:

Free charge accumulation

Maxwell electric stress

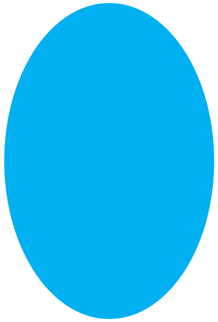
Liquid circulation flows

Oblate deformation

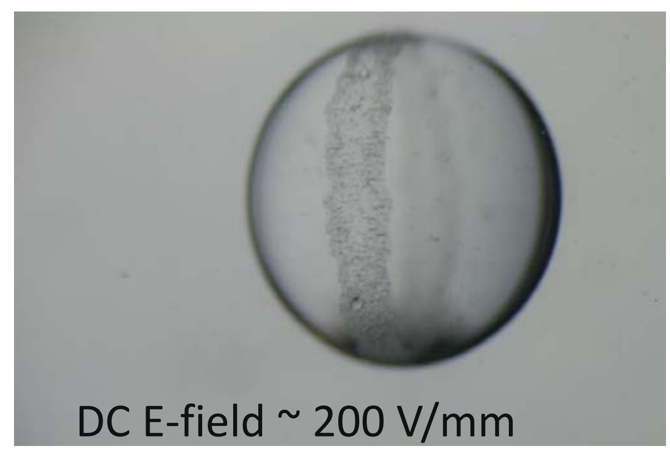


Adopted from [Taylor 1965]

Ribbon structure

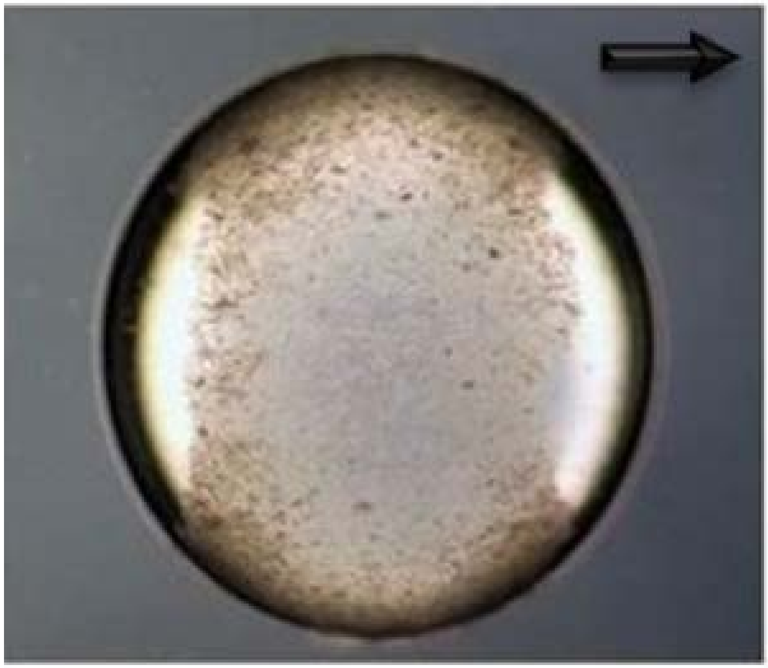


DC E-field ~ 200 V/mm



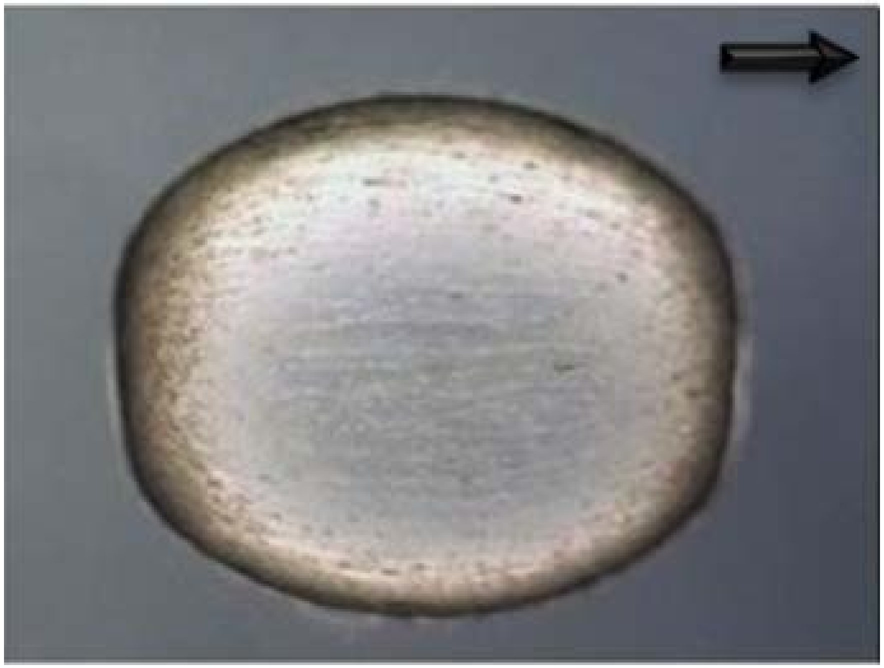
Electro-hydrodynamic Taylor flow

Oblate-to-Prolate transition



E=200 Vmm^{-1}

Electro-hydrodynamic flow

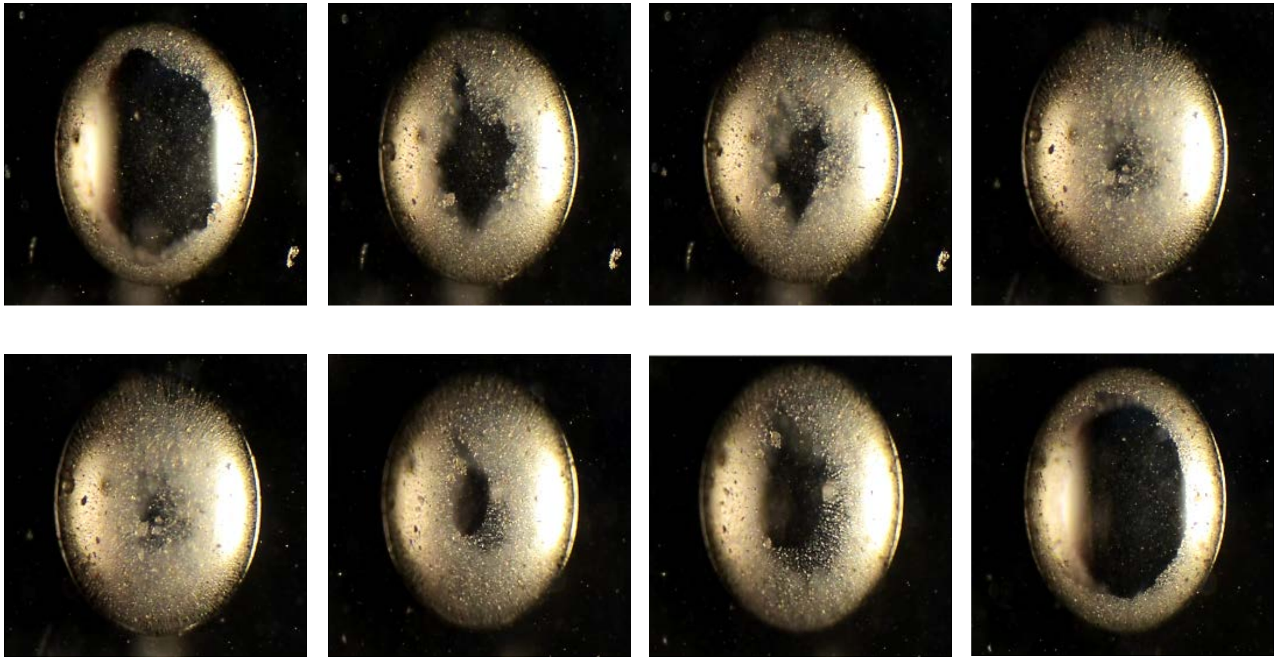


E=500 Vmm^{-1}

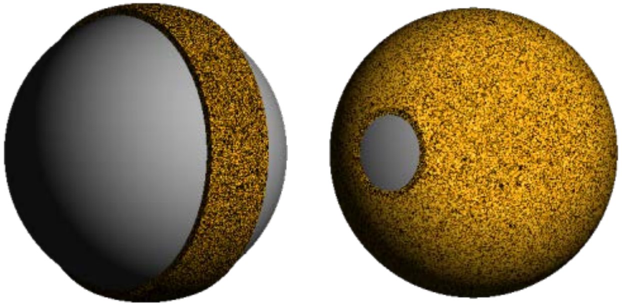
Dipole-dipole interactions

200 ⟶ 500 V/mm

200 ⟵ 500 V/mm



Electro-hydrodynamic flow



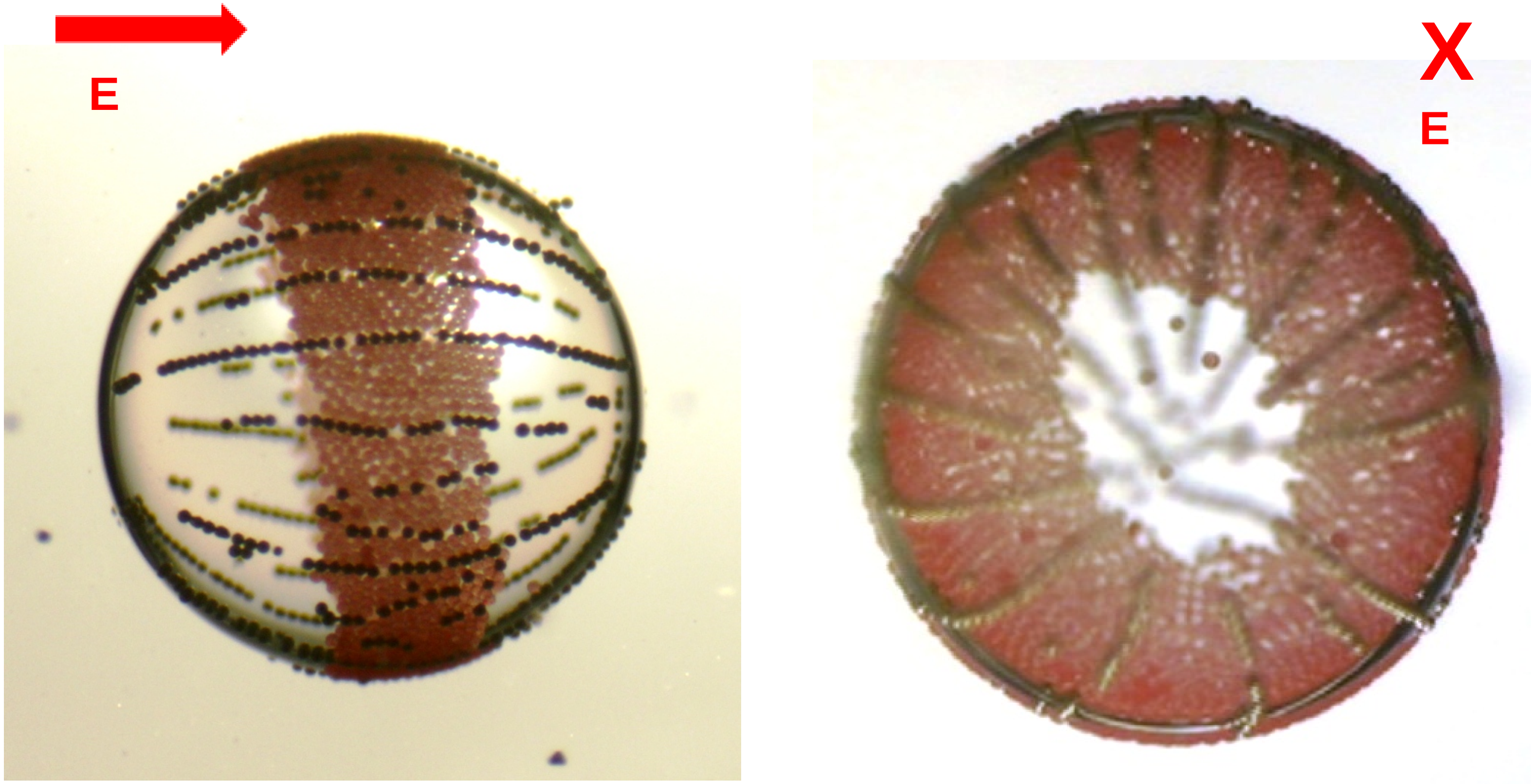
Dipole-dipole interactions

Active pupil-like colloidal shell (opening - closing)

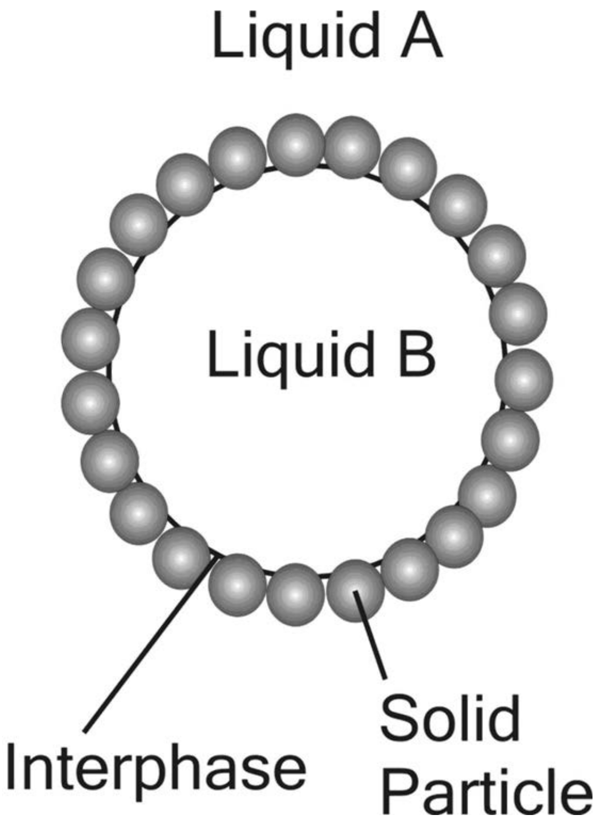
Active pupil-like colloidal shell (opening - closing)

Active structuring of colloidal armour on liquid drops, P. Dommersnes, Z. Rozynek, A. Mikkelsen, R.Castberg, K. Kjerstad, K. Hersvik & J. O. Fossum, Nature Communications 4, 2066 (2013)

NTNU



Electric field controlled particle structuring at droplet liquid-liquid interfaces



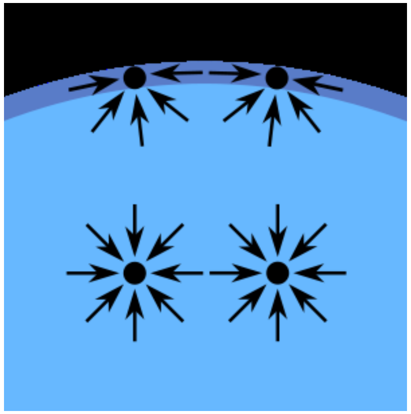
Surface Energy: $E = \gamma A$

$A = \text{Surface area}$ $\quad \gamma_{WA} = 0.0073\,\text{N/m}$

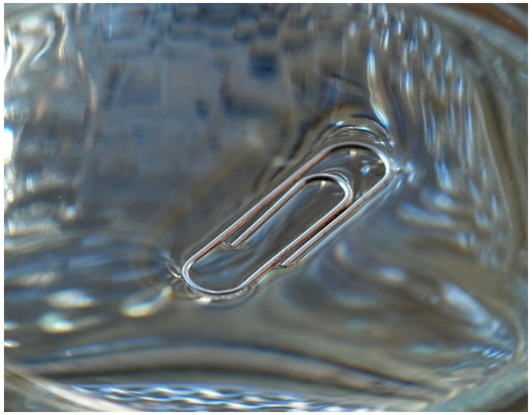
Capillary binding: A particle at the interface is trapped in a capillary barrier with a substantial energy cost of moving to either side of the liquid interface.

Origin of capillary binding:
Surface tension:

The forces on molecules of a liquid:

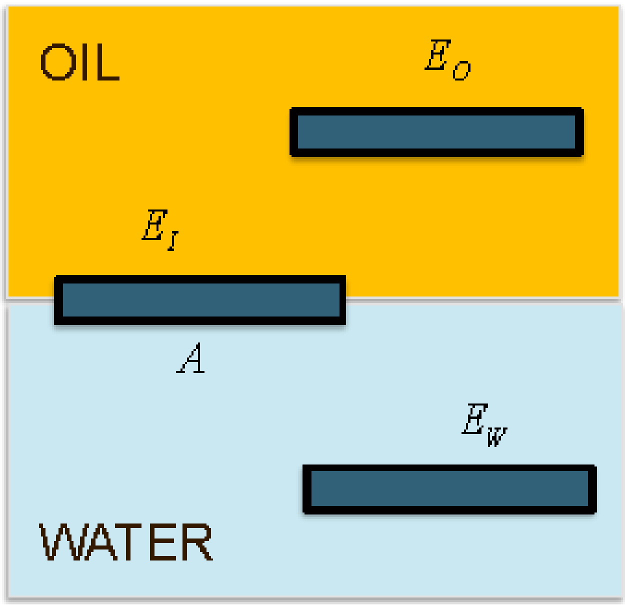


Surface tension preventing a paper clip from submerging



Capillary binding

Capillary binding of a flat solid particle at a liquid interface



Particle surface energy :

$$E_O = 2A\gamma_{SO}$$

$$E_W = 2A\gamma_{SW}$$

$$E_I = A\gamma_{SO} + A\gamma_{SW} - A\gamma_{OW}$$

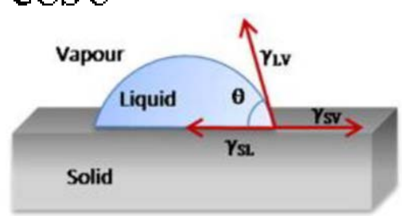
Energy gain :

$$E_I - E_O = -A\gamma_{OW}(1+\cos\theta)$$

$$E_I - E_W = -A\gamma_{OW}(1-\cos\theta)$$

Wetting angle Young's relation:

$$\gamma_{SO} = \gamma_{SW} + \gamma_{OW}\cos\theta$$



Energetically favorable to adsorb articles at the interface.

Typically:

$A_p\gamma_{OW}$ ~ 10000 kT for microparticles

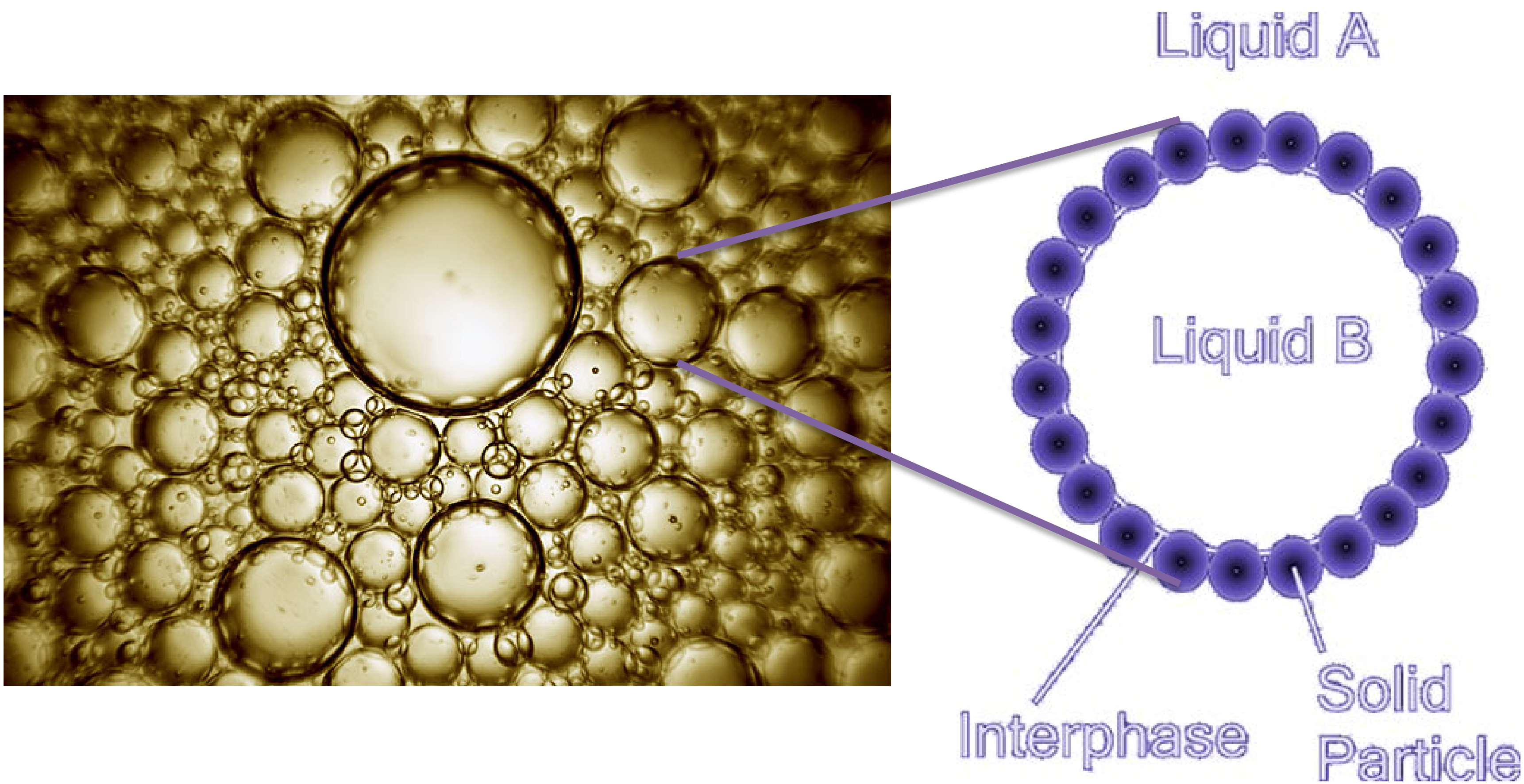
NTNU

Case 1: Partly covered drops ⇒ Coalescence
Case 2: Fully covered drops ⇒ No coalesence

Fully covered drops do not coalesce ⇒ Pickering emulsions: Experiments at NTNU Trondheim

NTNU

Colloidal particles as emulsion stabilizers: Pickering («physical») emulsions



Pickering («physical») emulsions

"Separation of Solids in the Surface-layers of Solutions and 'Suspensions' (Observations on Surface-membranes, Bubbles, Emulsions, and Mechanical Coagulation). — Preliminary Account." By W. RAMSDEN, M.A., M.D., Oxon., Fellow of Pembroke College, Oxford. Communicated by Professor F. GOTCH, F.R.S. Received June 8,—Read June 18, 1903.

J. Chem. Soc., Trans., 1907,**91**, 2001-2021

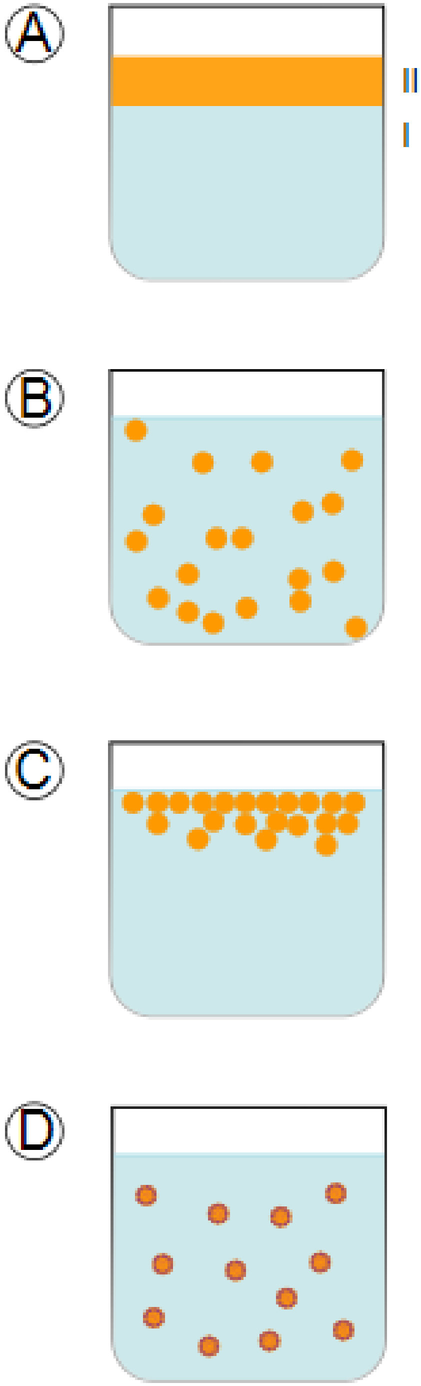
CXCVI.—*Emulsions.*

By SPENCER UMFREVILLE PICKERING, M.A., F.R.S.

IN the Sixth Report of the Woburn Experimental Fruit Farm (Eyre and Spottiswoode, 1906) were published the results of an examination of emulsions of paraffin oil in solutions of soft soap, such as are used for insecticidal purposes; this examination has now been extended with the double object of obtaining an emulsifying agent which would, for practical purposes, not be open to the objections presented by those containing soap, and also of elucidating the nature of emulsification. The subject had already been investigated by Ramsden (*Proc. Roy. Soc.*, 1903, **72**, 156), but his work, unfortunately, did not come under the notice of the writer until that here described had been completed. It is satisfactory to find, however, that Ramsden, pursuing a different line of enquiry, should have arrived at an explanation of emulsification which is essentially the same as that given here.

Percival Spencer Umfreville Pickering (1858 –1920)

«Classical» («chemical») emulsions



Legend

- Phase I
- Phase II
- Surfactant

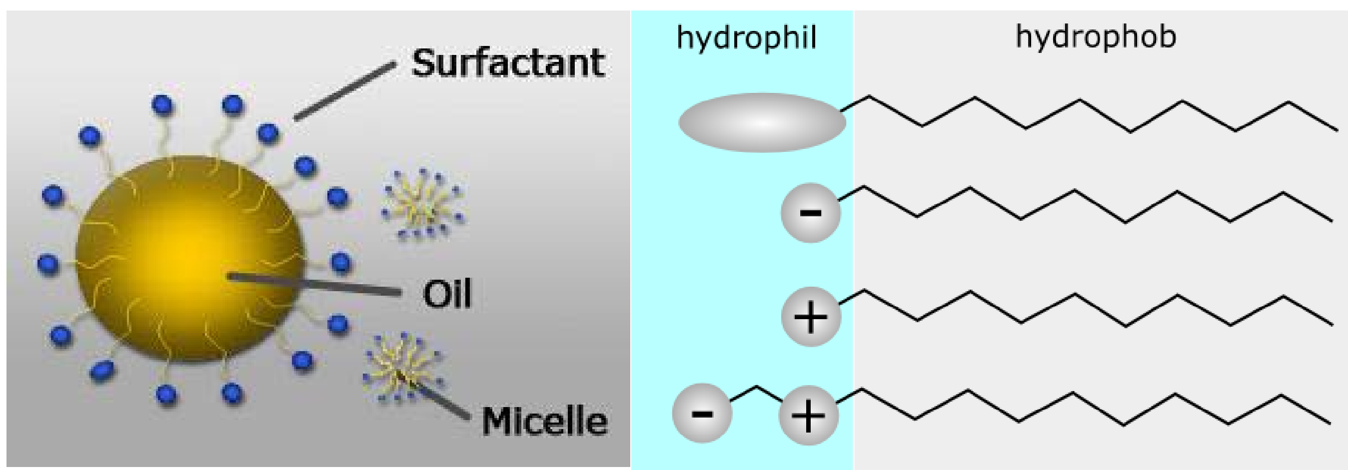
A. Two immiscible liquids, not emulsified

B. Emulsion of Phase II dispersed in Phase I

C. The unstable emulsion progressively separates

D. Surfactant positions itself on interface between Phases I and II, stabilizing emulsion

$E_{bind} > \sim k_B T$

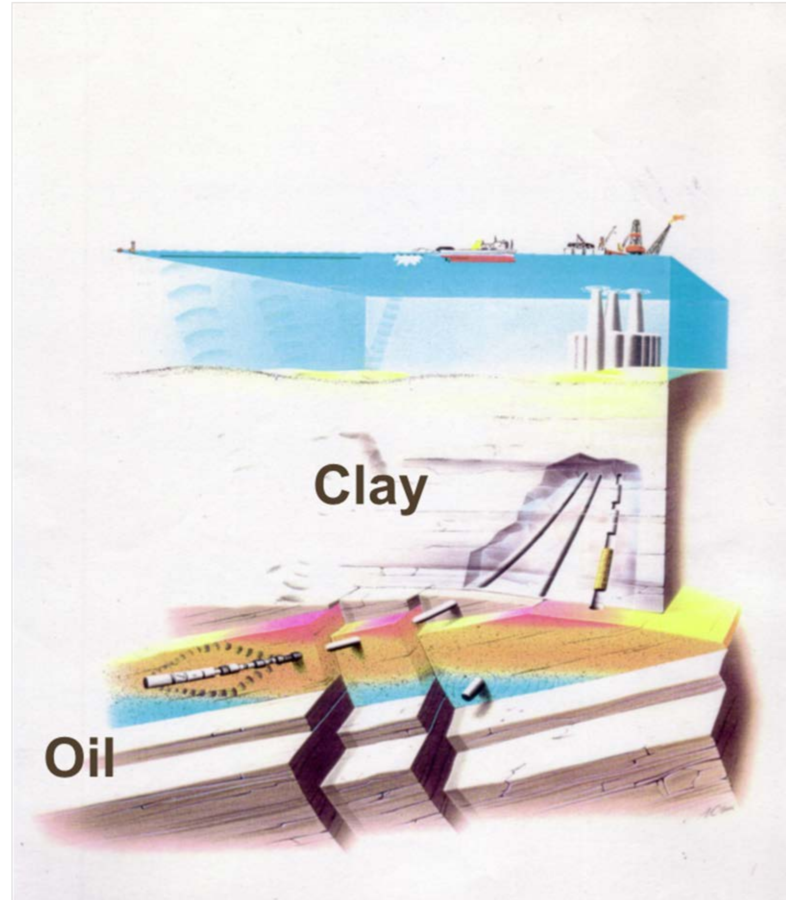


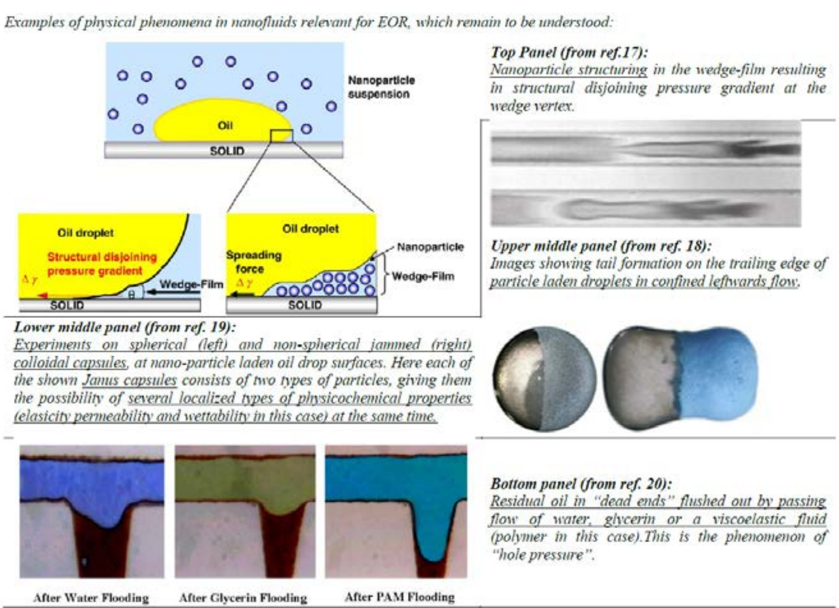
Classical» («chemical») emulsions

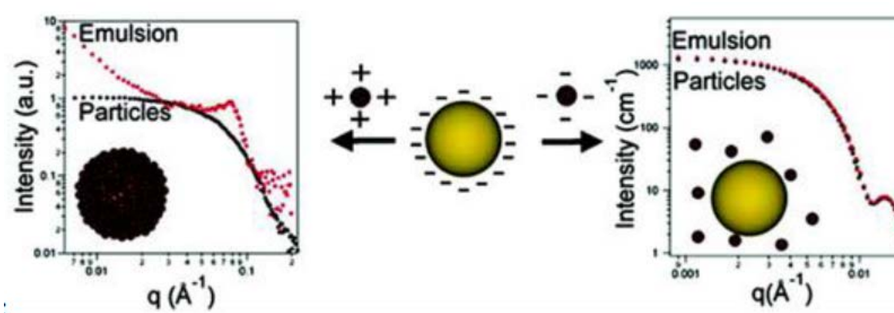
Experimental results indicate that some nanoparticles (silica, clay etc.) are good EOR agents => **Nanofluids**.

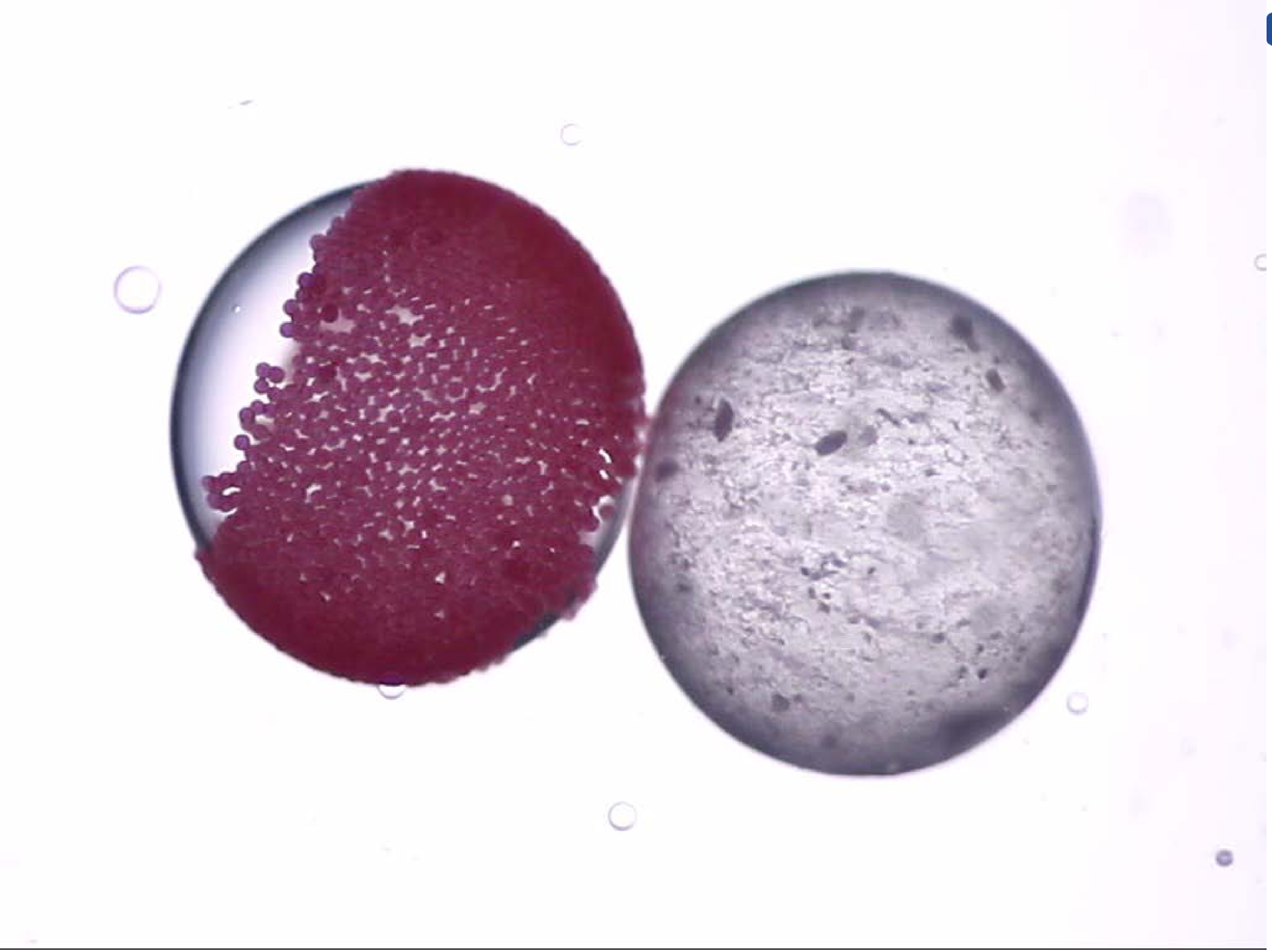
The mechanisms through which oil is enhanced using these nano agents are not well understood.

Important factors could include change of rock wettability, reduction of interfacial tension, reduction of oil viscosity, reduction of mobility ratio and permeability alterations.



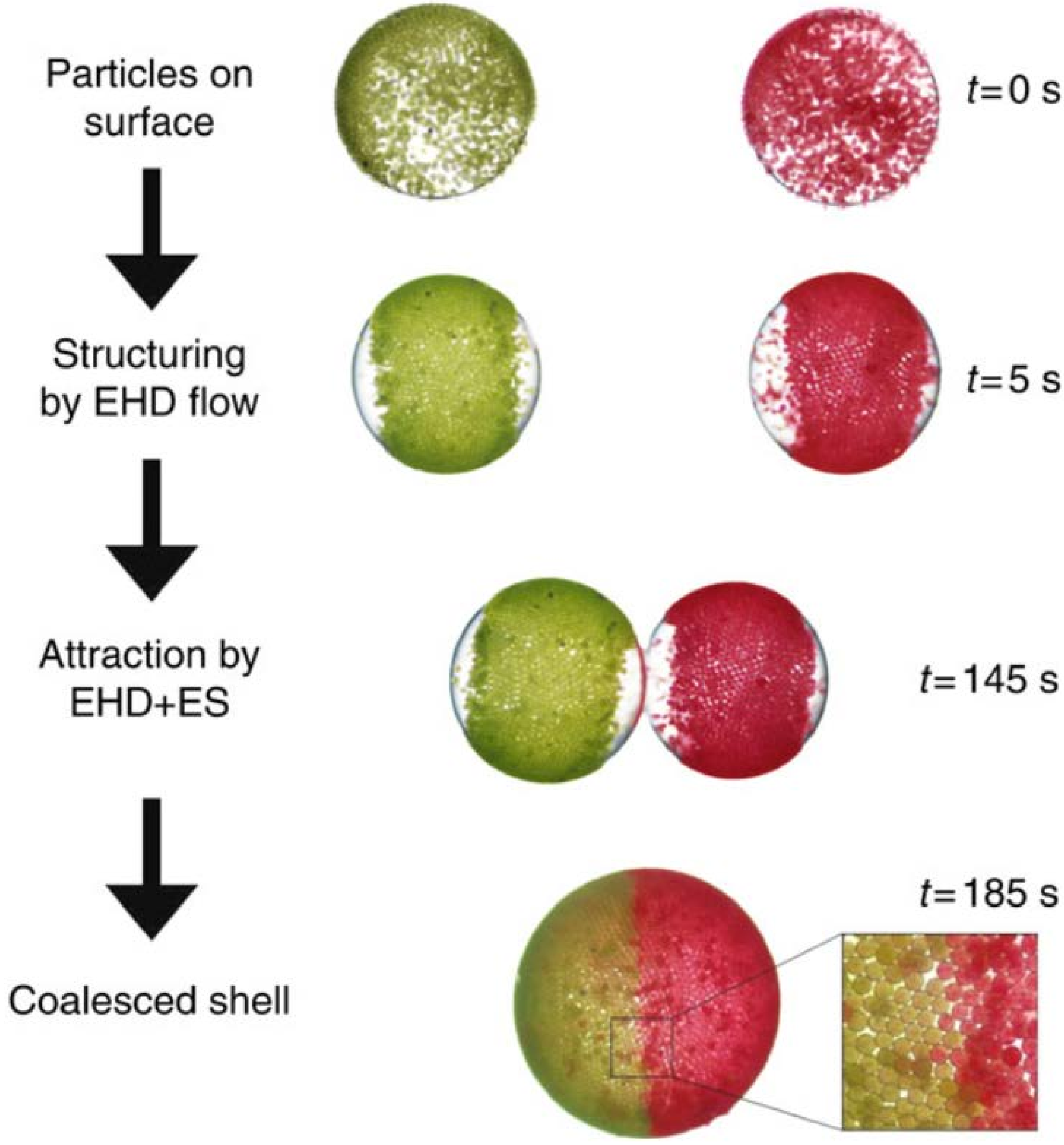






Janus shells with clay and PE particles, Experiments at NTNU Trondheim

Electroformation of Janus and patchy capsules, Z. Rozynek, A. Mikkelsen, P.Dommersnes & J. O. Fossum, Nature Communications 5, 3945 (2014)



Fabrication of Janus **shell**

a

b

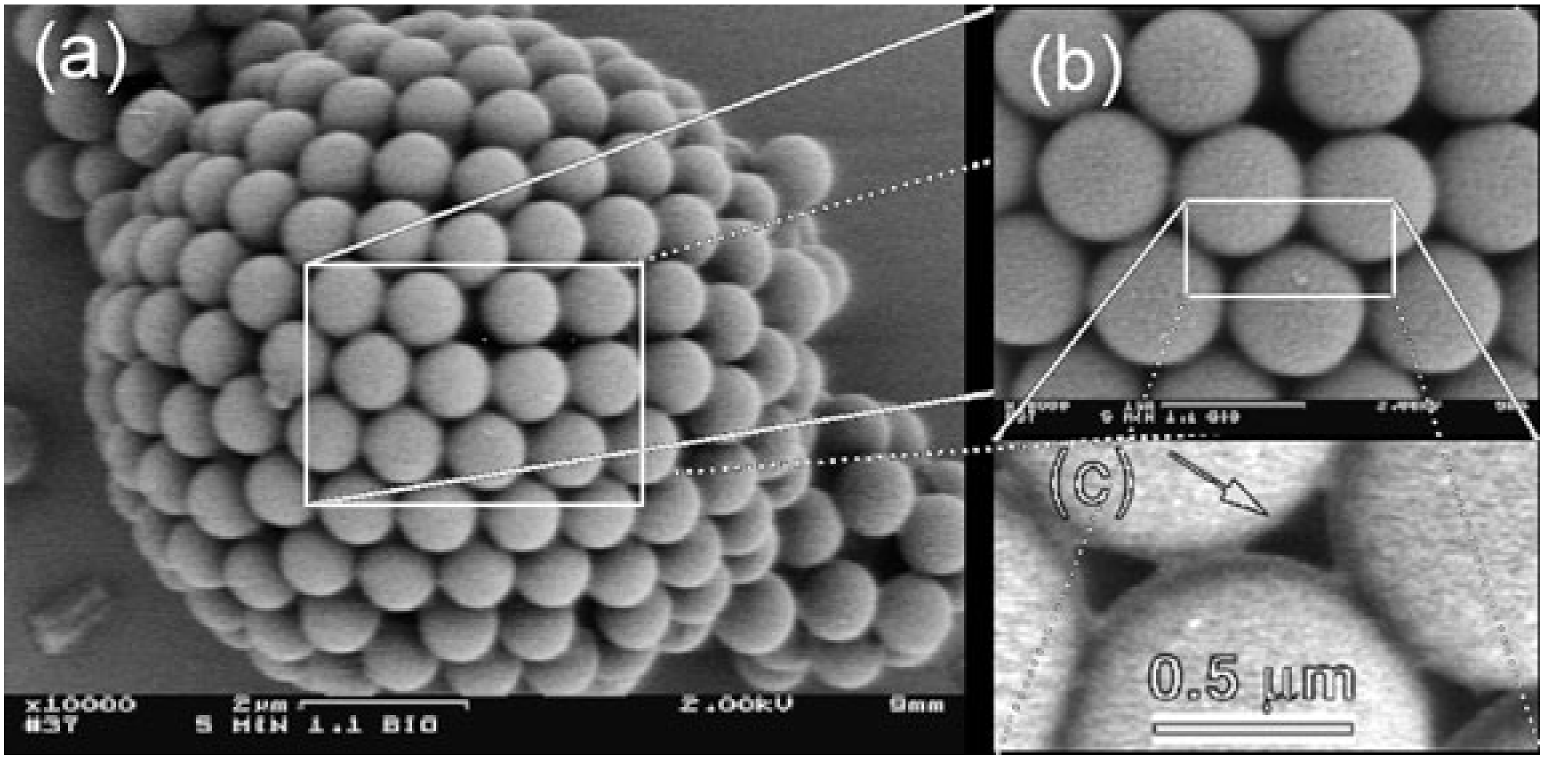
glass (500 nm) and blue PE (20 µm) particles

PS (1 µm) and clay mineral (~1 µm) particles

Arrested shells : Small particles:

Experiments at NTNU Trondheim

Colloidosomes

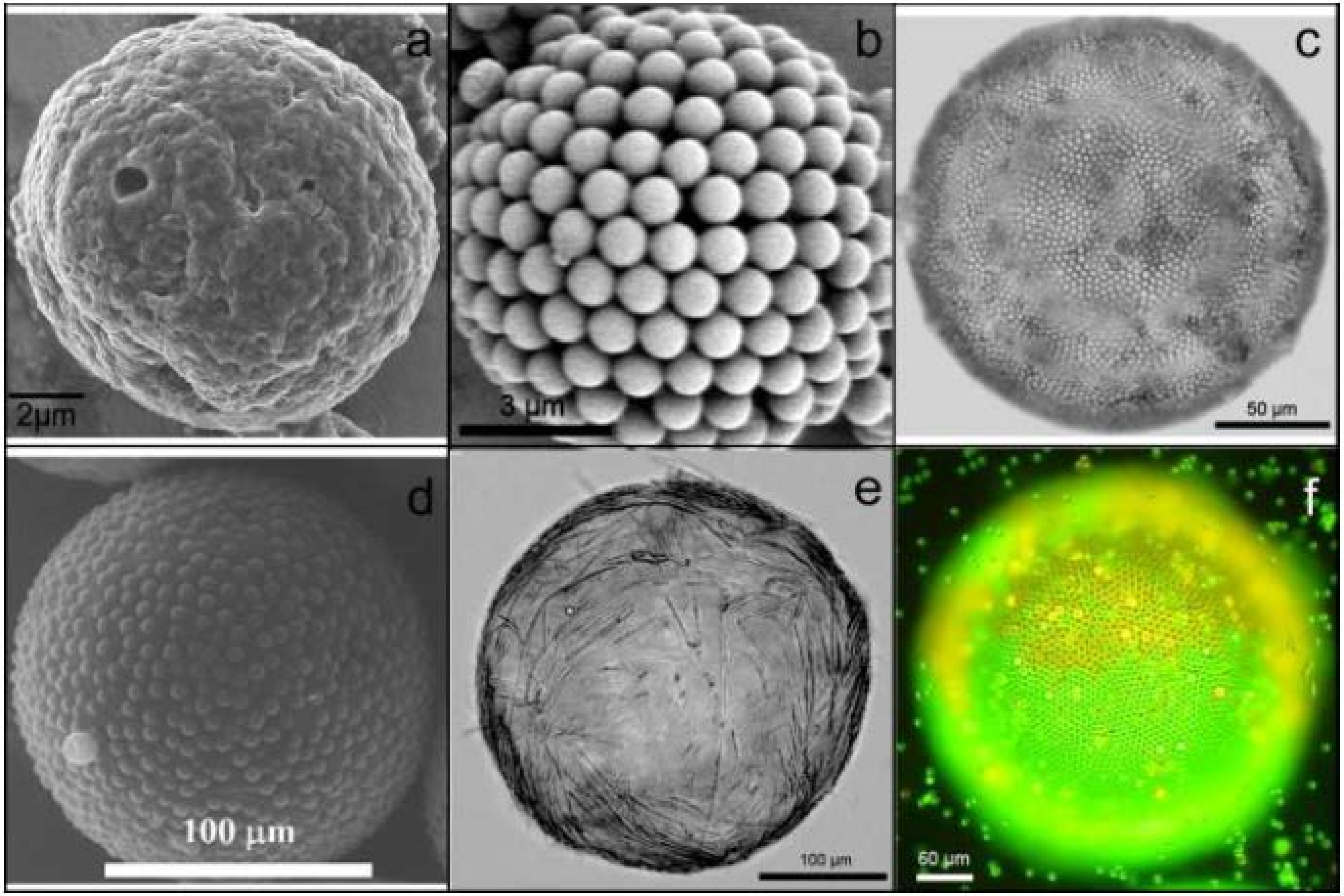


A.D. Dinsmore et. Al., Science, **298**, 1006 (2002)

Pickering (1907) : Emulsions

Dinsmore et al. Science (2002): "Colloidosomes"

NTNU



Dinsmore et.al.

Colloidal clay shells: Example

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Soft Matter

Dynamic Article Links

Cite this: *Soft Matter*, 2011, **7**, 2600

www.rsc.org/softmatter

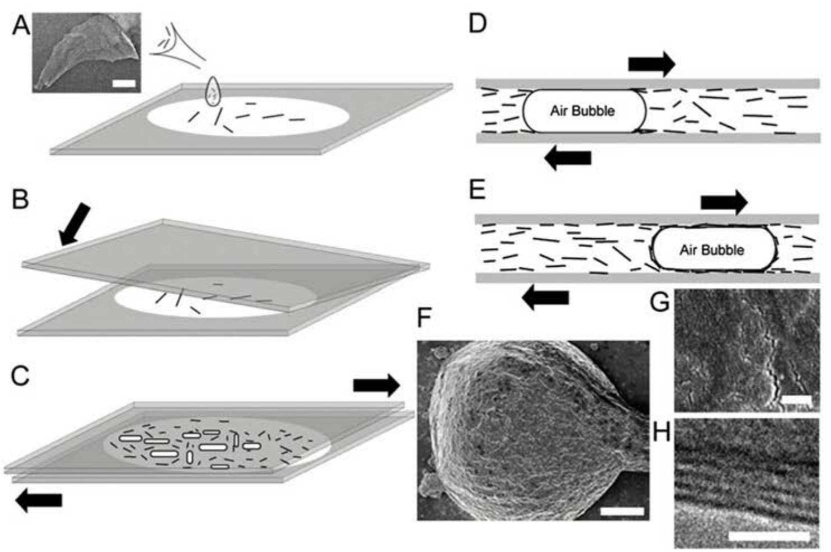
PAPER

Semi-permeable vesicles composed of natural clay†

Anand Bala Subramaniam,[*a] Jiandi Wan,[b] Arvind Gopinath[c] and Howard A. Stone[*b]

Received 21st November 2010, Accepted 3rd January 2011

DOI: 10.1039/c0sm01354d



Journal of Dispersion Science and Technology, 31:632–640, 2010

ISSN: 0193-2691 print/1532-2351 online
DOI: 10.1080/01932690903218062

Rheological Properties of Particle-Stabilized Emulsions

Sébastien Simon, Stefan Theiler, Agnethe Knudsen, Gisle Øye, and Johan Sjöblom

Ugelstad Laboratory, Department of Chemical Engineering, The Norwegian University of Science and Technology (NTNU), Trondheim, Norway

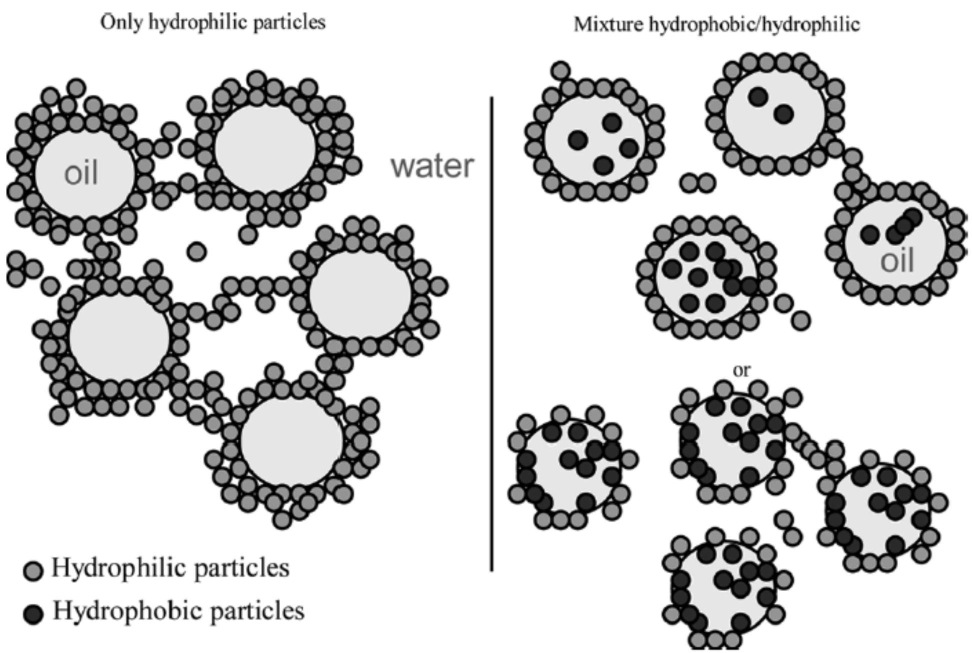
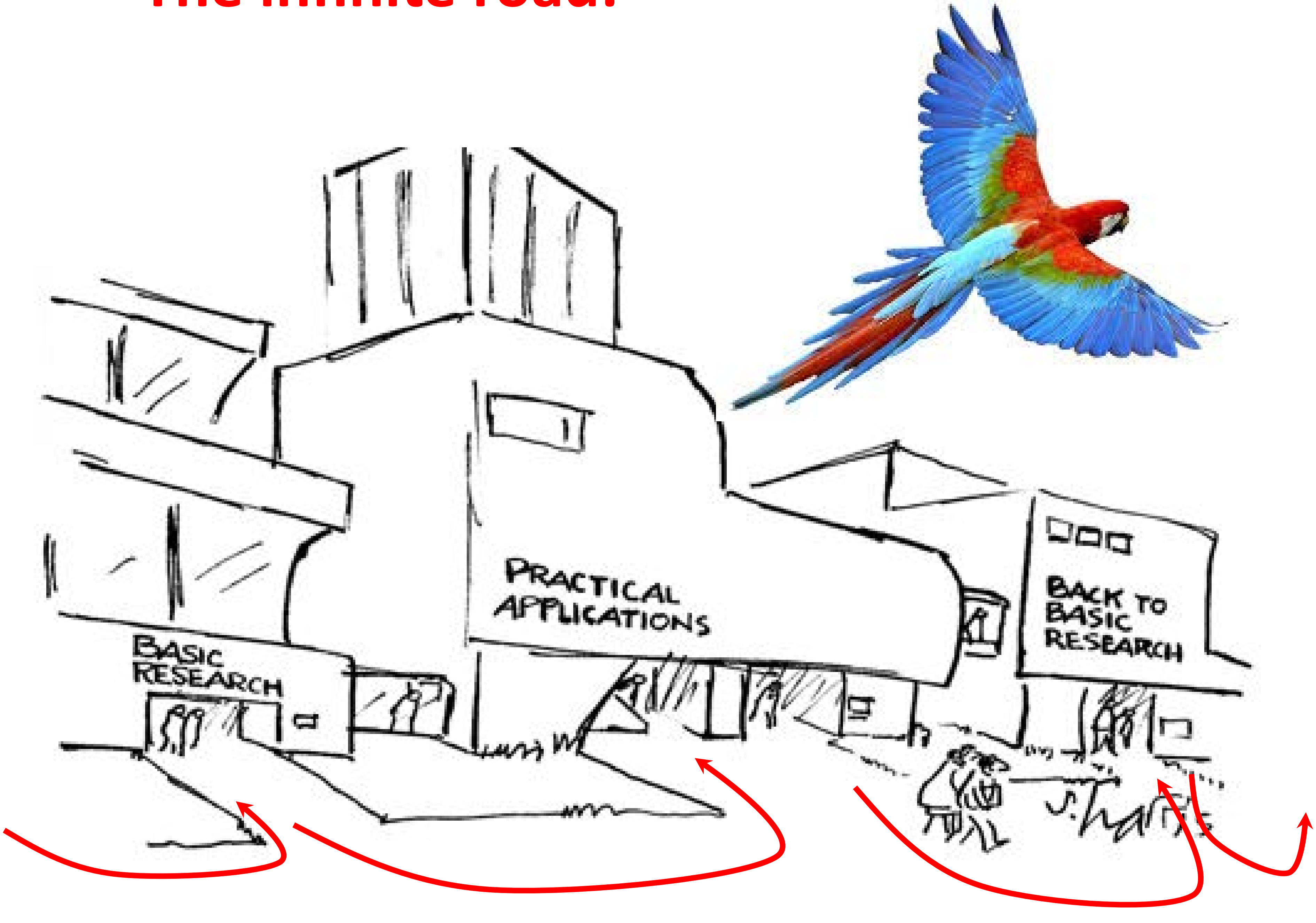


FIG. 12. Sketch of structure of o/w emulsions stabilized by only hydrophilic particles (left) and mixtures of hydrophilic and hydrophobic particles (right).

The infinite road:



Permanent and safe storage of nuclear waste

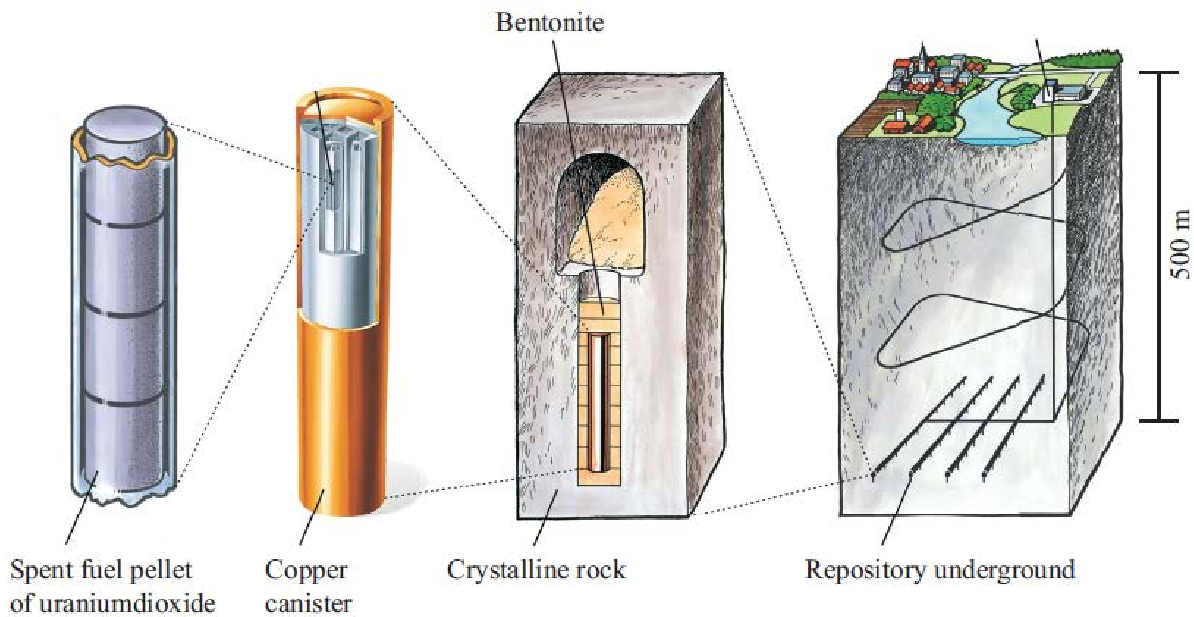
NTNU

The Bentonite Barrier

Swelling properties, redox chemistry and mineral evolution

P. Daniel Svensson

LUND UNIVERSITY



DOCTORAL DISSERTATION
by due permission of the Faculty of Engineering, Lund University, Sweden.

To be defended in public at the Center for Chemistry and Chemical Engineering,
Lecture Hall K:C, on March 9, 2015, at 13:15.

Faculty opponent

Prof. Jon Otto Fossum, Norwegian University of Science and Technology

Synthetic clays?

Permanent plugging for safe abandonment of terminated oil & gas wells

NTNU

IRIS (International Research Institute of Stavanger):

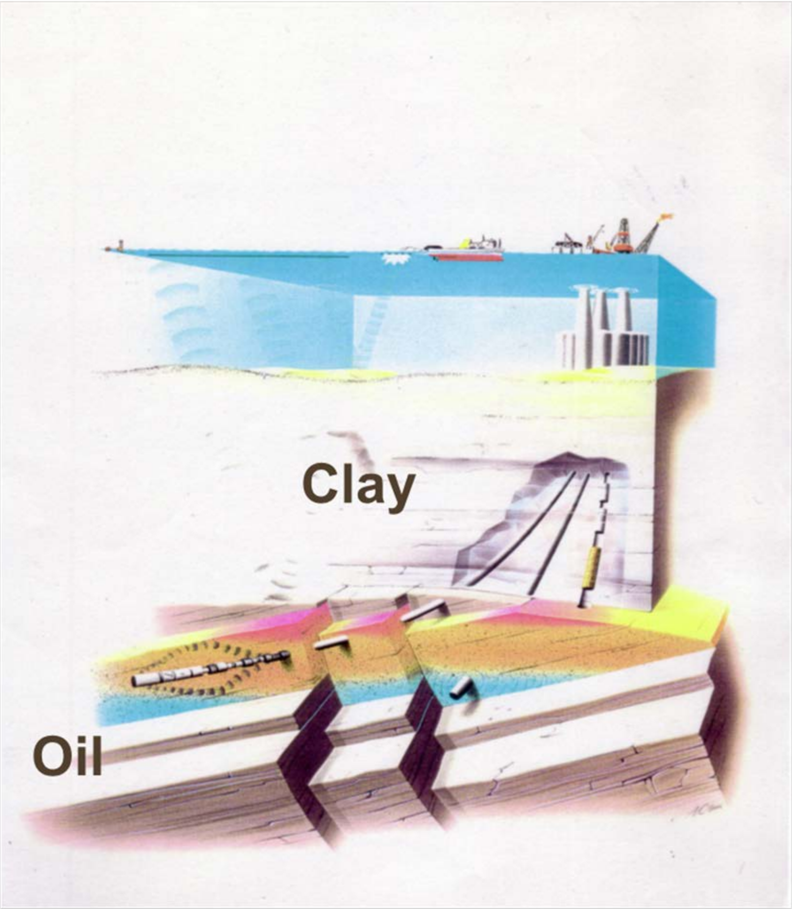
The average time for a P&A operationis 35 days

For Statoil only, the company has planned to permanently abandon approximately 1200 wells in the next 40 years

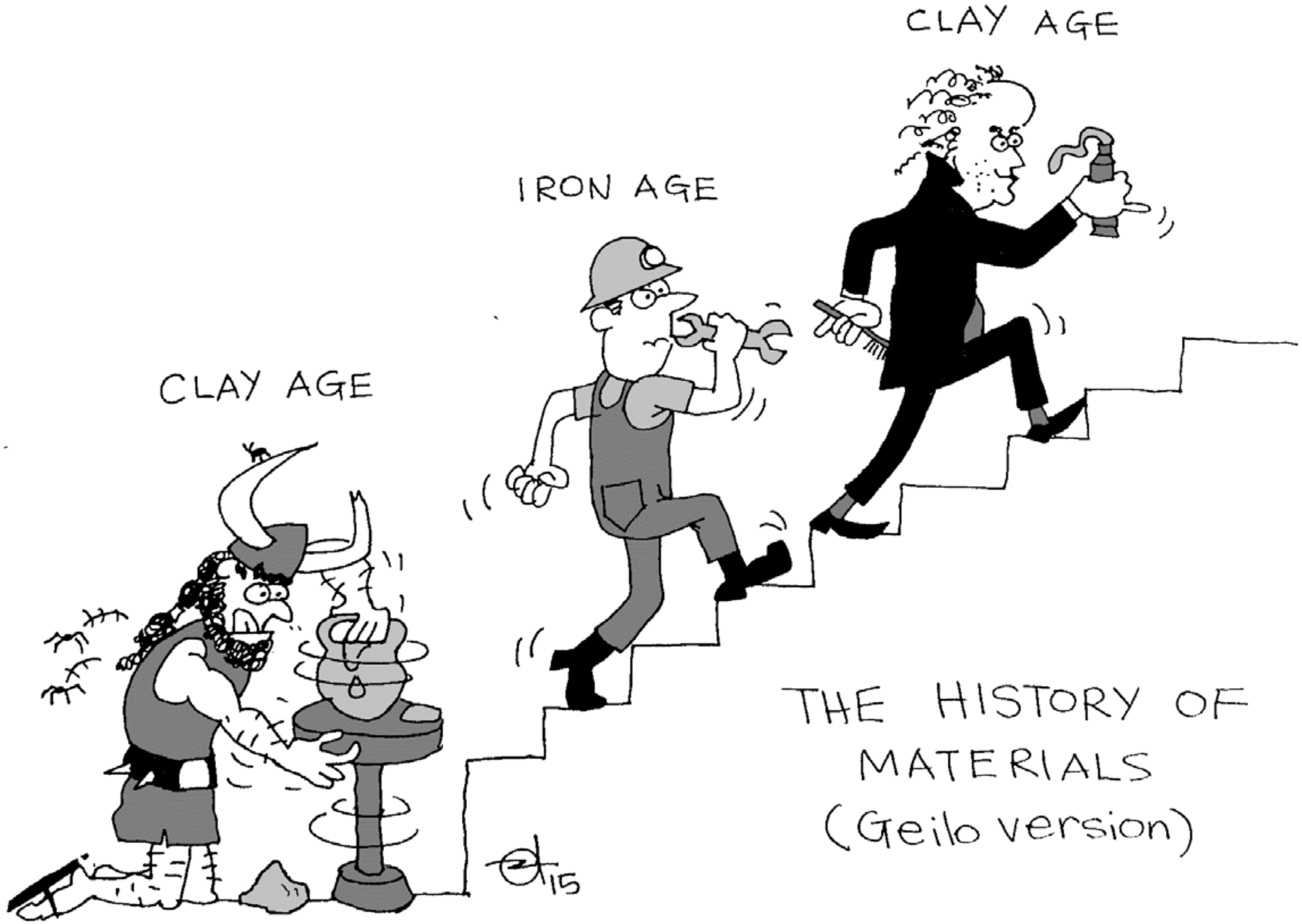
On the UK sector, a total number of 4600 wells are to be PP&Aed over the next 15 years.

Due to these large numbers, there is great interest in trying out new technologies and methods for P&A that can reduce the time and/or equipment costs.

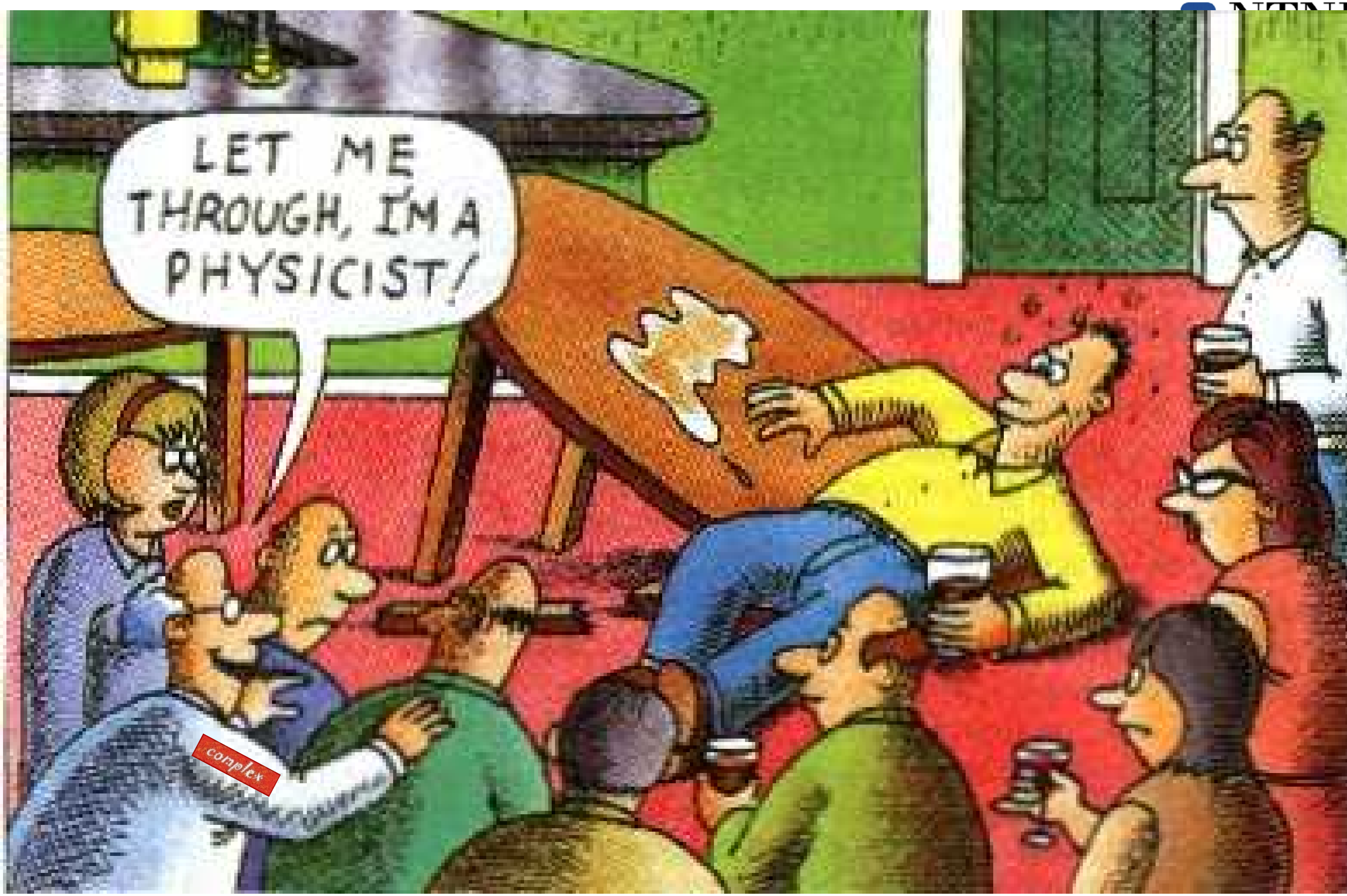
For the Norwegian continental shelf estimates suggest that with present day technology this may cost around **360 Billion NOK ≈ 30 Billion EUR.**

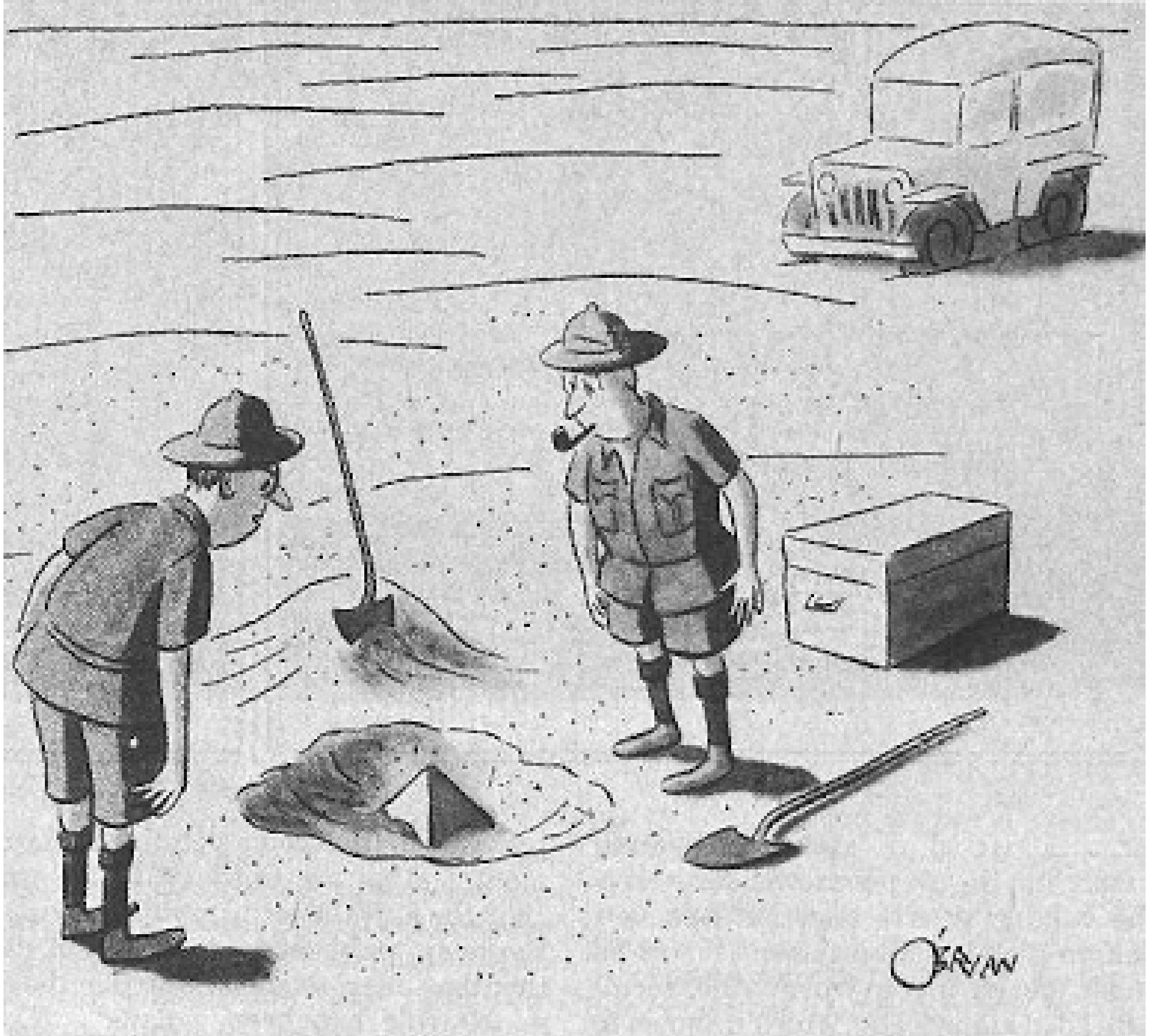


Key technological challenges: Design of material strength, cementation, adhesion properties and integration with other materials.



Drawn by Ernesto Altshuler


LET ME THROUGH, I'M A PHYSICIST!
complex



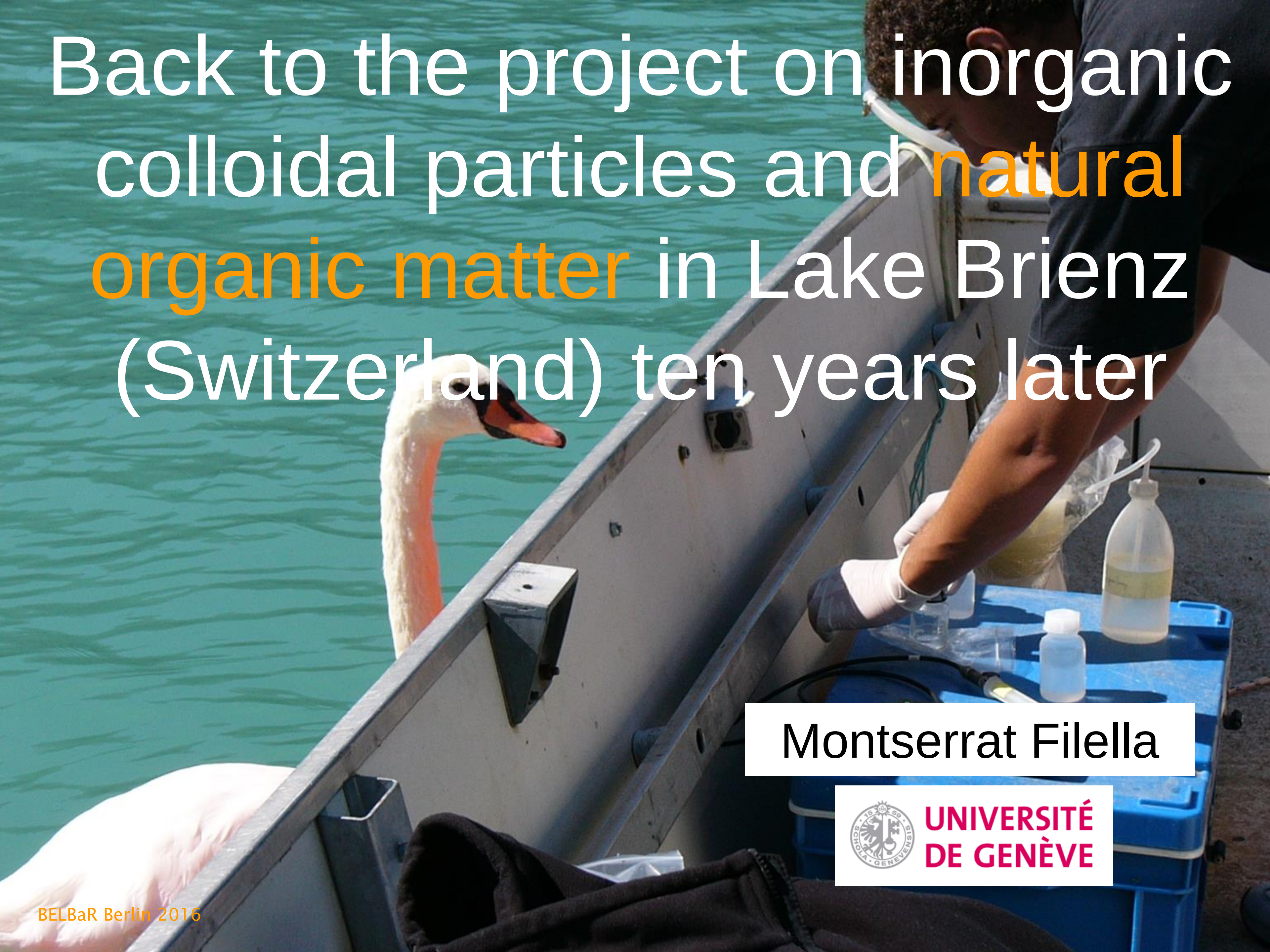
"This could be the discovery of the century. Depending, of course, on how far down it goes."

Thank you for your attention!

Clay baths will prolong your life:


Back to the project on inorganic colloidal particles in Lake Brienz (Switzerland) ten years later
Montserrat Filella
UNIVERSITÉ DE GENÈVE
BELBaR Berlin 2016

Back to the project on inorganic colloidal particles and natural organic matter in Lake Brienz (Switzerland) ten years later

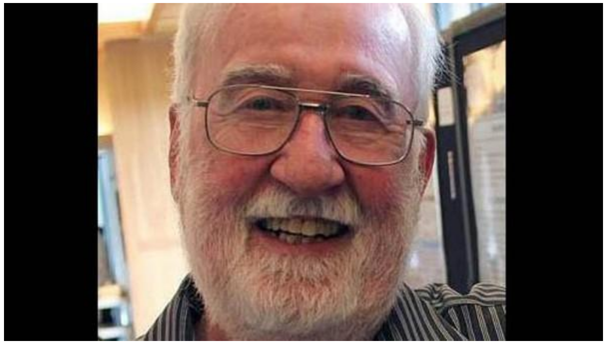


Montserrat Filella

UNIVERSITÉ DE GENÈVE

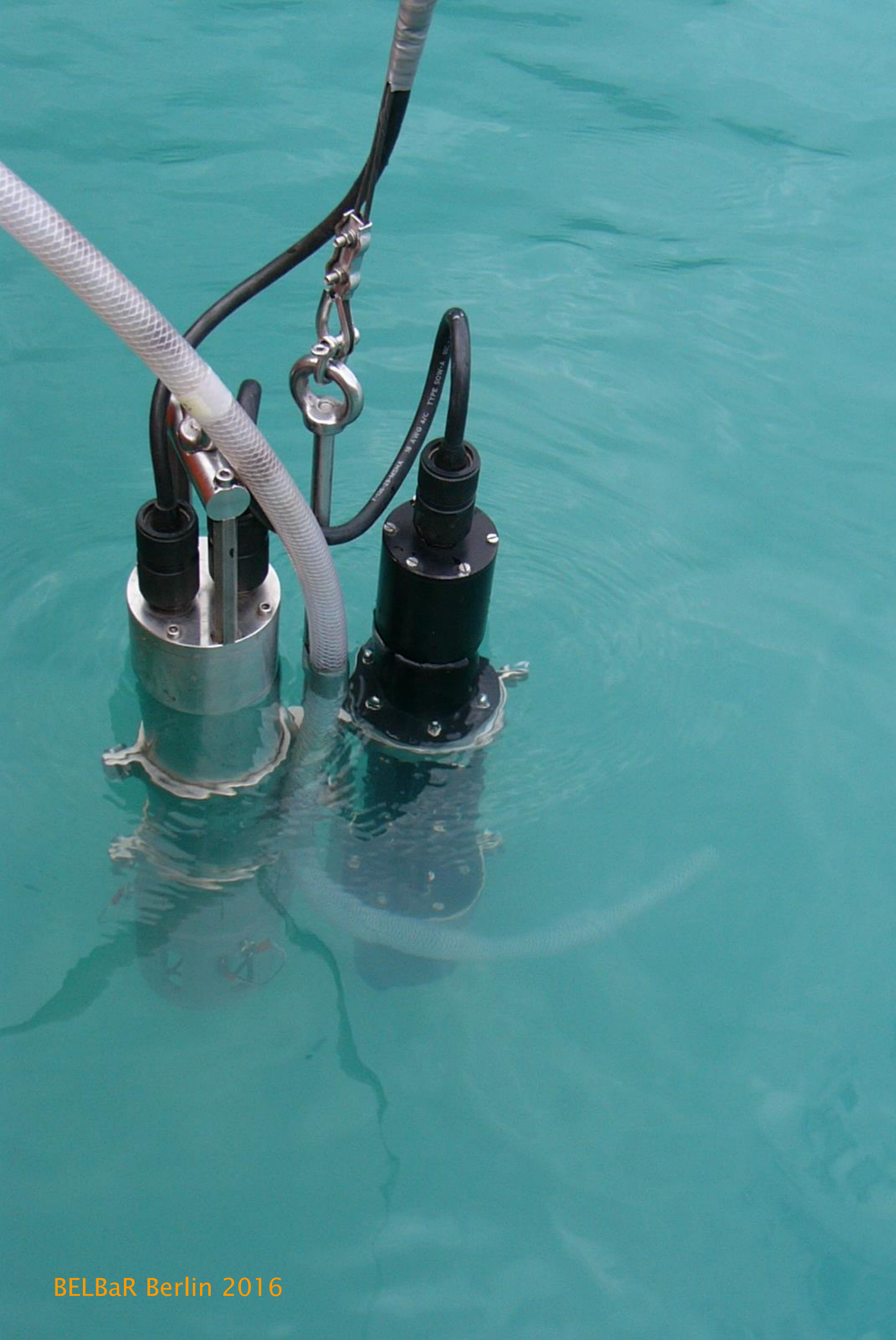
stop

David Sackett (1934-2015)



The sins of expertness and a proposal for redemption

BMJ 2000 ; 320 doi: http://dx.doi.org/10.1136/bmj.320.7244.1283 (Published 06 May 2000)
Cite this as: *BMJ* 2000;320:1283



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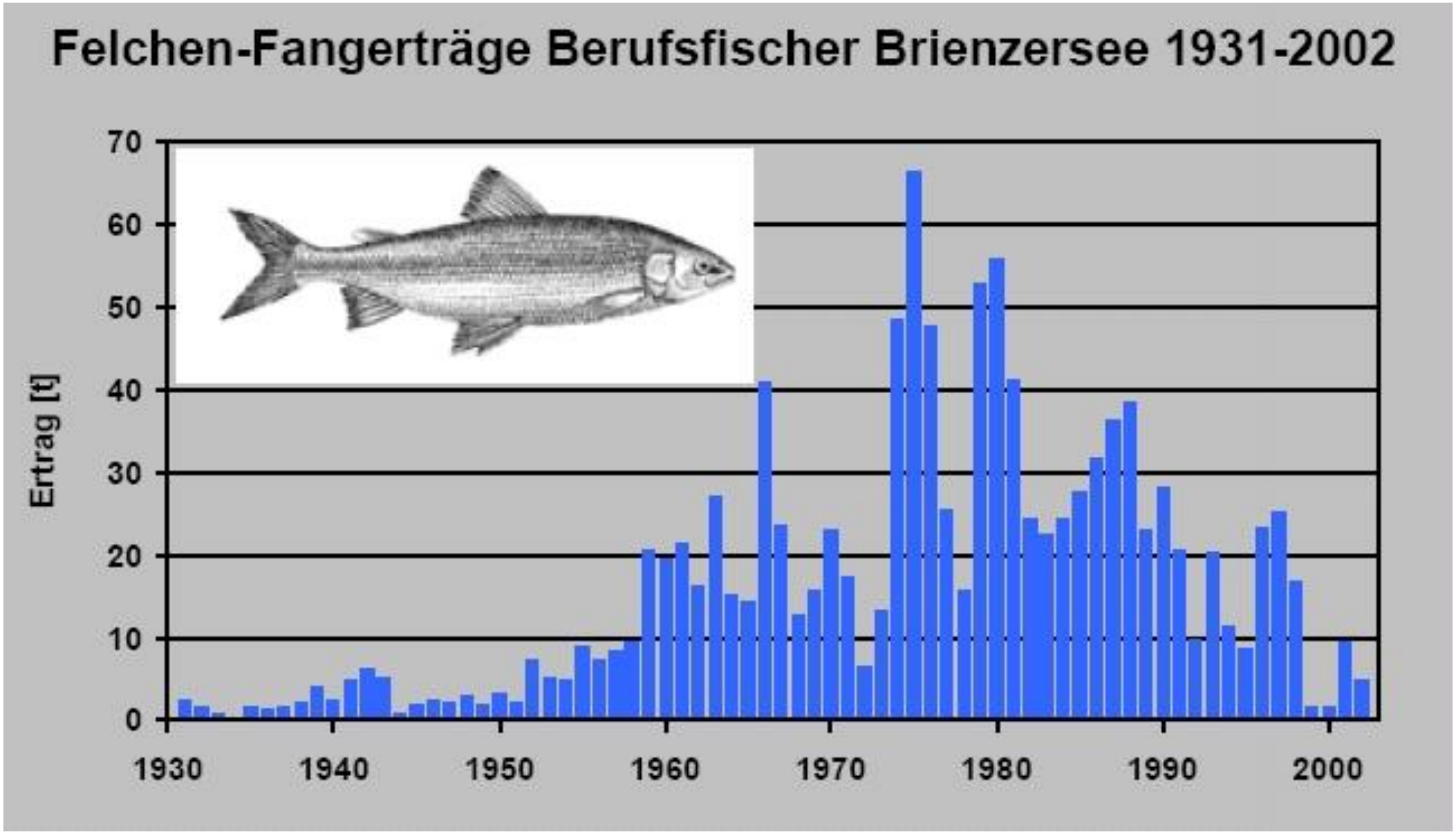
example of **environmental** study + **method** development

the **system**

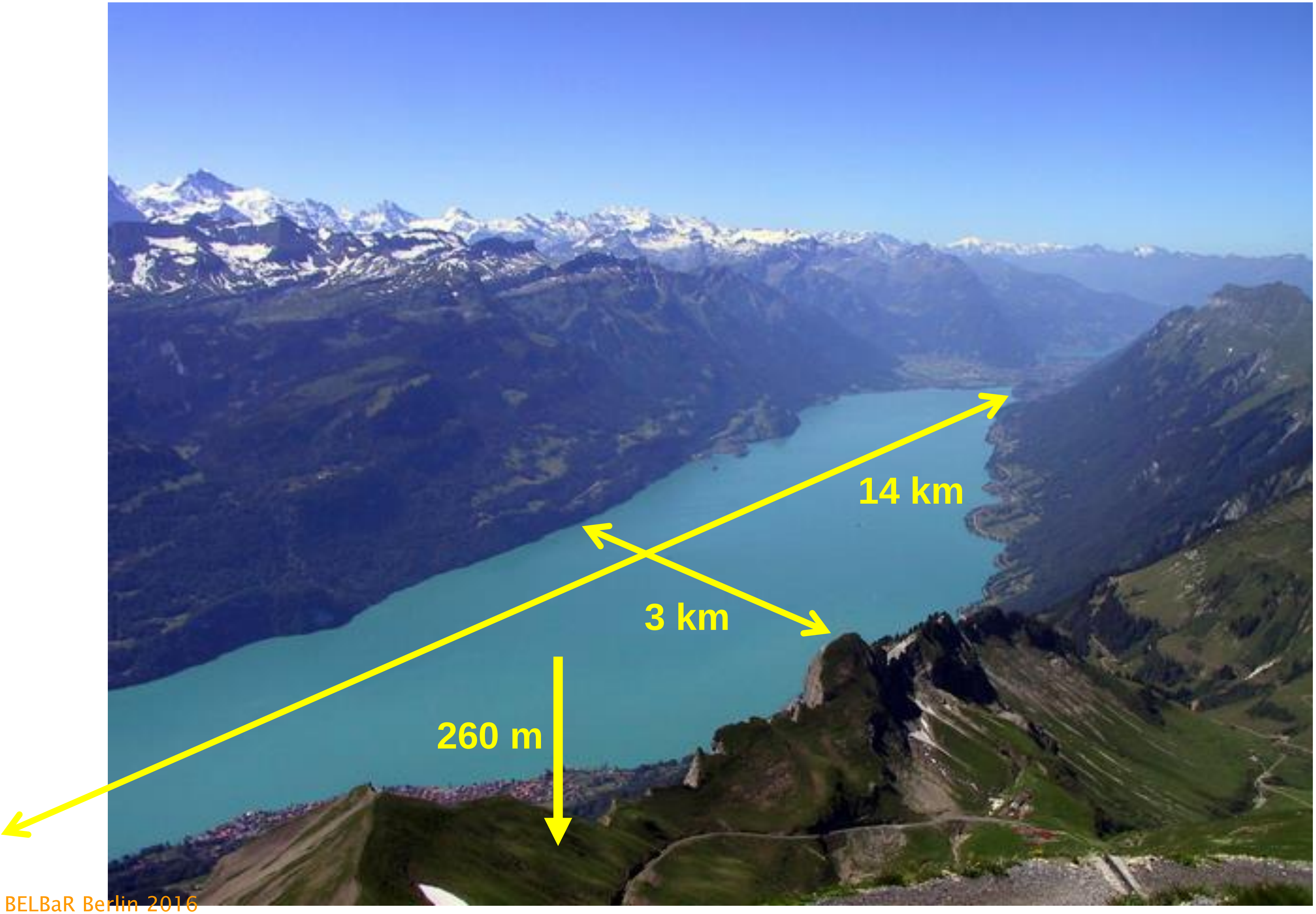
BELBaR Berlin 2016

the **problem**



Felchen-Fangerträge Berufsfischer Brienzersee 1931-2002
Ertrag [t]
0
10
20
30
40
50
60
70
1930
1940
1950
1960
1970
1980
1990
2000

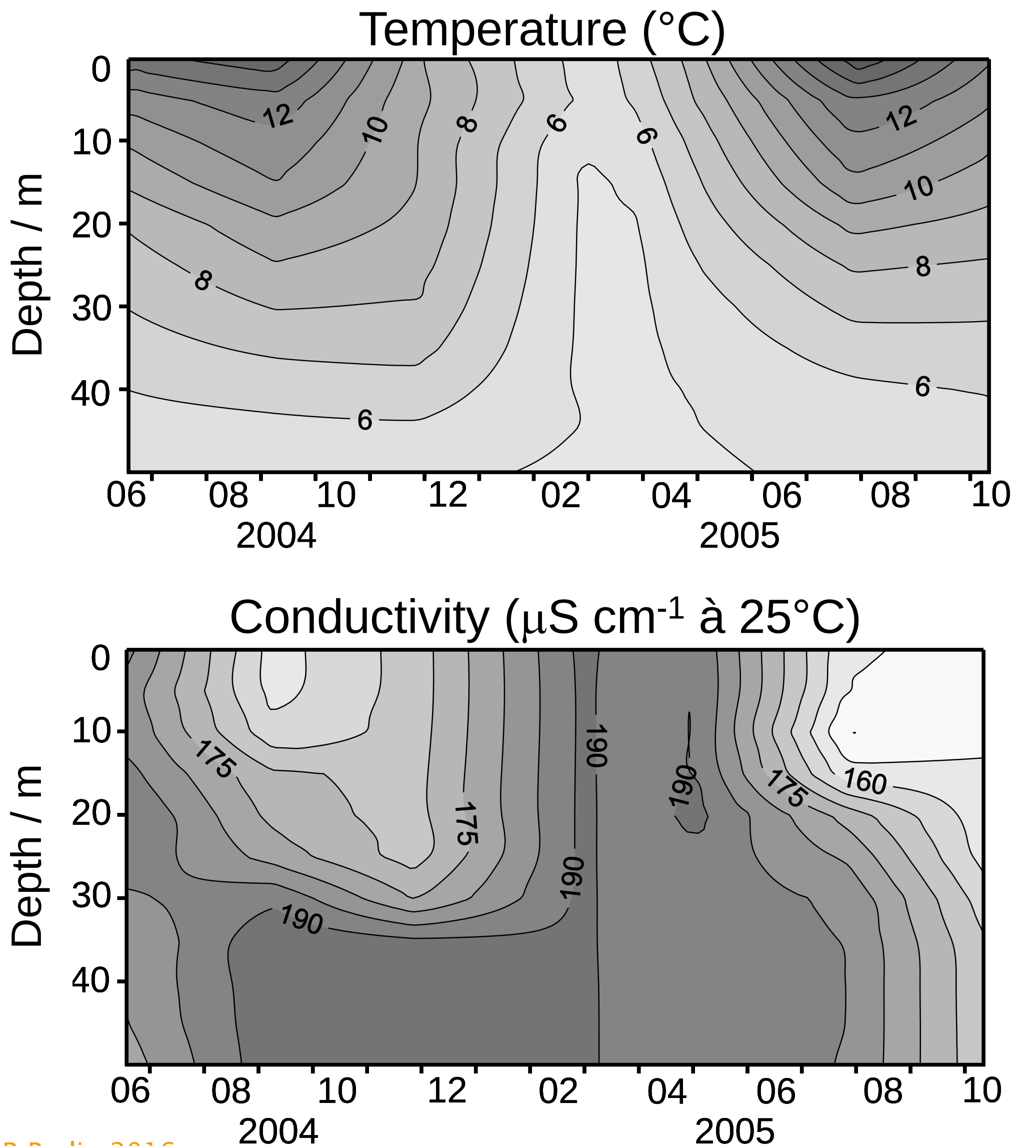
the **system**



the system

10 km

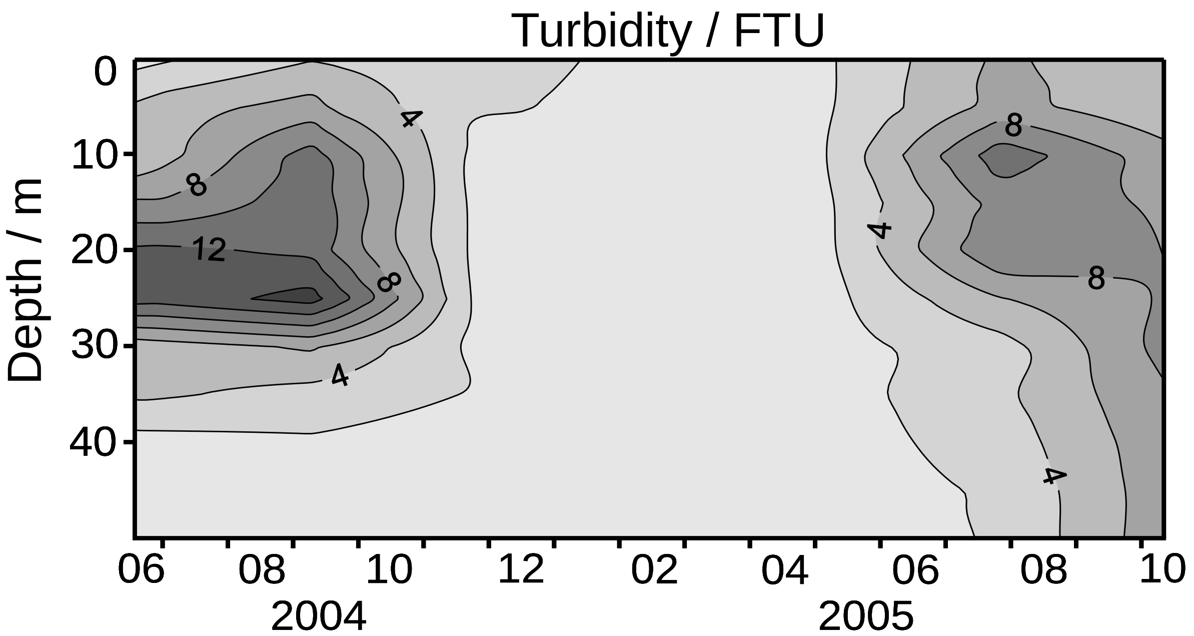
the **system**



- stratification
- river intrusion

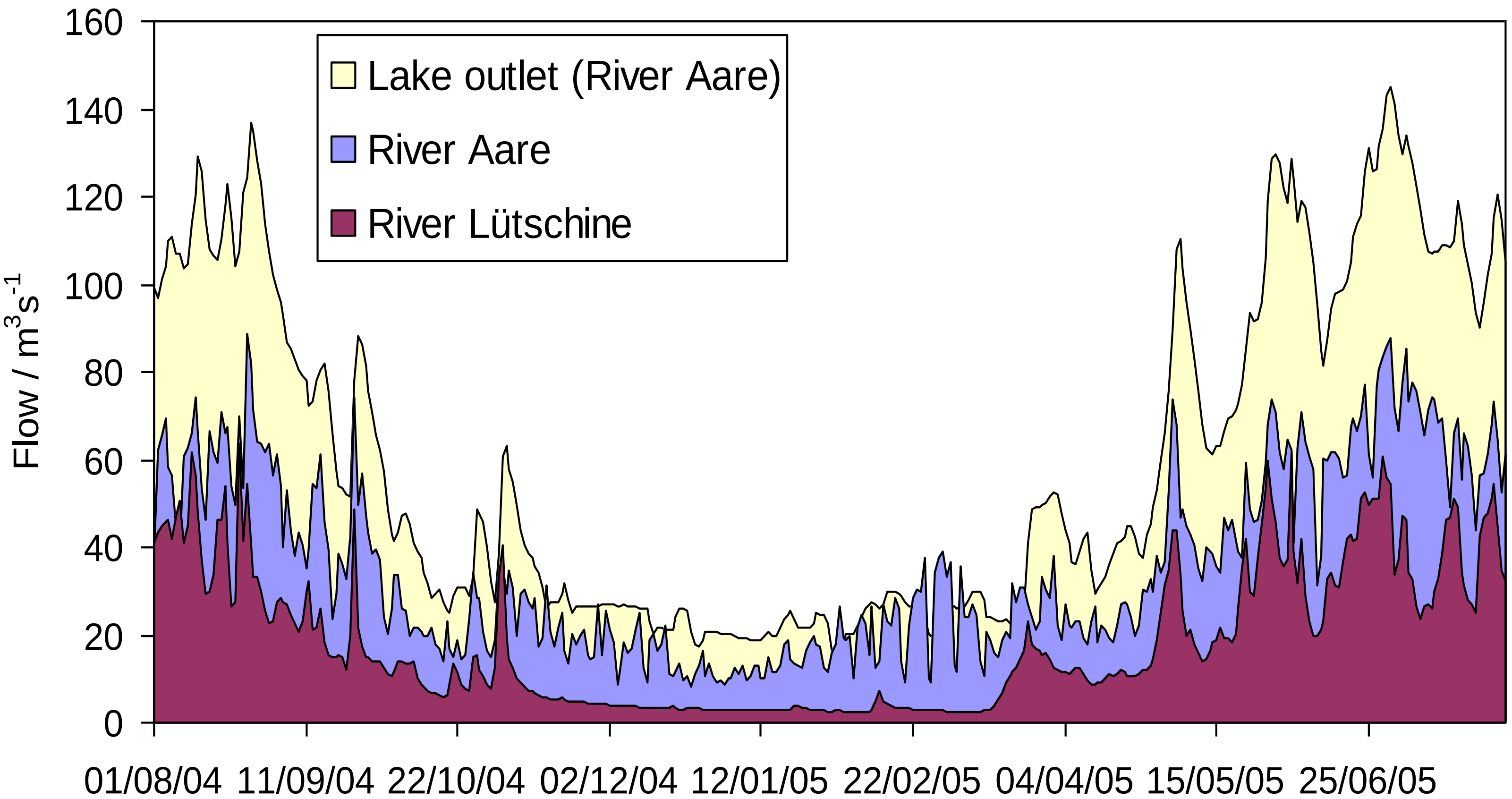
V. Chanudet and M. Filella, The fate of inorganic colloidal particles in Lake Brienz. AQUATIC SCIENCES, **69**, 199-211 (2007)

the **system**



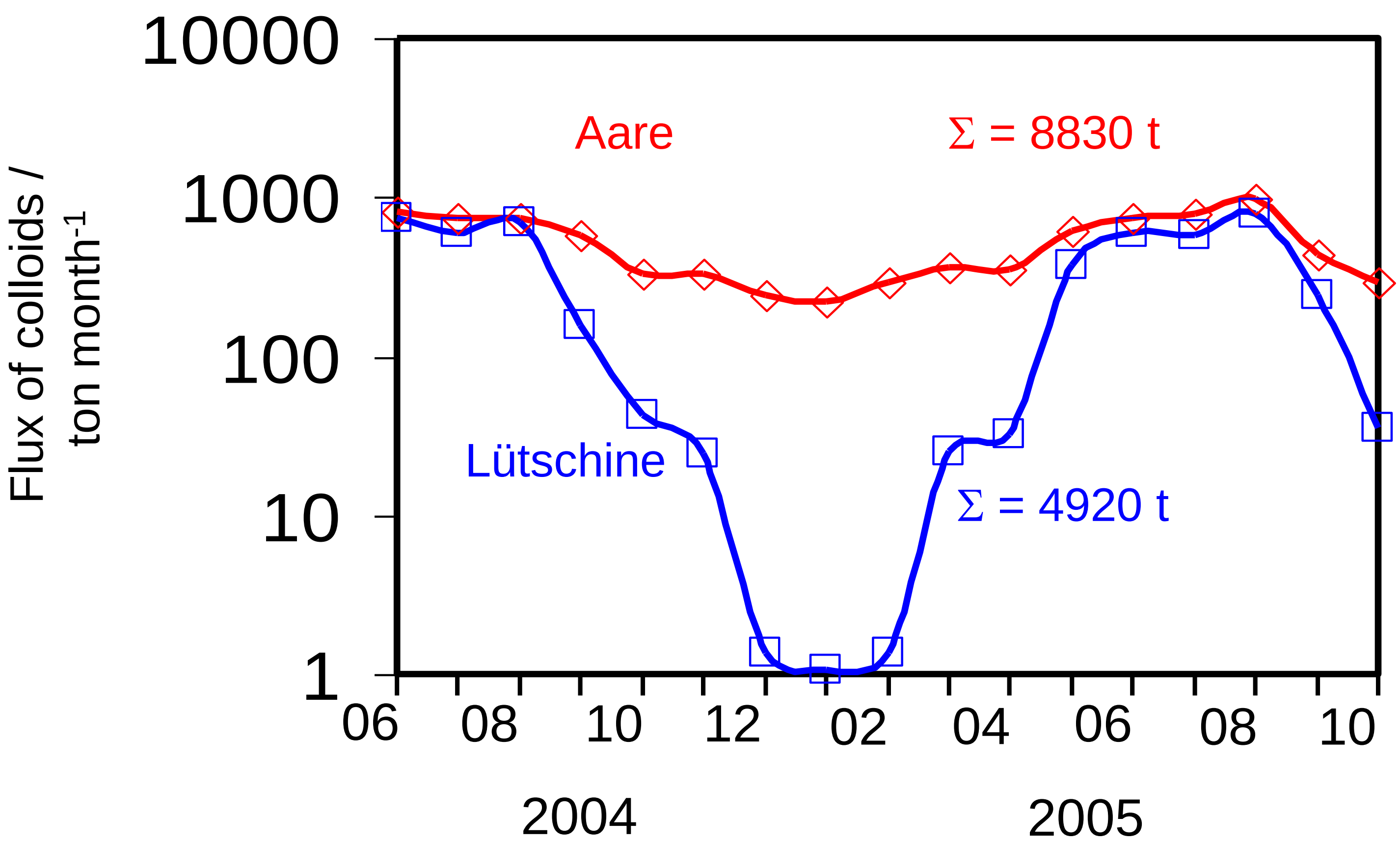
- winter : weak and constant
- summer: river intrussion
- October 2005

the **system**



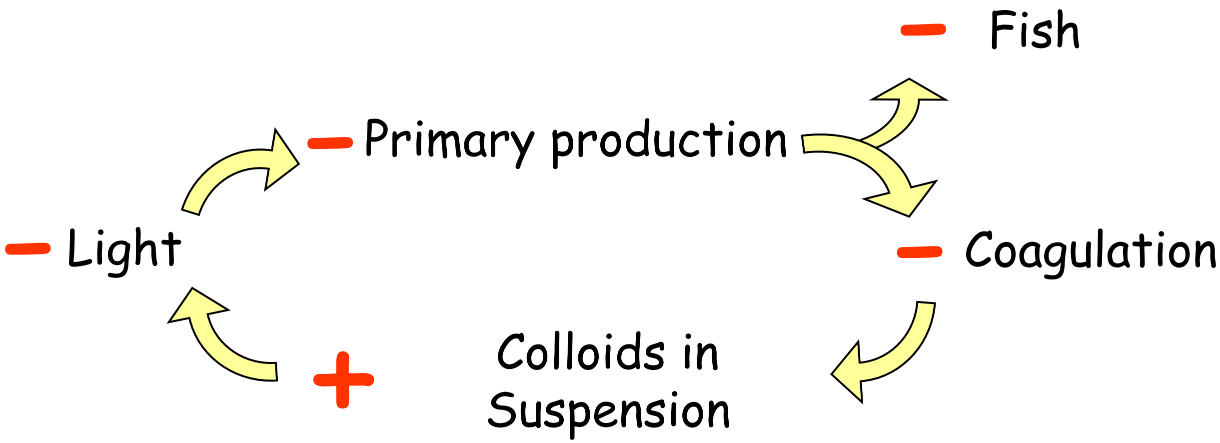
Lake outlet (River Aare)
River Aare
River Lütschine
Flow / m^{3}s^{-1}
160
140
120
100
80
60
40
20
0
01/08/04
11/09/04
22/10/04
02/12/04
12/01/05
22/02/05
04/04/05
15/05/05
25/06/05

the **system**



Flux of colloids / ton month-1
10000
1000
100
10
1
Aare
Σ = 8830 t
Lütschine
Σ = 4920 t
06
08
10
12
02
04
06
08
10
2004
2005

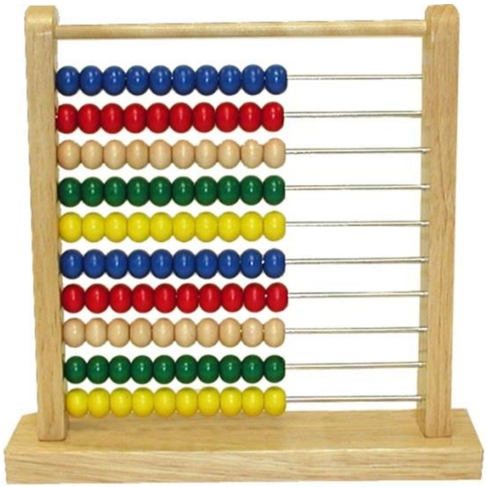
work **hypothesis**



our approach

size

amount

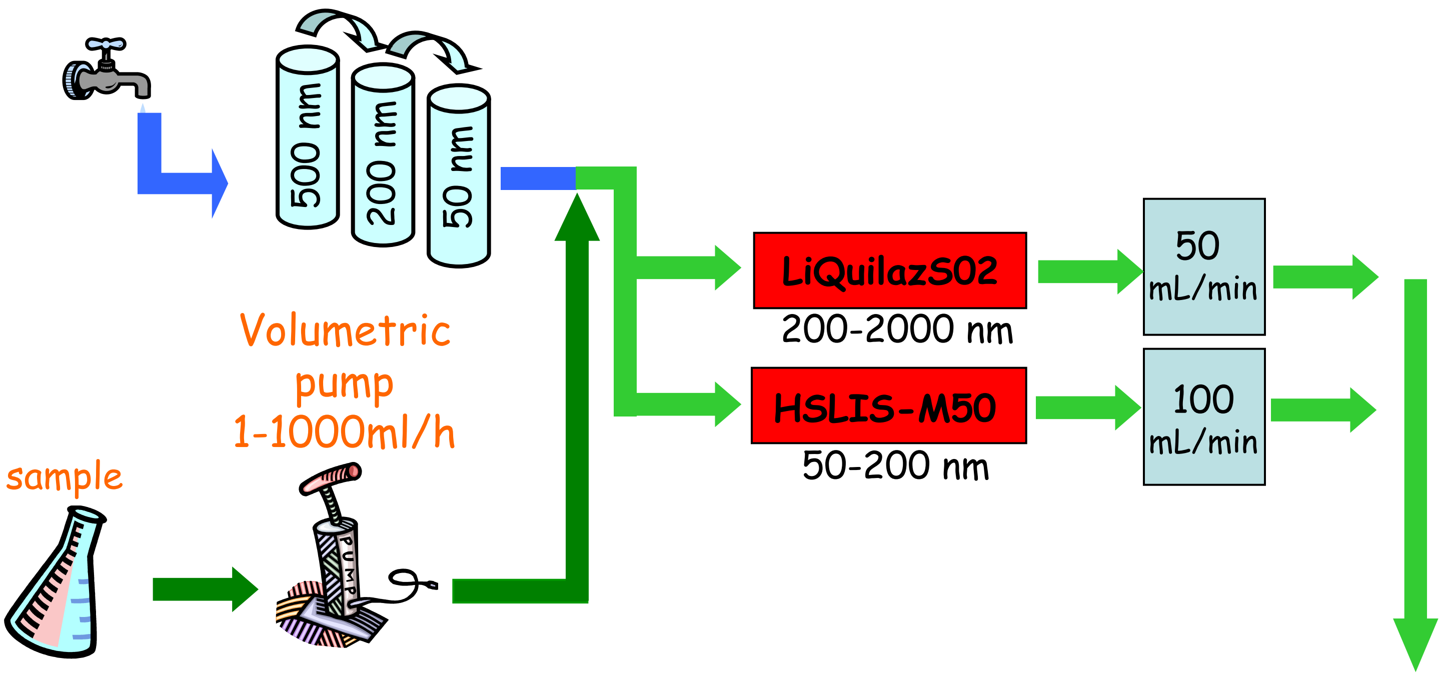


type

SPC

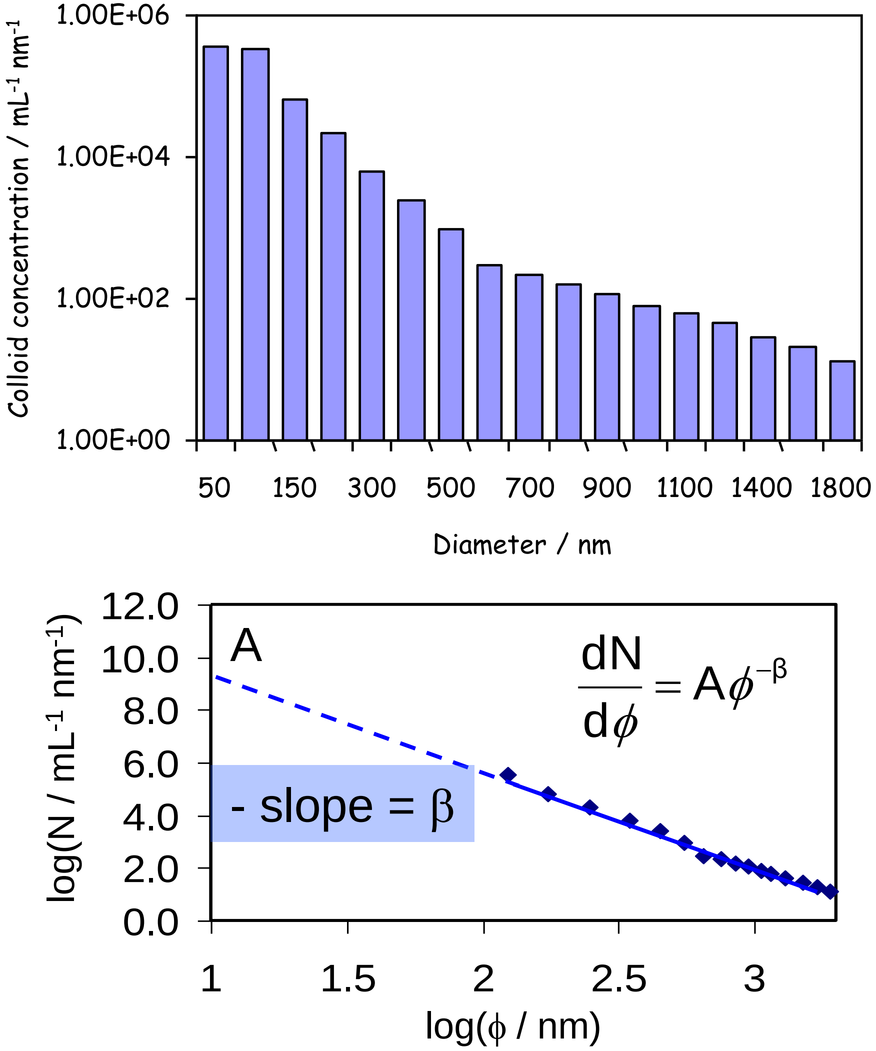
TEM-EDS-SAED

- Determination of particle size distributions: Single Particle Counter (SPC)



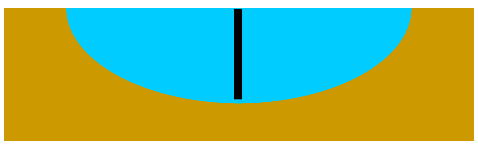
colloid **size**

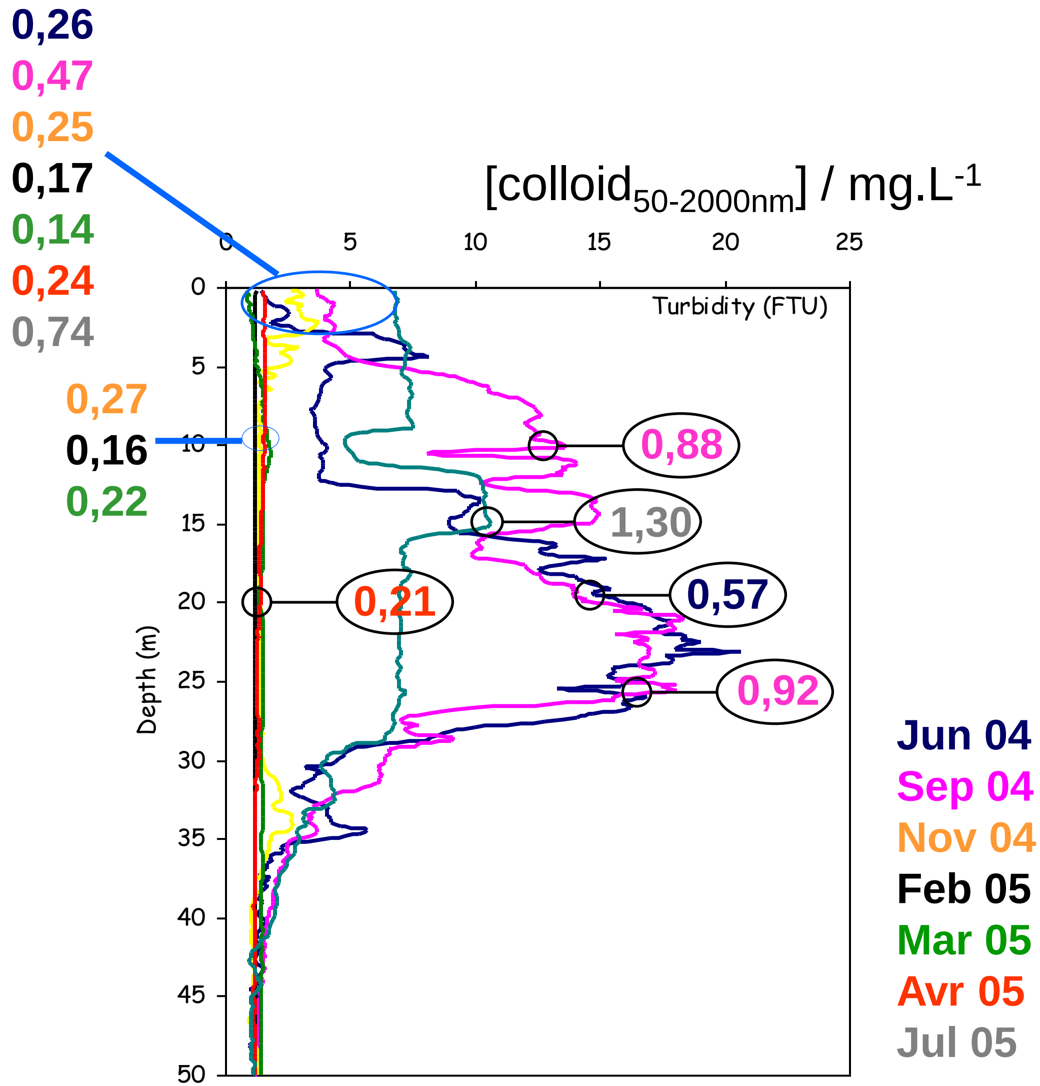
colloid **size**



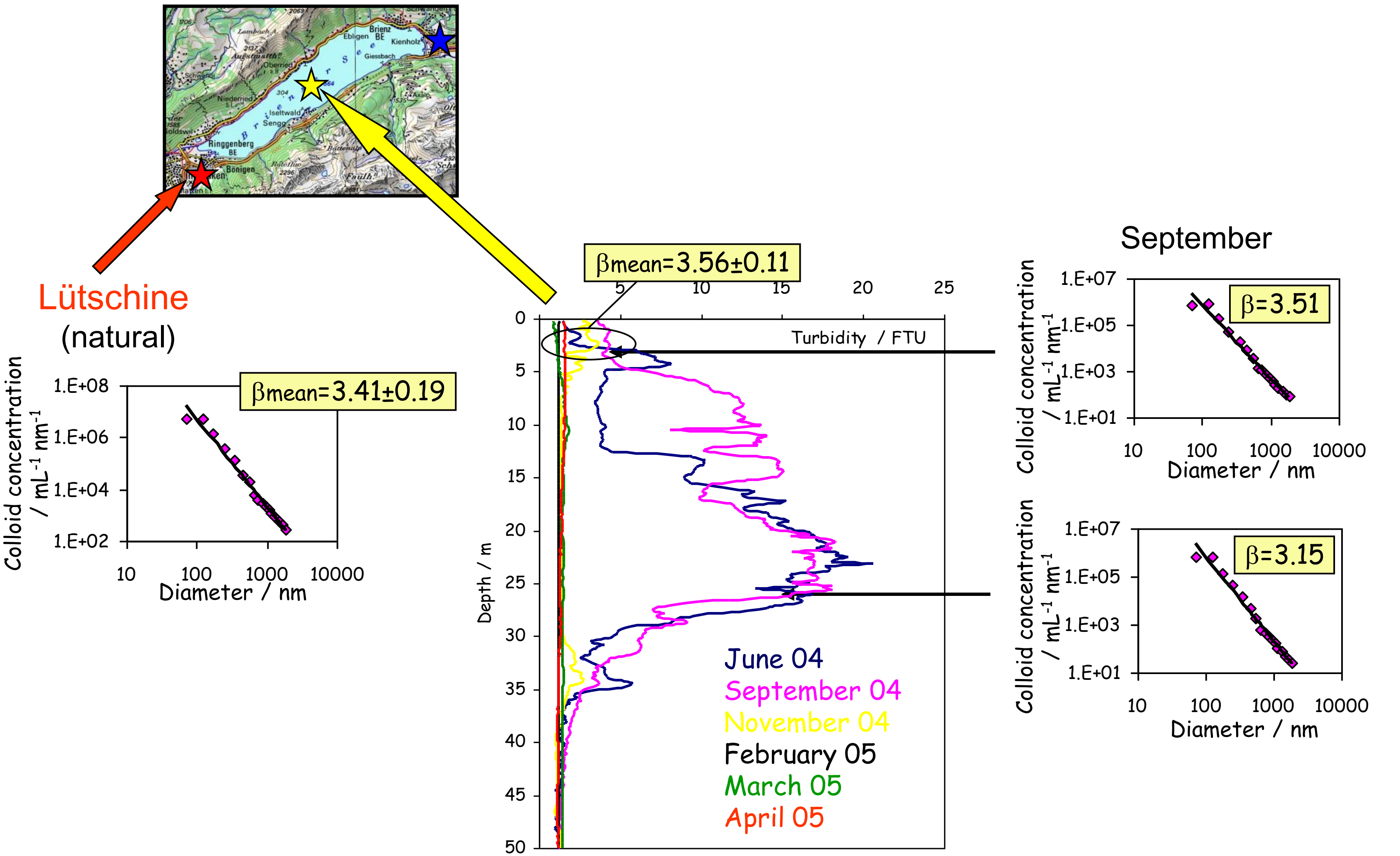
V. Chanudet and M. Filella, Size and composition of inorganic colloids in a peri-alpine, glacial flour-rich lake. GEOCHIM. COSMOCHIM. ACTA, 72, 1466-1479 (2008)

colloid **size**





colloid **size**

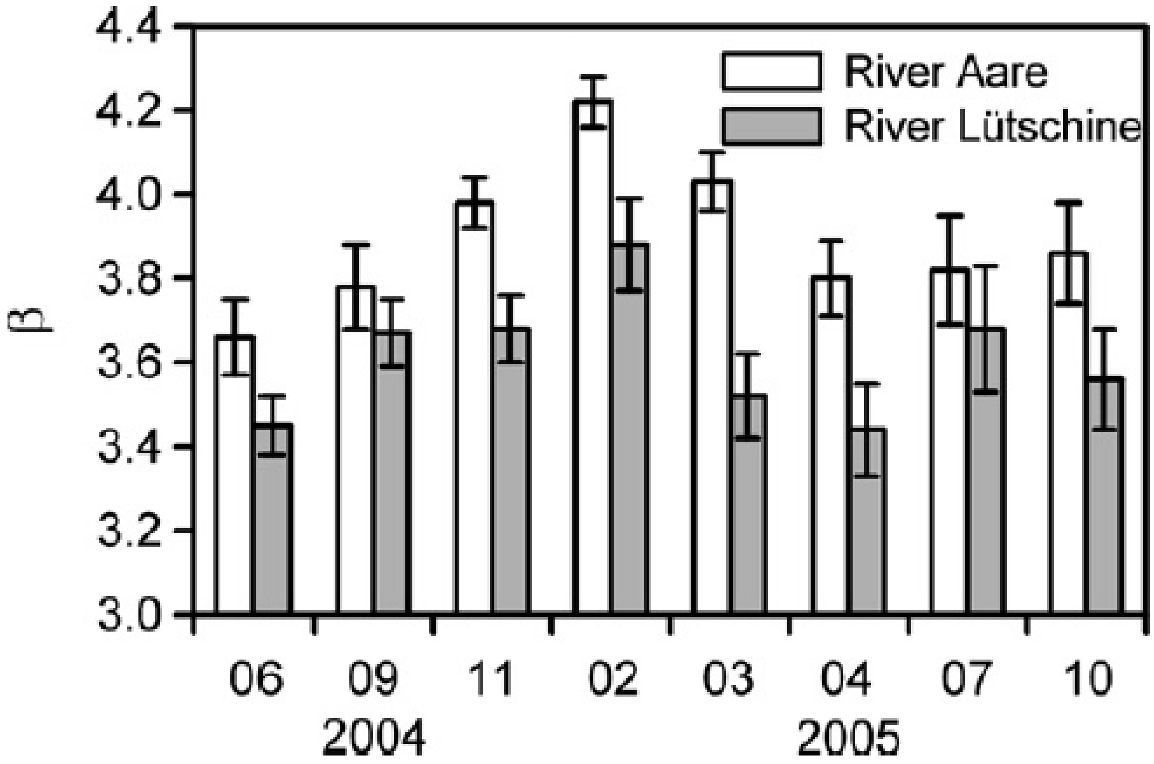


colloid **size**

	Brienz 1 m	*Brienz max turbidity*
June	4.0	**3.0**
Sep.	3.5	**3.1**
Nov.	3.5	3.5
Feb.	3.5	3.5
Mar.	3.7	3.7
Apr.	3.5	3.5
July	3.4	**3.2**
Oct.	3.5	3.4

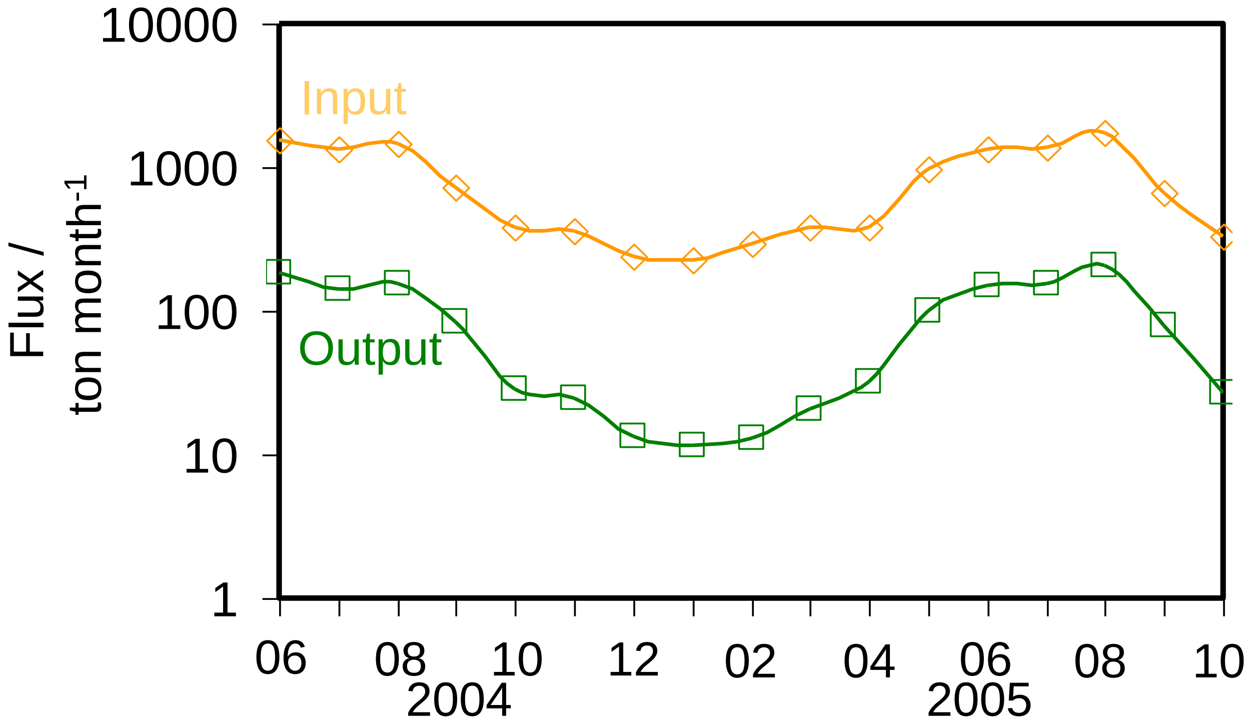
- $\beta_{turbidity} < \beta_{surface}$
- coagulation-sedimentation and or direct influence of rivers in the plume

colloid **size**



- $\beta_{\text{Lütschine}} < \beta_{\text{Aare}}$
- dams, chemical-induced aggregation, **mineralogy**

colloid **size**

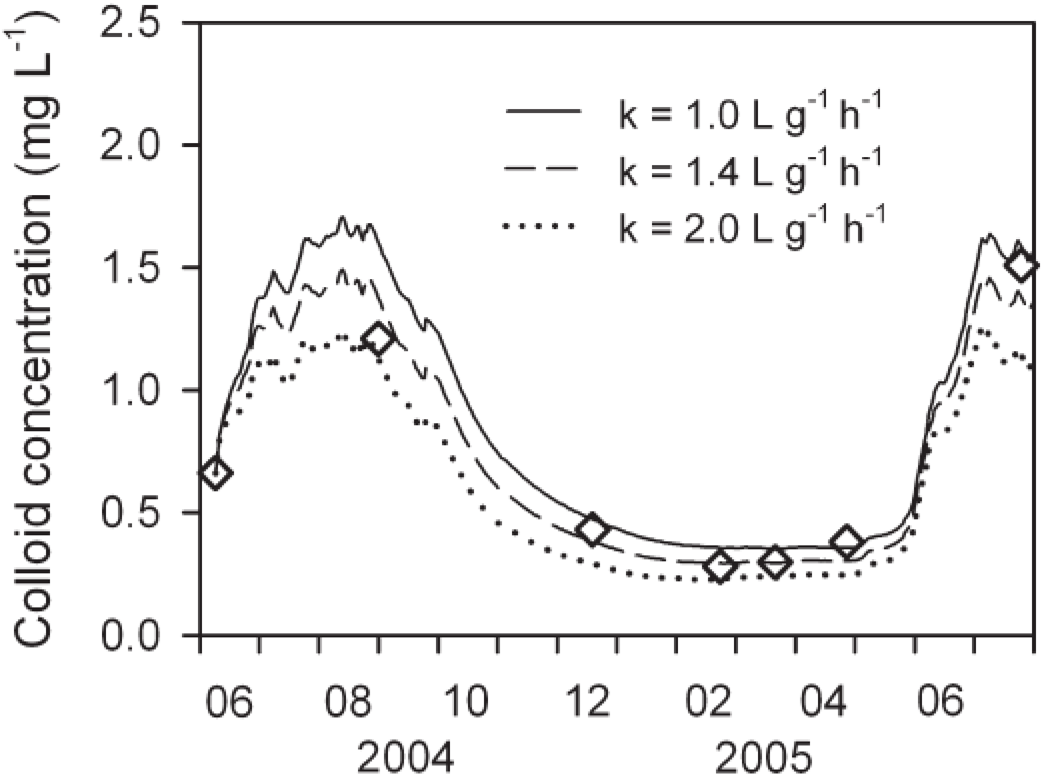


Total input : 13750 ton

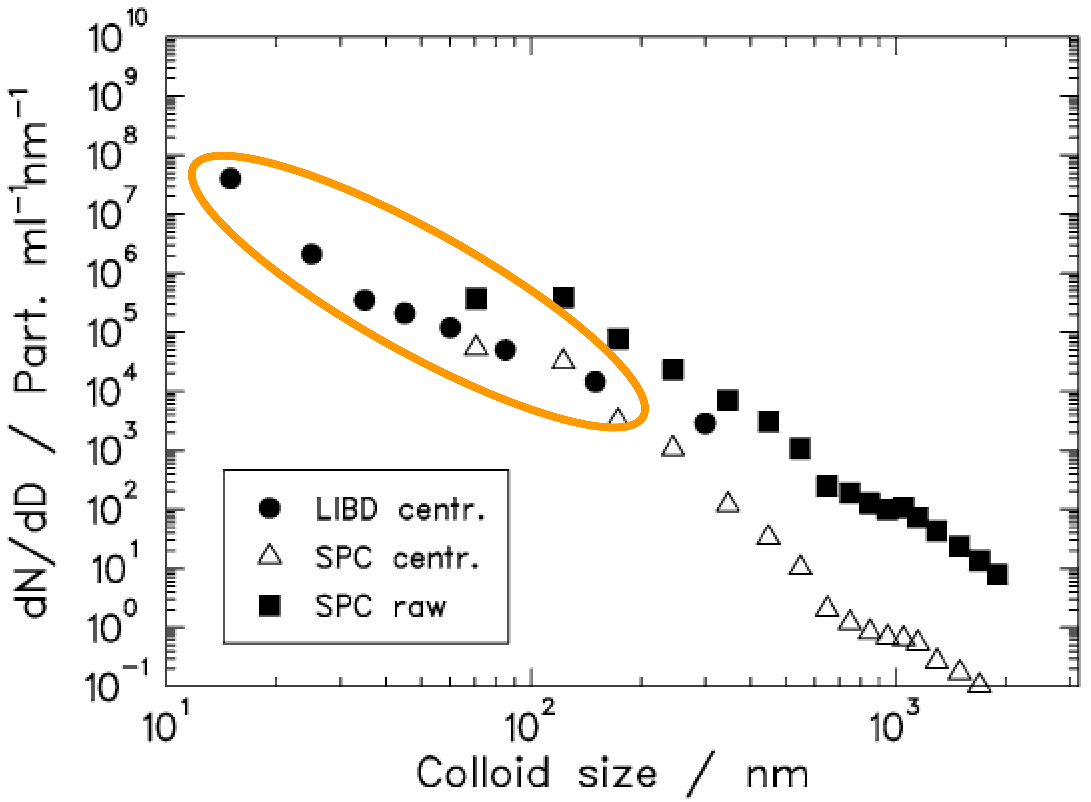
Total output : 1430 ton

≈ 90% colloids « lost » in the lake

colloid **size**



LIBD and SPC measurements

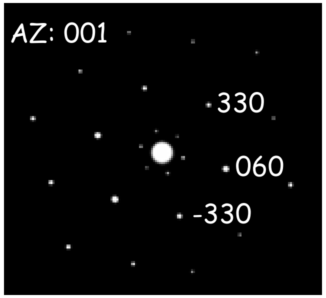


C. Walther, S. Büchner, M. Filella and V. Chanudet, Probing particle size distributions in natural surface waters from 15 nm to 2 µm by a combination of LIBD and Single Particle Counting. J. COLL. INTERFACE SCI., **301**, 532-537 (2006)

colloid composition

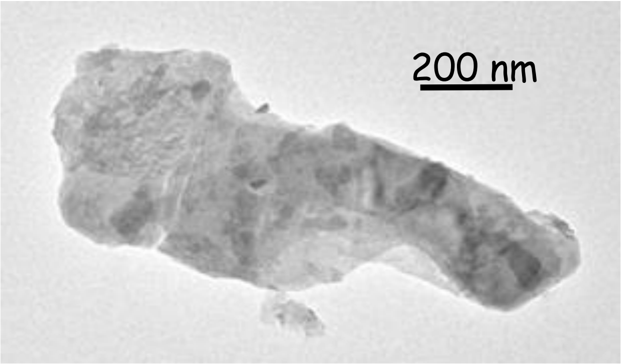
For each particle:

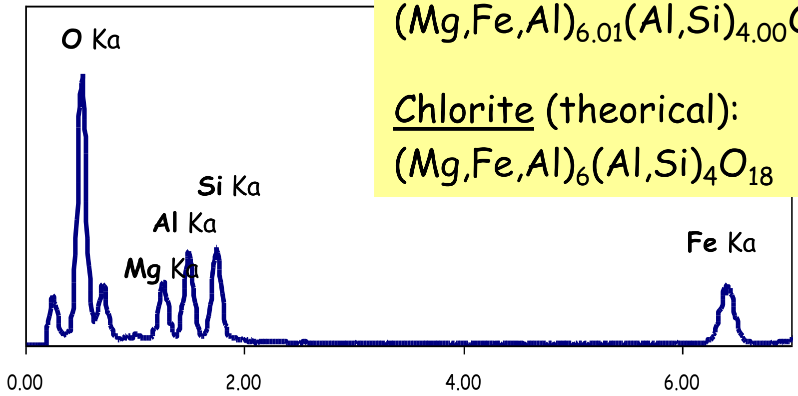
- shape (TEM)
- size (TEM)
- chemical composition (EDS)
- crystallography (SAED)



Monoclinic. class:2/m

chlorite



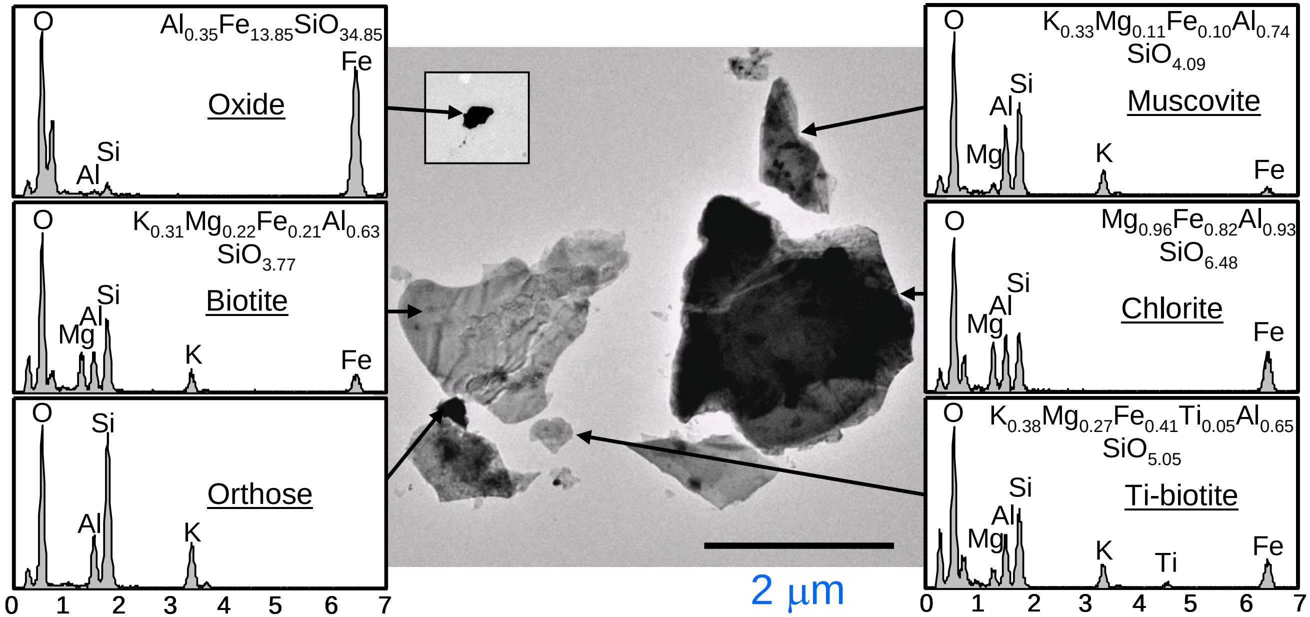


EDS: $Mg_{0.72}Fe_{0.75}Al_{0.98}Si_1O_{7.08}$
or
$(Mg,Fe,Al)_{6.01}(Al,Si)_{4.00}O_{20.53}$

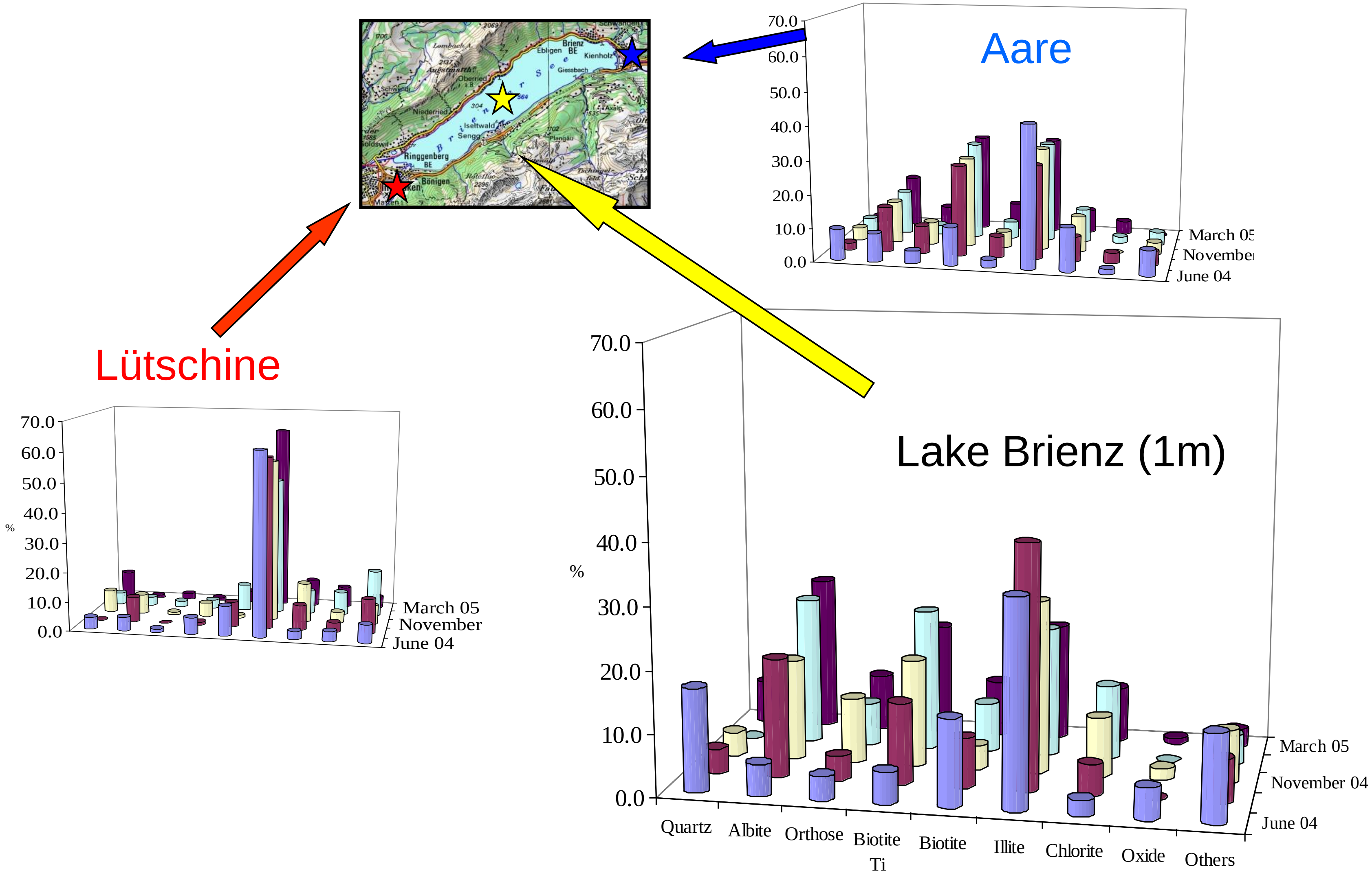
Chlorite (theorical):
$(Mg,Fe,Al)_6(Al,Si)_4O_{18}$

V. Chanudet and M. Filella, A non-perturbing scheme for the mineralogical characterisation and quantification of inorganic colloids in natural waters. ENVIRON. SCI. TECHNOL., **40**, 485-490 (2006)

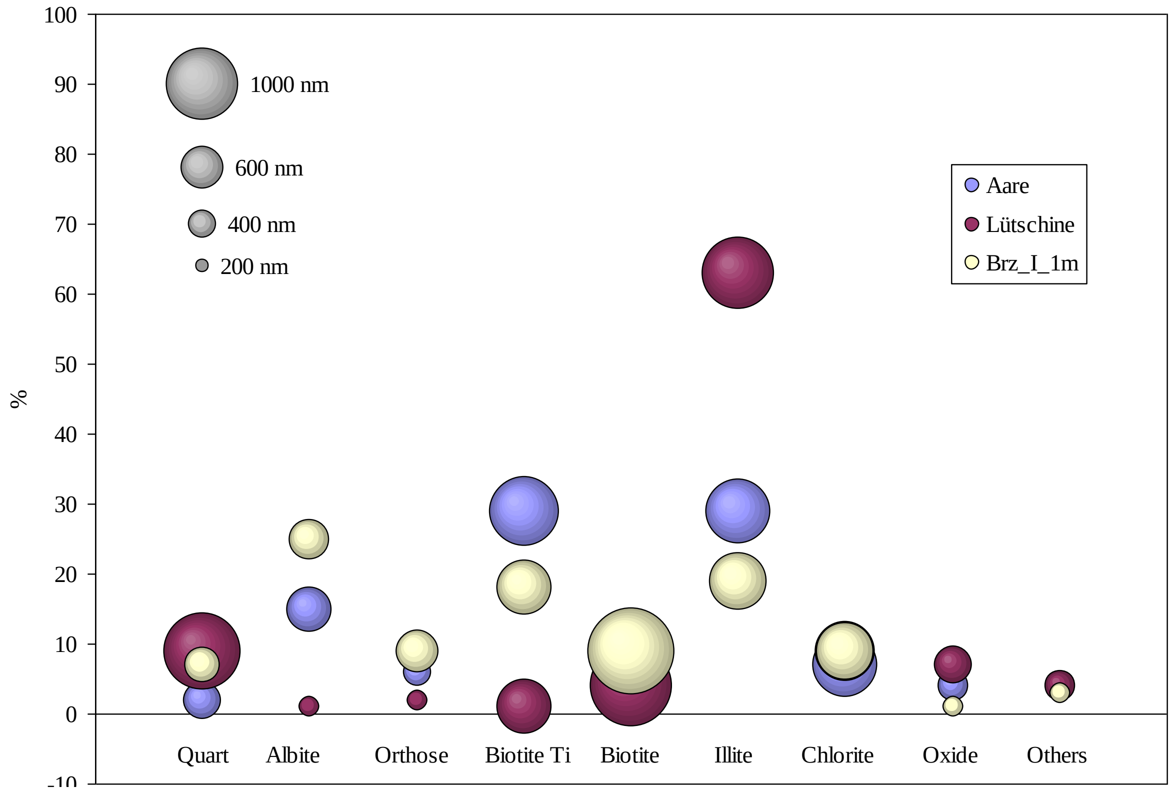
colloid **composition**



colloid **composition**

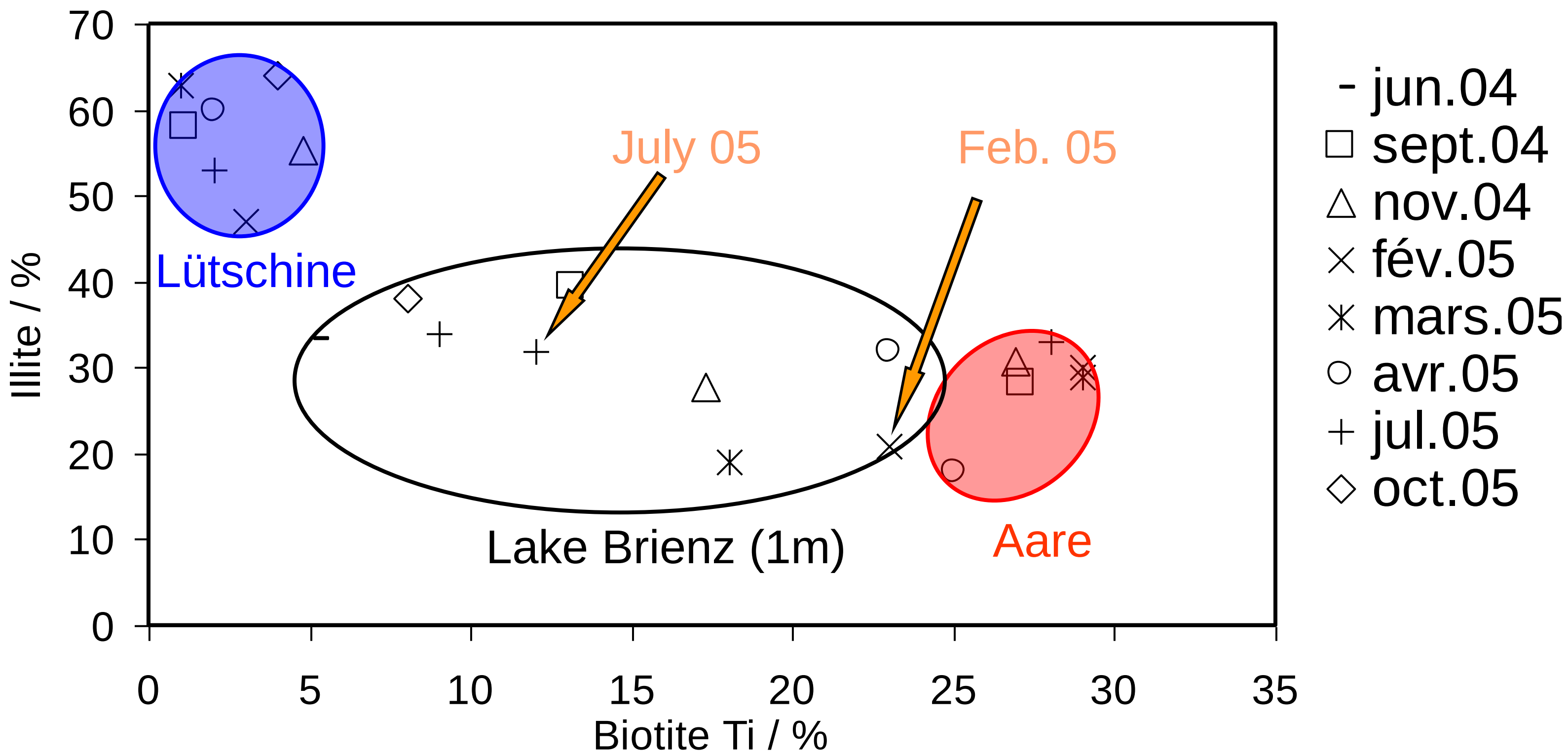


colloid composition and size



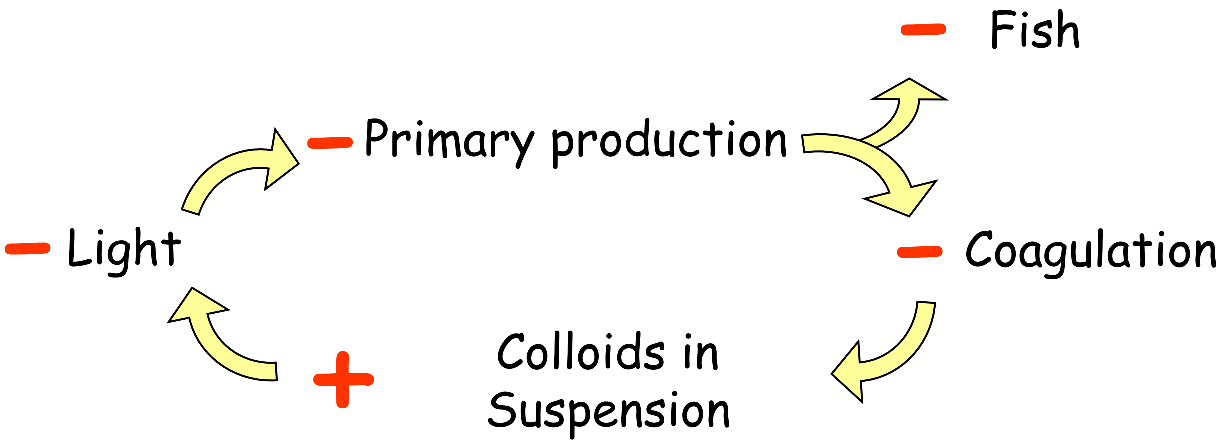
V. Chanudet and M. Filella, Size and composition of inorganic colloids in a peri-alpine, glacial flour-rich lake. GEOCHIM. COSMOCHIM. ACTA, **72**, 1466-1479 (2008)

colloid composition **and** size

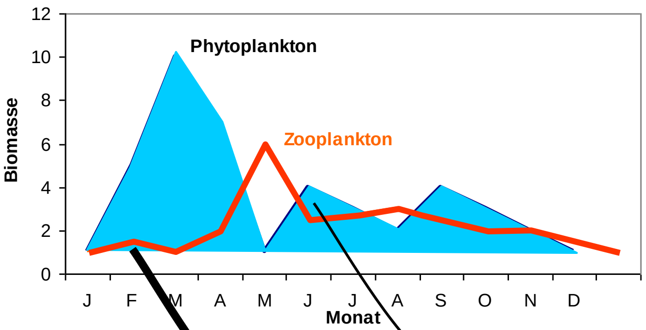


Winter : ≈ Aare
Summer : contribution from Lütschine

work **hypothesis**



why to quantify different types of NOM



Suspension

Organic matter

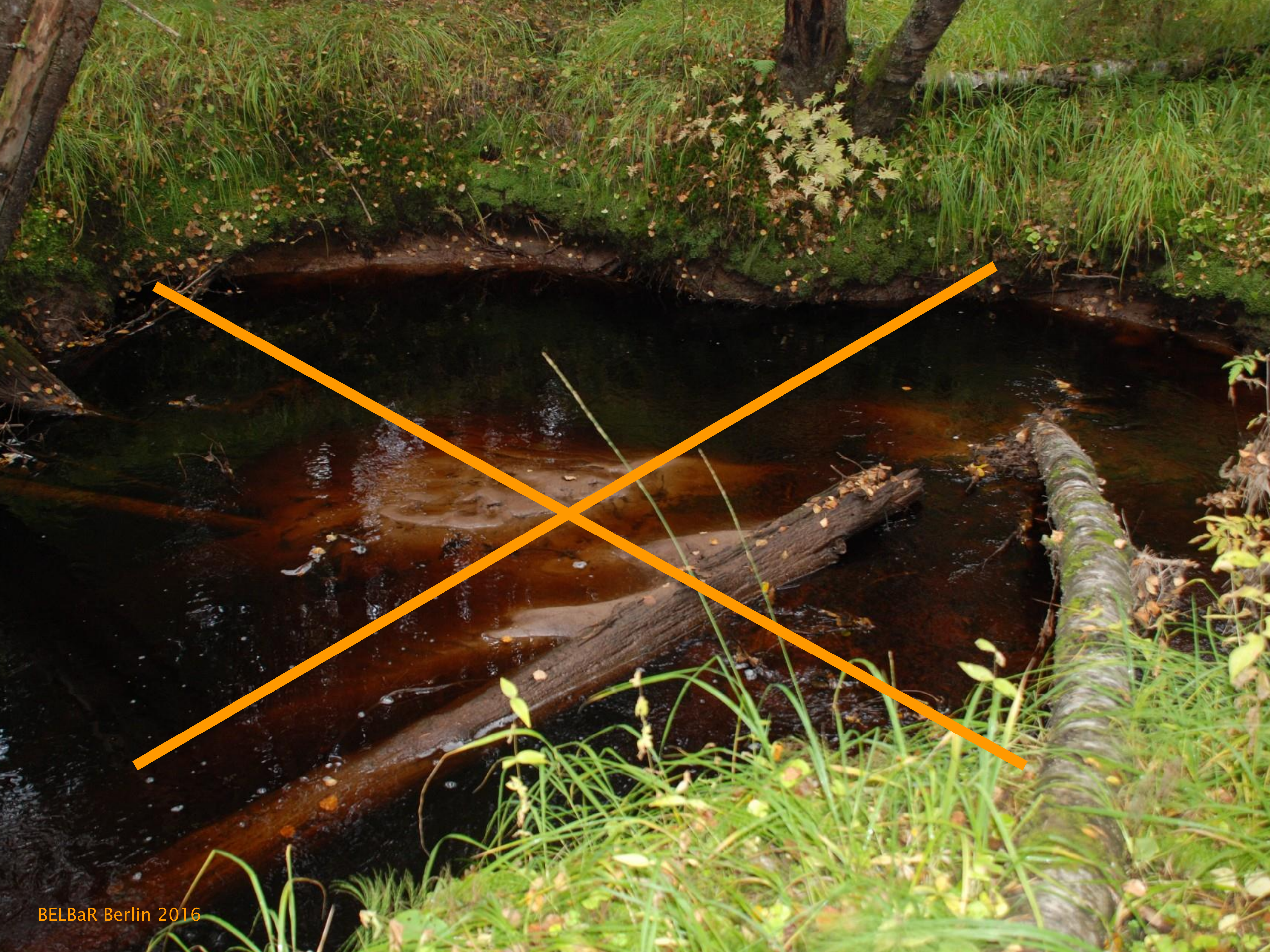
Coagulation

ROM/humics/hydrophobe

for

against

Sedimentation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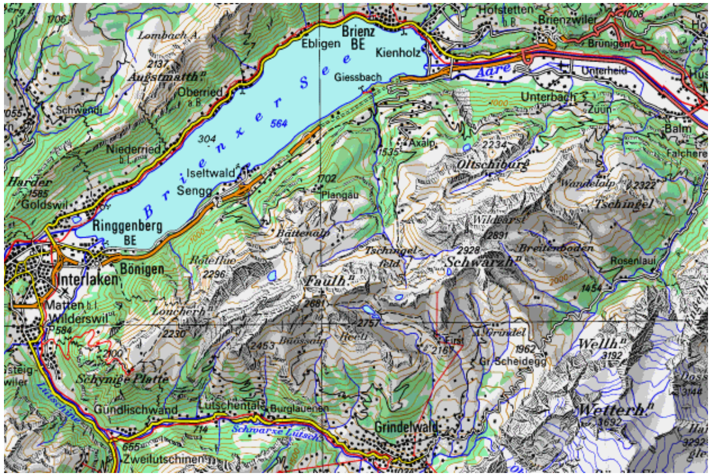
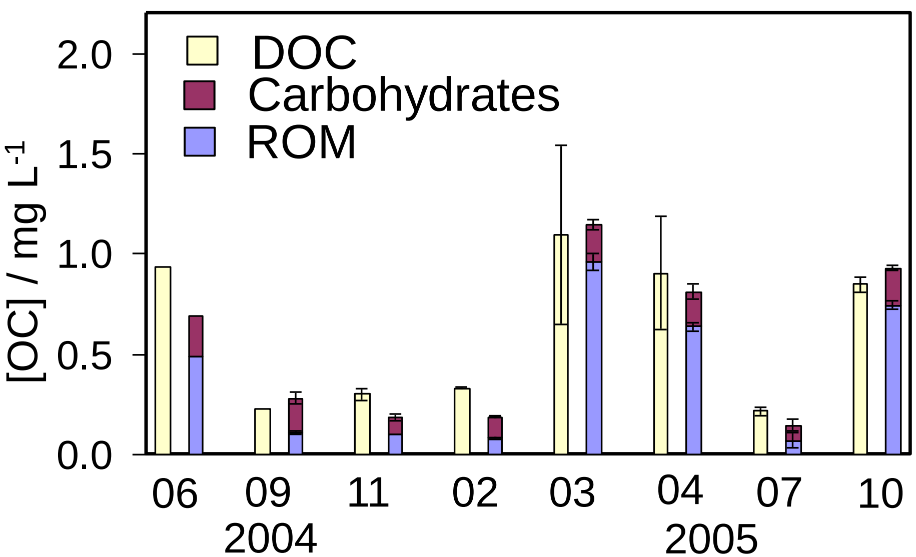
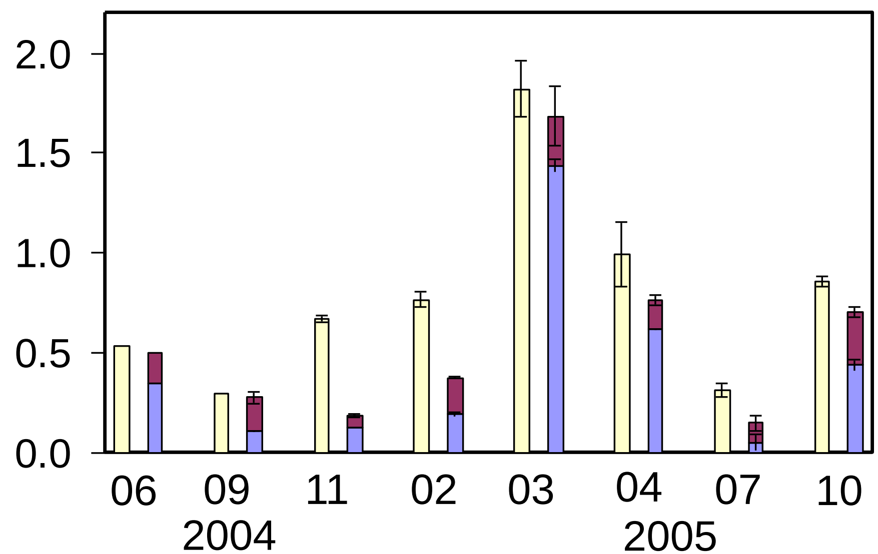
river **seasonal** variations



Aare River

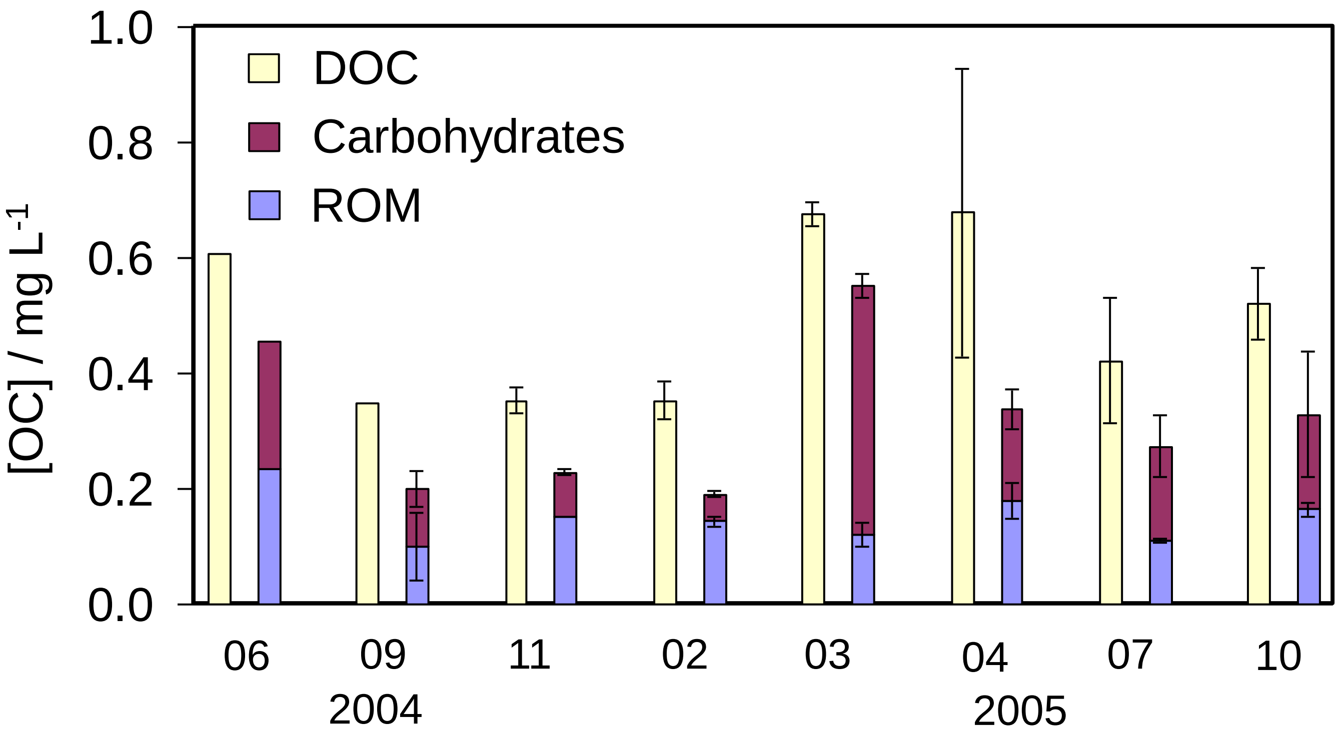


Lütschine River



V. Chanudet and M. Filella, Submicron organic matter in a peri-alpine, ultra-oligotrophic lake. ORGANIC GEOCHEMISTRY, **38**, 1146-1160 (2007)

lake **seasonal** variations



lake NOM

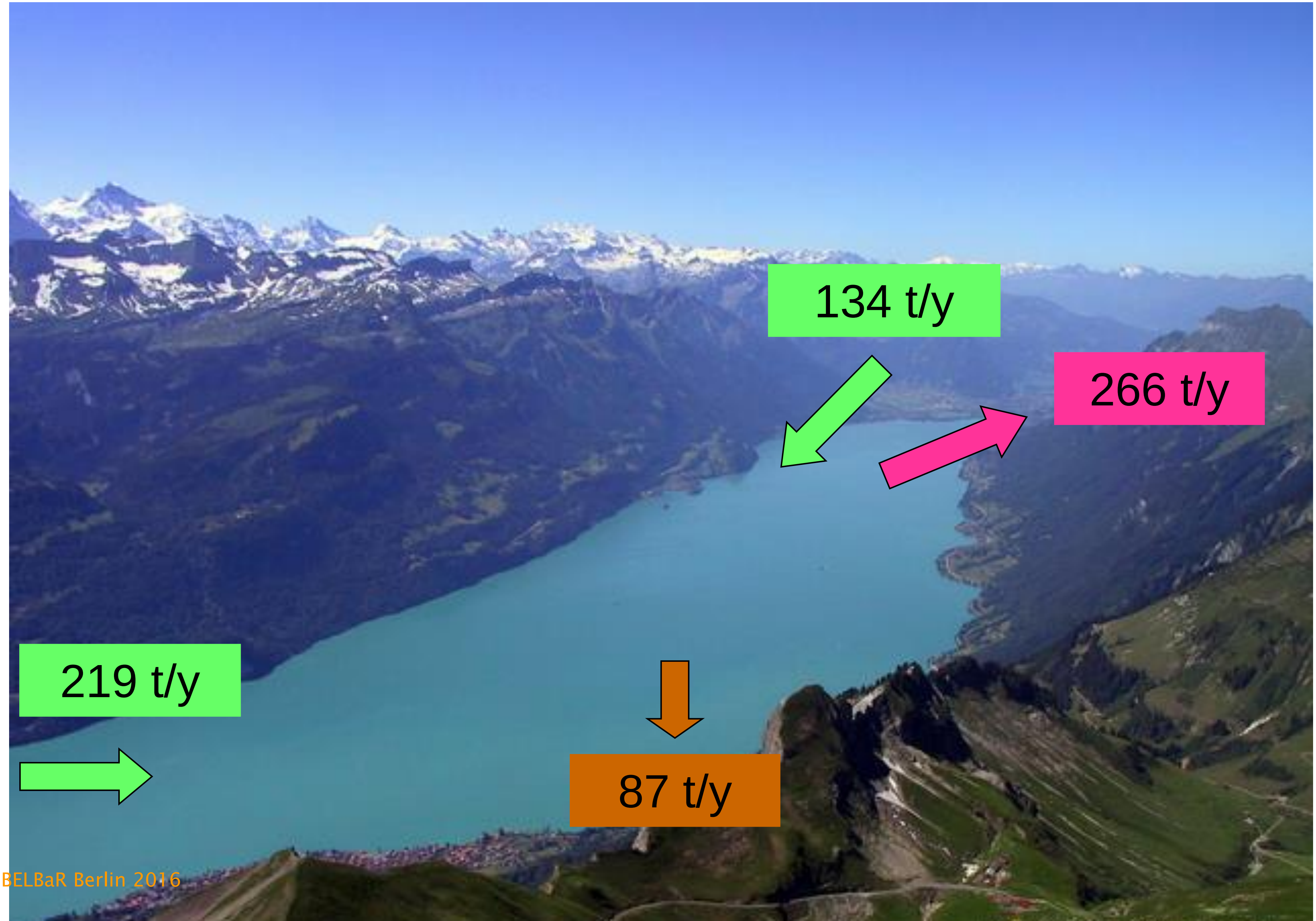
- Low and constant *ROM/humics/ hydrophobe* concentrations

  0.1 – 0.2 mg C L^{-1}

- Low polysaccharide concentrations, seasonal variations

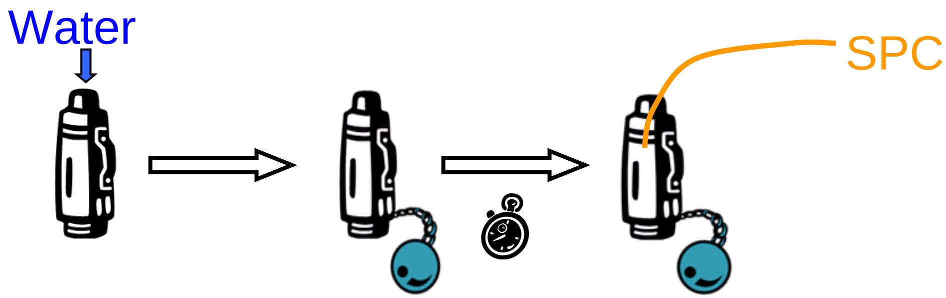
  0.1 – 0.4 mg C L^{-1}

mass balance studies: *ROM/humics/hydrophobe*



coagulation studies

Procedure



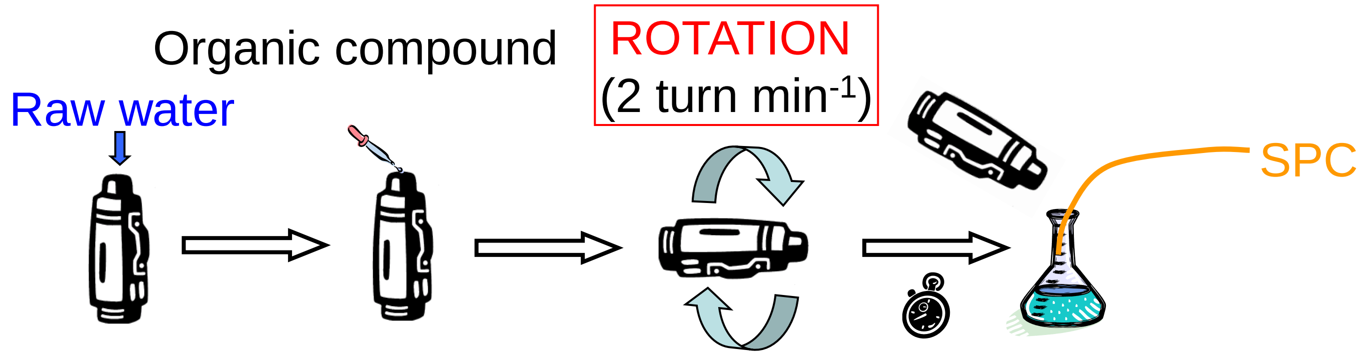
coagulation studies

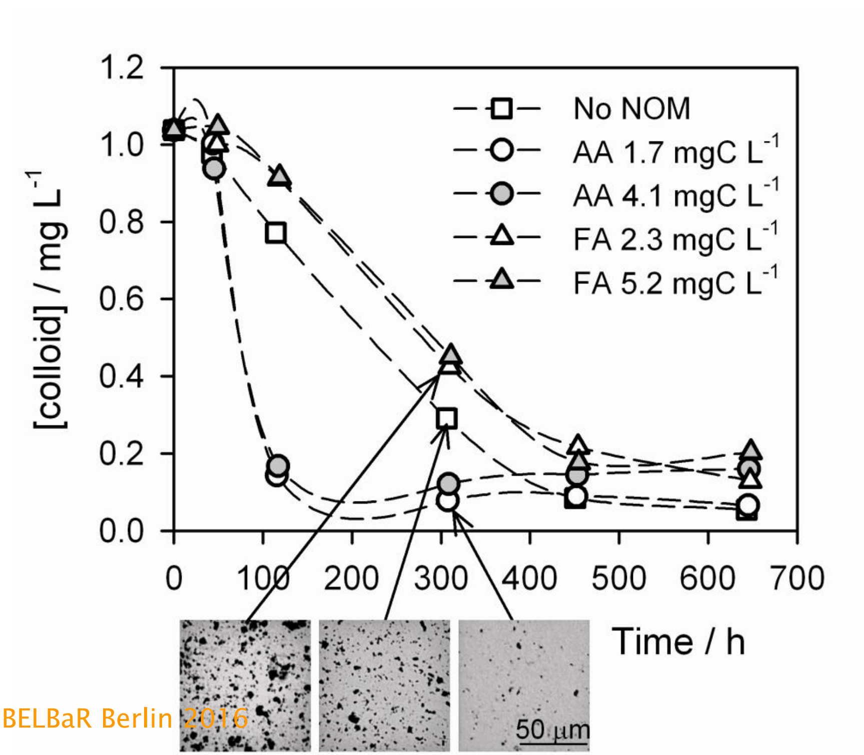
System	Date	k_n[a] (10^{-13} L h^{-1})	dN/dt at t_0[b] (10^8 L^{-1} h^{-1})	k_m[a] (L g^{-1} h^{-1})
Lake Brienz, 1 m depth	Nov 2004	2.05 ± 0.08	1.42 ± 0.06	29 ± 2
	Feb 2005	2.5 ± 0.3	0.74 ± 0.09	34 ± 3
	Mar 2005	2.81 ± 0.09	0.87 ± 0.04	34 ± 2
	Apr 2005	4.4 ± 0.6	2.4 ± 0.3	55 ± 8
	Jul 2005	2.0 ± 0.2	9 ± 1	33 ± 3
	Aug 2005	1.9 ± 0.3	7.5 ± 1.3	36 ± 3
	Sep 2005	2.30 ± 0.05	8.2 ± 0.2	30 ± 1
	Oct 2005	2.0 ± 0.3	6.2 ± 0.8	28 ± 3
Lake Thun	Sep 2005	2.84 ± 0.04	1.20 ± 0.02	46 ± 1
	Oct 2005	3.1 ± 0.2	0.38 ± 0.02	62 ± 7
River Aare	Nov 2004	0.017 ± 0.001	25 ± 1	0.5 ± 0.1
River Lütschine	Nov 2004	1.75 ± 0.03	1.08 ± 0.03	21 ± 1
	Feb 2005	1.7 ± 0.2	0.20 ± 0.02	51 ± 5
KWO outlet	Mar 2005	0.017 ± 0.003	34 ± 6	0.61 ± 0.03

- max. when higher productivity
- no coagulation in Aare waters

V. Chanudet and M. Filella, The fate of inorganic colloidal particles in Lake Brienz. AQUATIC SCIENCES, **69**, 199-211 (2007)

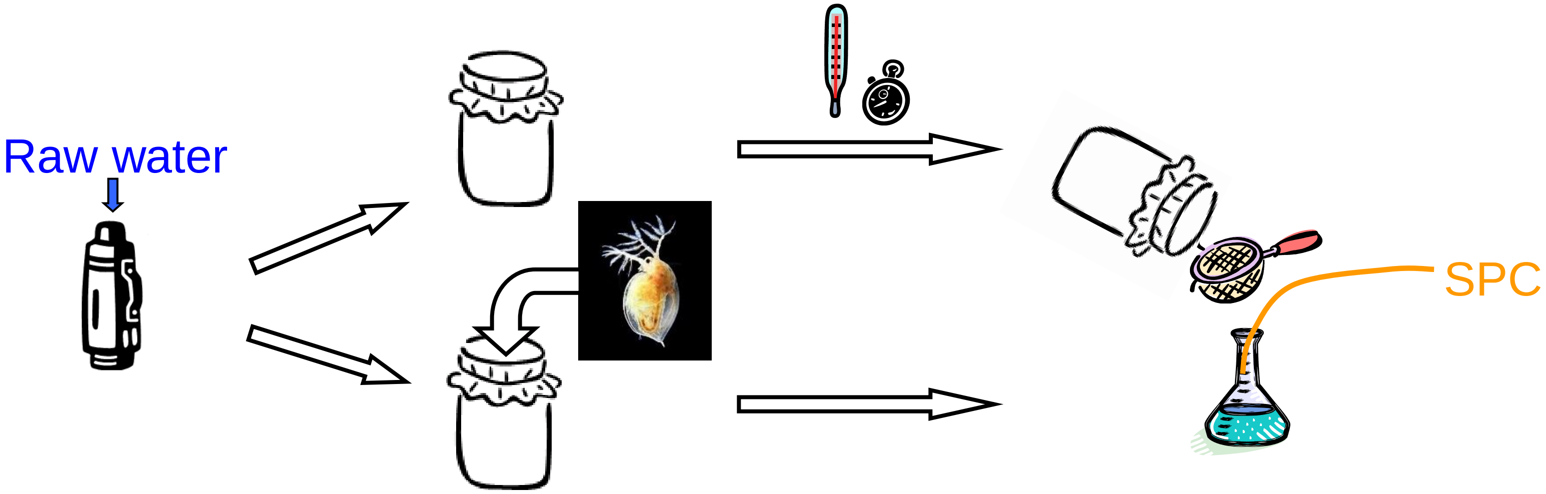
coagulation studies





Organic compound	*[ ] mgC L⁻¹*	***k*produit / *k*ref**
Alginic acid	0.3	**0.9**
	1.7	**2.7 ± 0.5**
	4.1	**2.0**
Dextran	1.7	**1.1**
Galacturonic acid	1.7	**0.4**
Polygalacturonic acid	1.7	**1.2**
Fulvic acid	2.3	**0.8**
	5.2	**0.8**

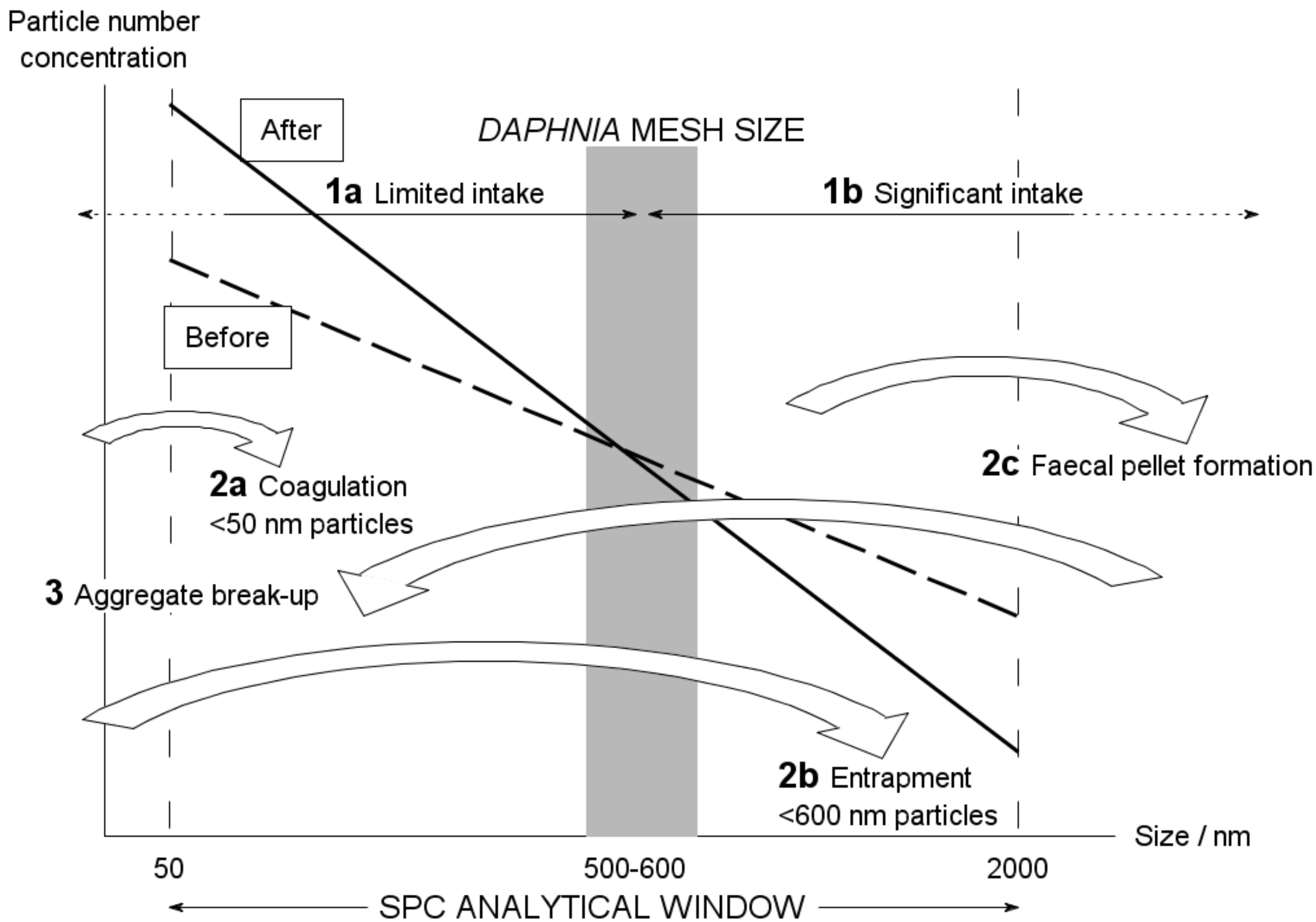
coagulation studies: Daphnia



- Faecal pellet formation only for particles bigger than Daphnia mesh size (500-600 nm)
- Not enough Daphnia in Lake Brienz

M. Filella, C. Rellstab, V. Chanudet and P. Spaak, Effect of the filter feeder Daphnia on the particle size distribution of inorganic colloids in freshwaters. WATER RES., **42**, 1919-1924 (2008)

coagulation studies: Daphnia



work **hypothesis**

− Fish

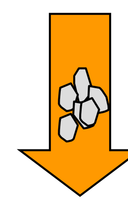
− Primary production

− Light

− Coagulation

\+ Colloids in Suspension

10 – 20 x 

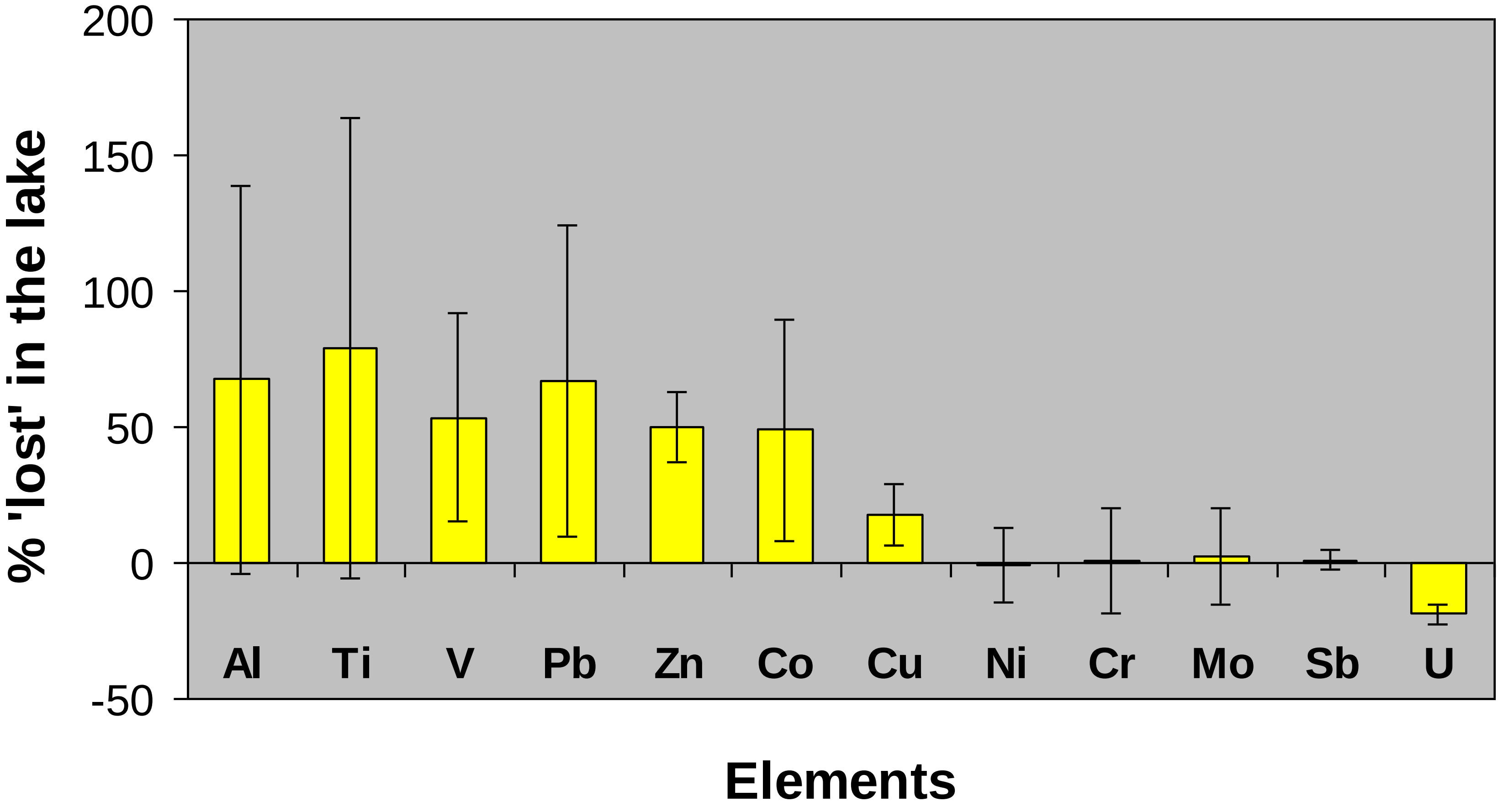
= 2 x 

any **solution**?

more

- trace element fate
- colloids in ice
- colloids in mine groundwater
- phosphate fate
- NOM sorption on ‘real’ inorganic colloids

trace element fate

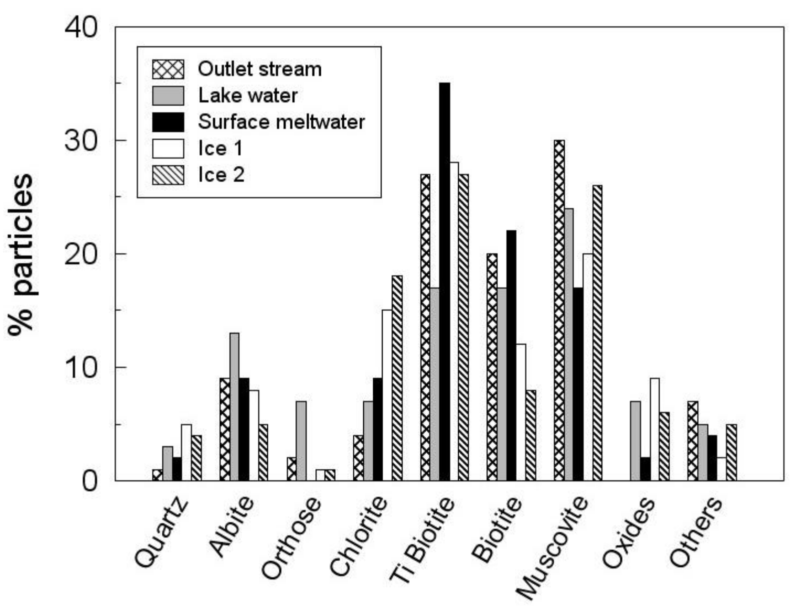


colloids in **ice**

colloids in ice

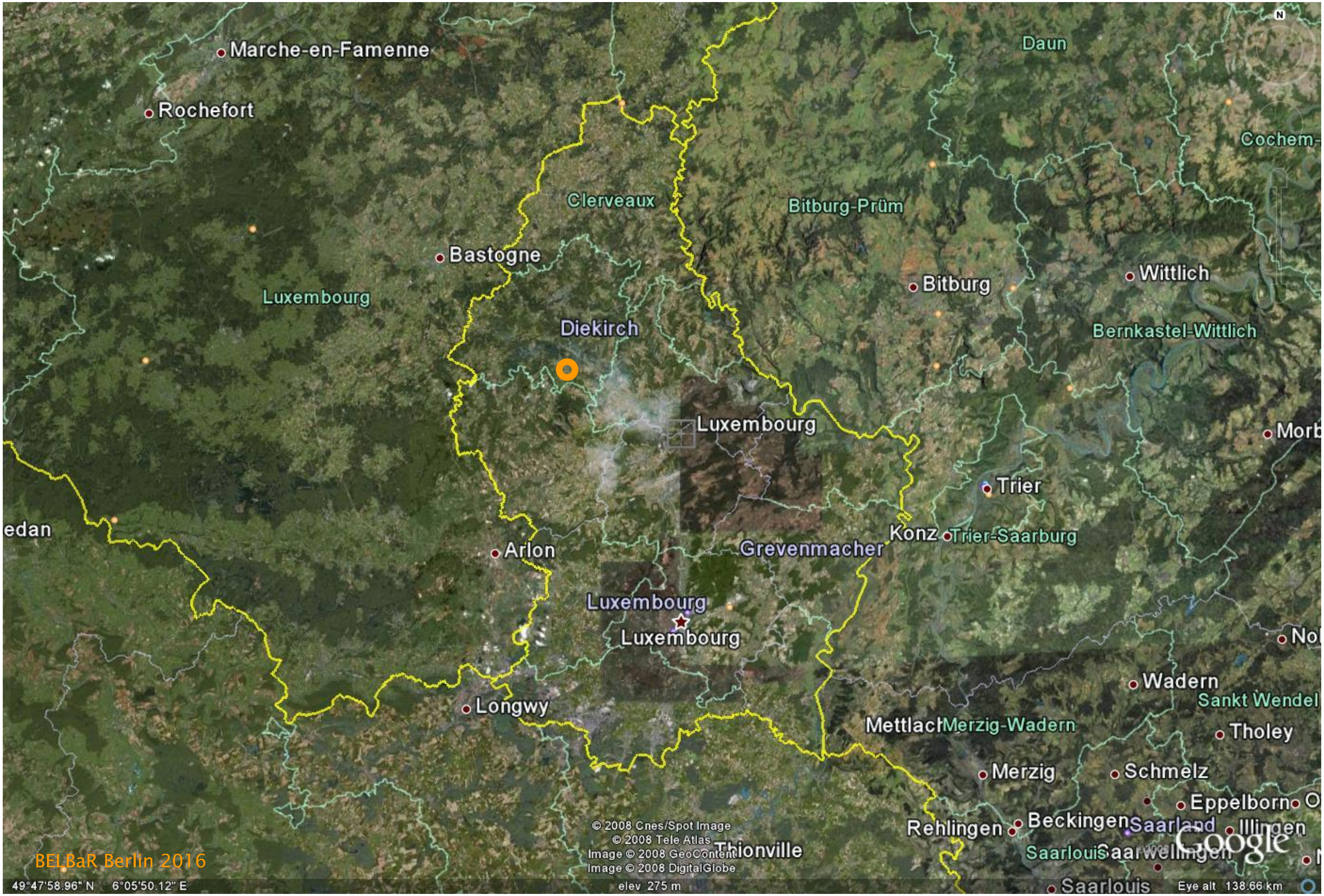
colloids in **ice**

Sample	β^a	Colloid number[b] / mL^{-1}	Colloid mass[c] / mg L^{-1}	TSS[d] / mg L^{-1}
Glacier ice 1	3.3 ± 0.2	$(4.08 \pm 0.10)\times10^7$	0.58 ± 0.02	60.2 ± 0.2
Glacier ice 2	3.0 ± 0.2	$(6.12 \pm 0.10)\times10^7$	1.31 ± 0.04	105.0 ± 0.3
Glacier surface meltwater	4.0 ± 0.1	$(9.93 \pm 0.03)\times10^7$	0.74 ± 0.01	16.0 ± 0.2
Glacier outlet stream	4.0 ± 0.1	$(1.01 \pm 0.01)\times10^9$	7.3 ± 0.1	176.1 ± 0.4
Lake water	4.2 ± 0.1	$(1.16 \pm 0.01)\times10^9$	8.4 ± 0.1	59.5 ± 0.5

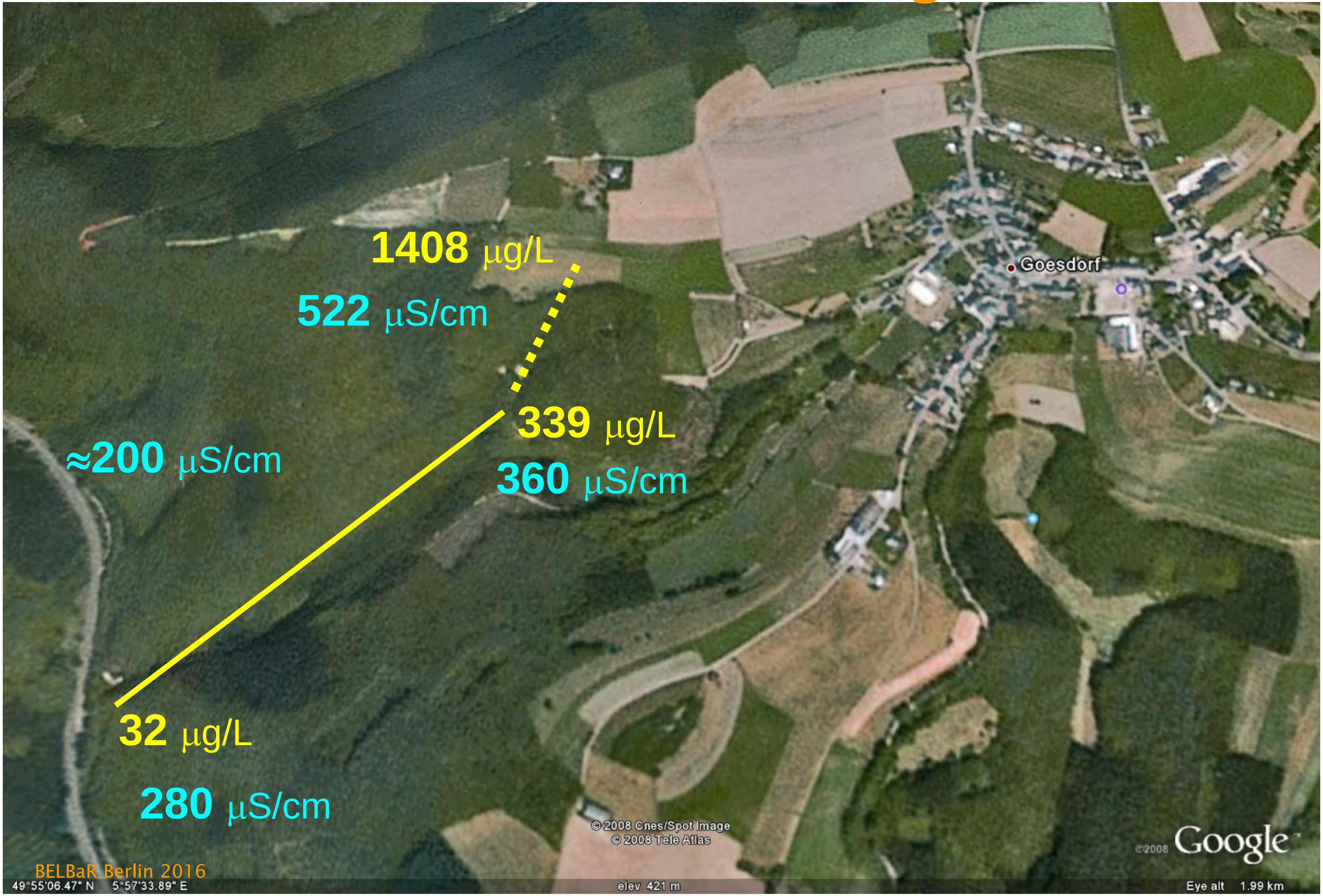


V. Chanudet and M. Filella, Particle size and mineralogical composition of inorganic colloids in glacier-melting water and overlying ice in an Alpine glacier, the Oberaargletscher, Switzerland. J. GLACIOLOGY, **52**, 473-475 (2006)

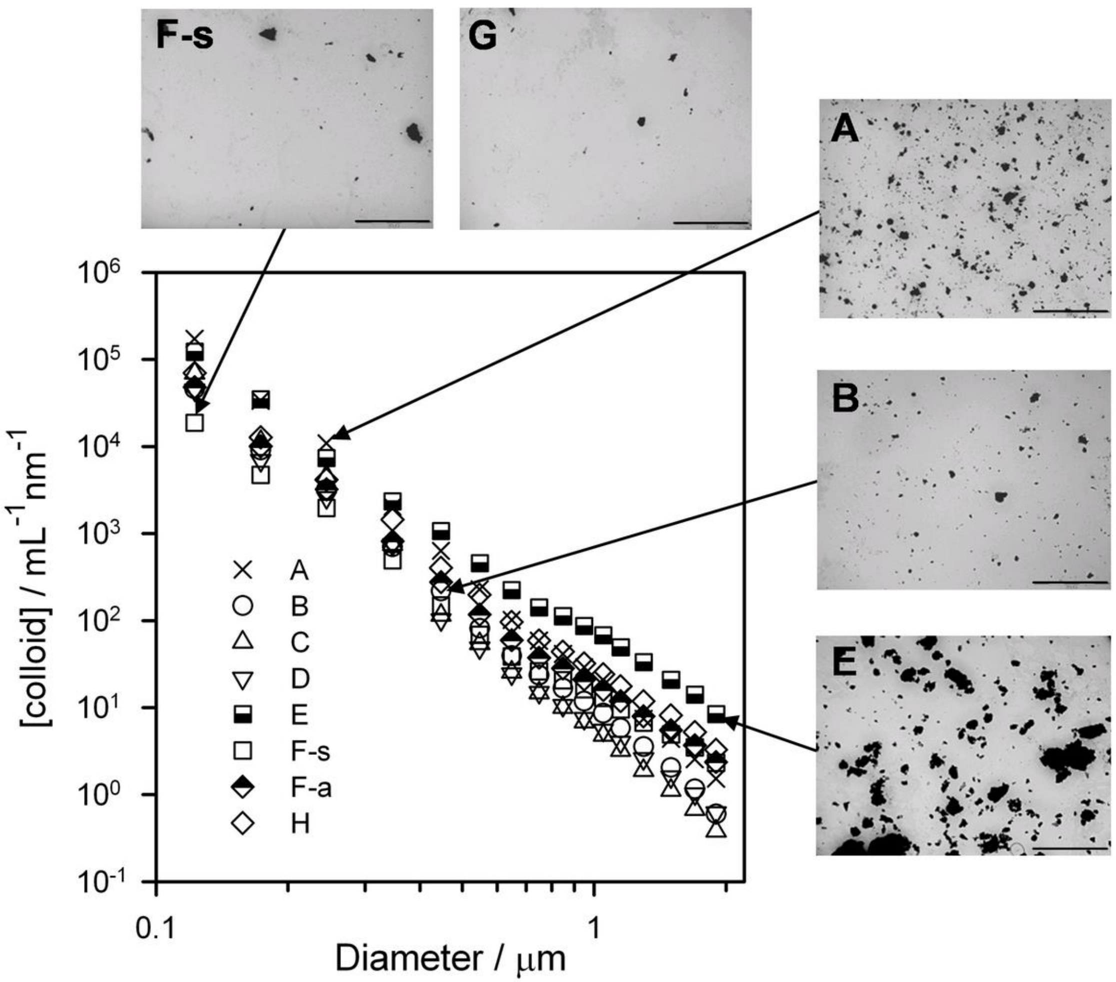
colloids in a mine groundwater



colloids in a mine groundwater

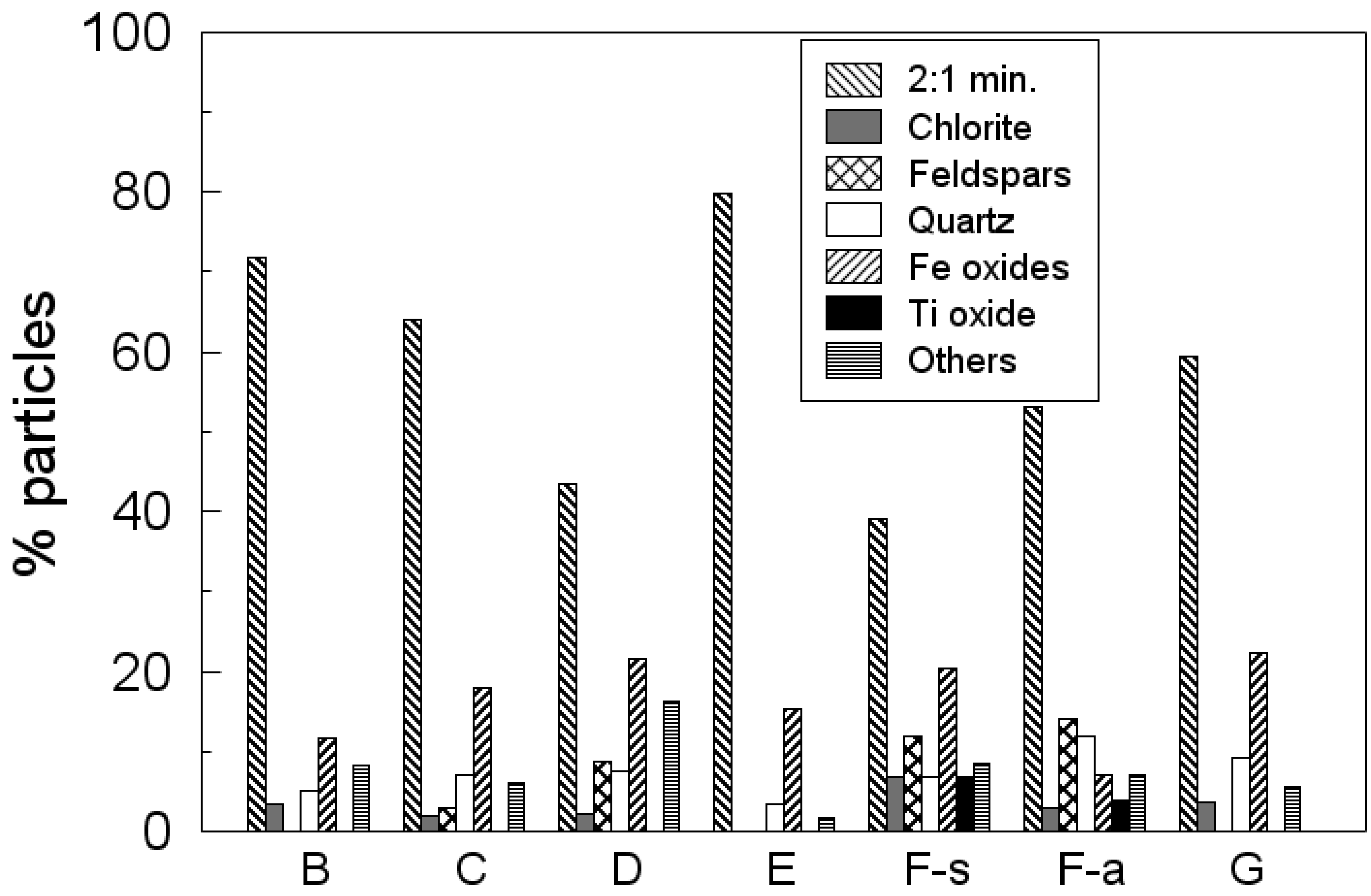


colloids in a mine **groundwater**

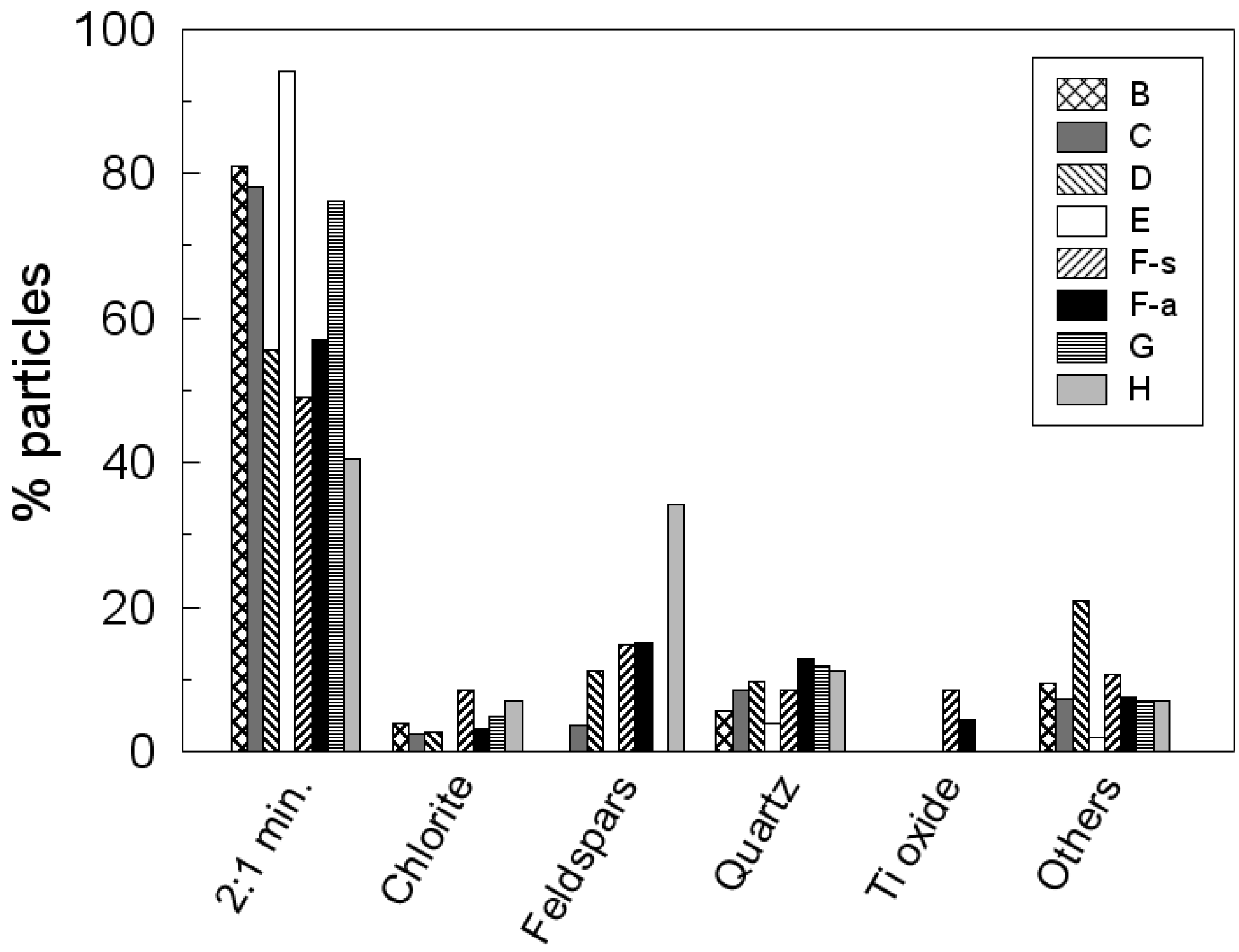


M. Filella, V. Chanudet, S. Philippo and F. Quentel, Particle size and mineralogical composition of inorganic colloids in draining waters of the adit of an abandoned mine, Goesdorf, Luxembourg. APPLIED GEOCHEM., **24**, 52-61 (2009)

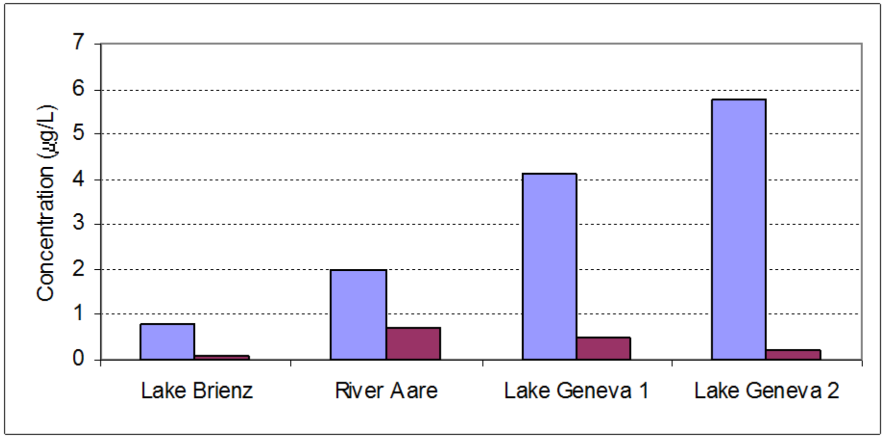
colloids in a mine groundwater



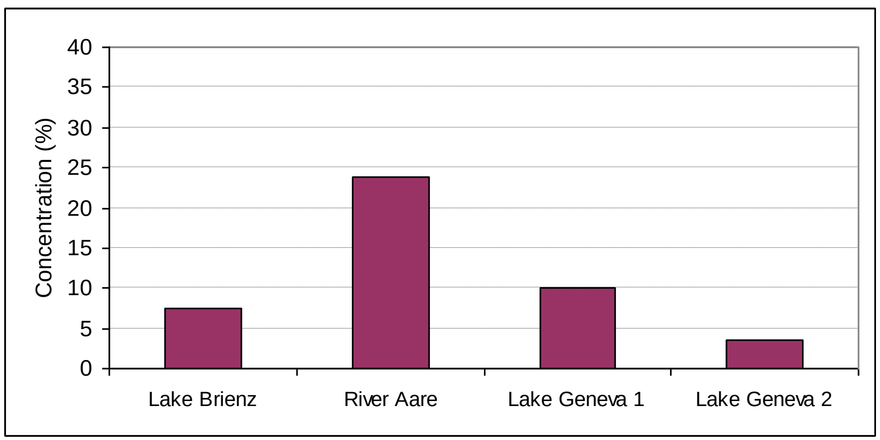
colloids in a mine **groundwater**

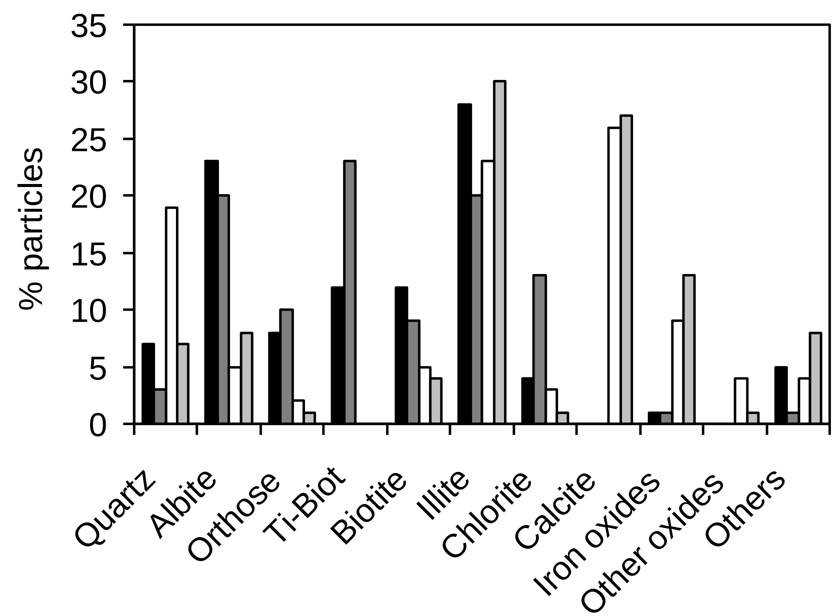


phosphate fate



System	Total colloid surface (3 kDa – 1.2 µm.)[f] / mm^2 mL^{-1}	Colloidal-P surface density[g] / ng cm^{-2}
Lake Brienz	23	32
River Aare	1437	5
Lake Geneva 1	37	134
Lake Geneva 2	11	188





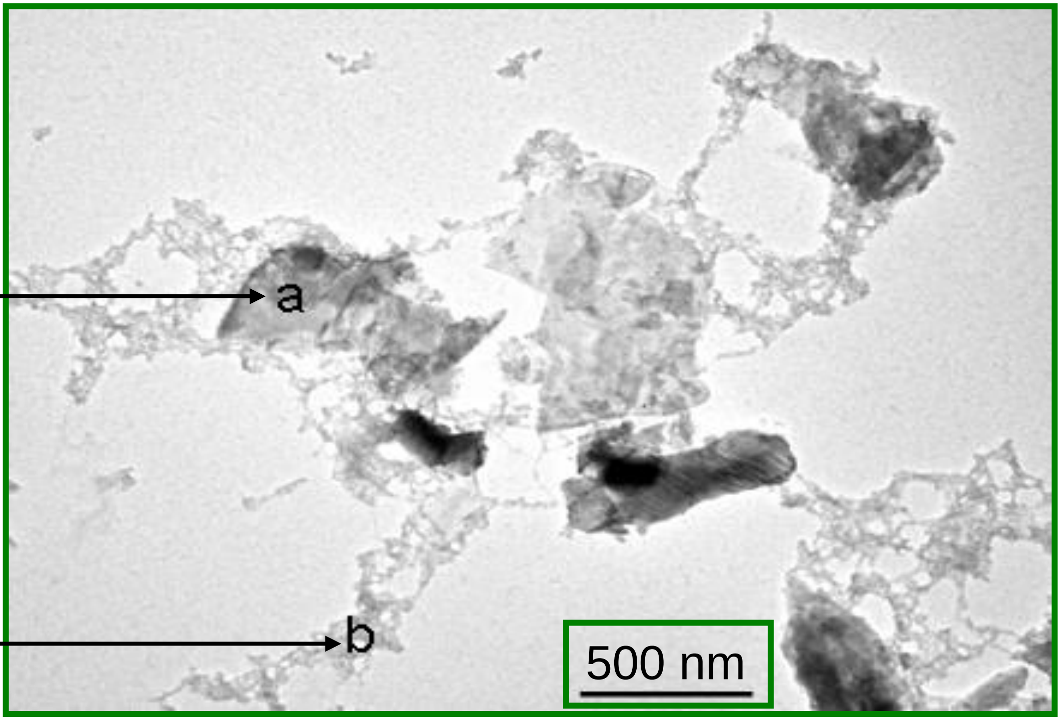
M. Filella, C. Deville, V. Chanudet and D. Vignati, ariability of the colloidal molybdate reactive phosphorous concentrations in freshwaters. WATER RES., **40**, 3185-3192 (2006).

traditional observation method

TEM + Rutenium red

Mineral particle

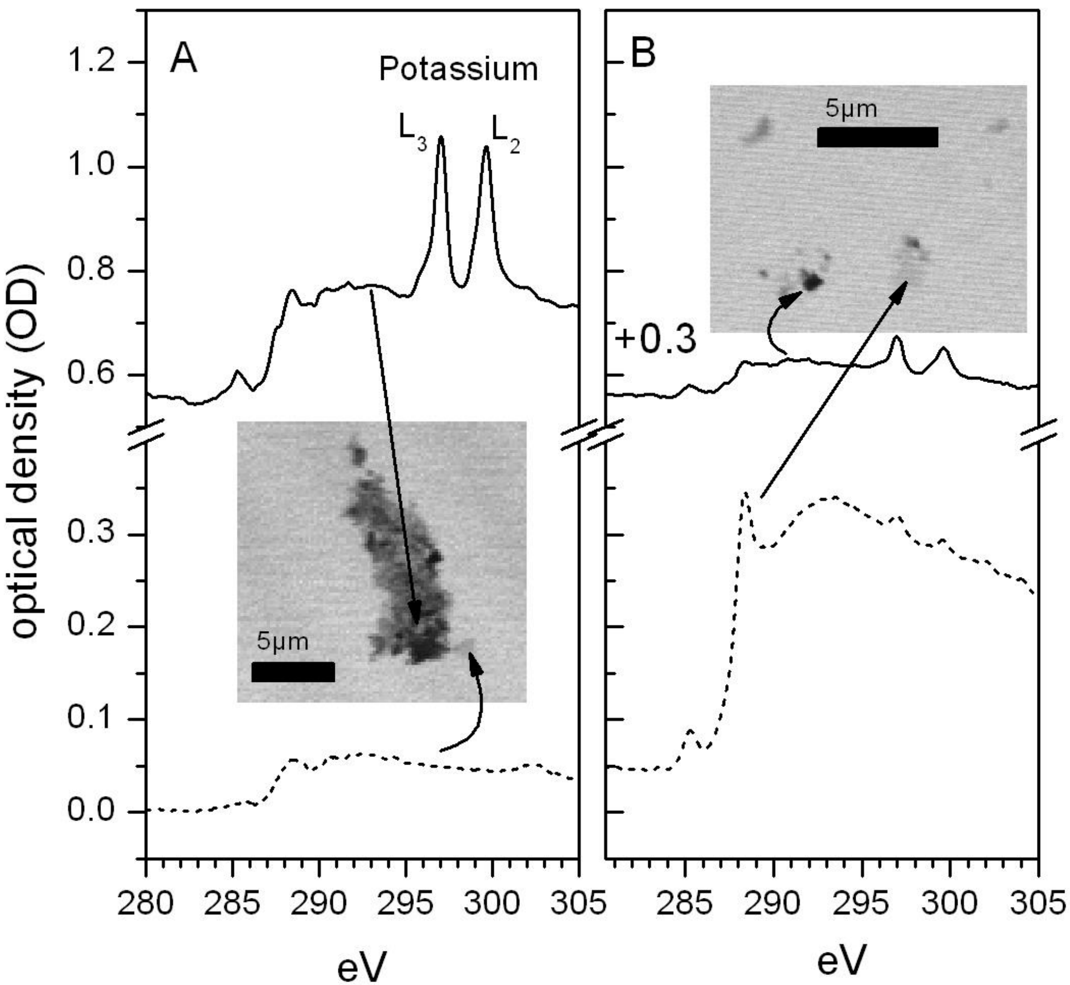
Polysaccharides
(fibrils)



STXM and C K-edge spectroscopy

Lütschine River

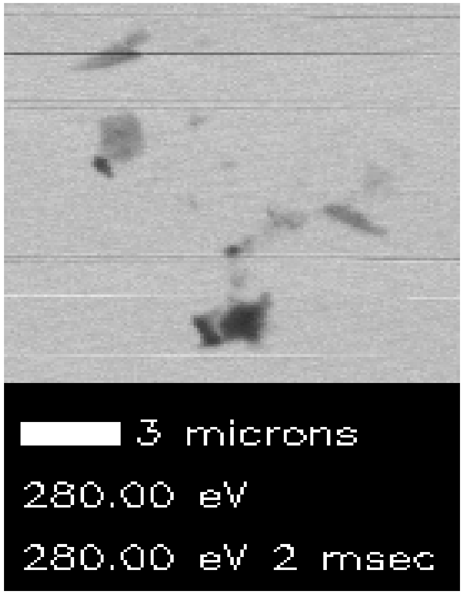
Aare River

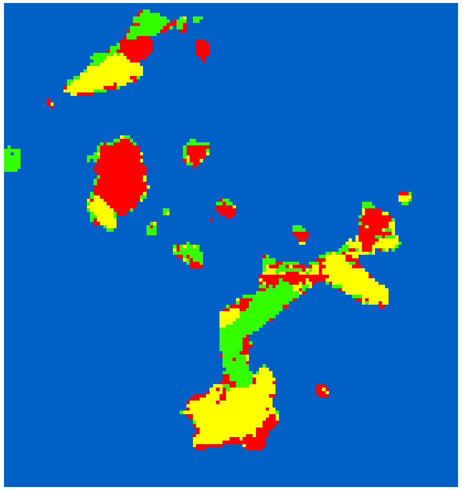


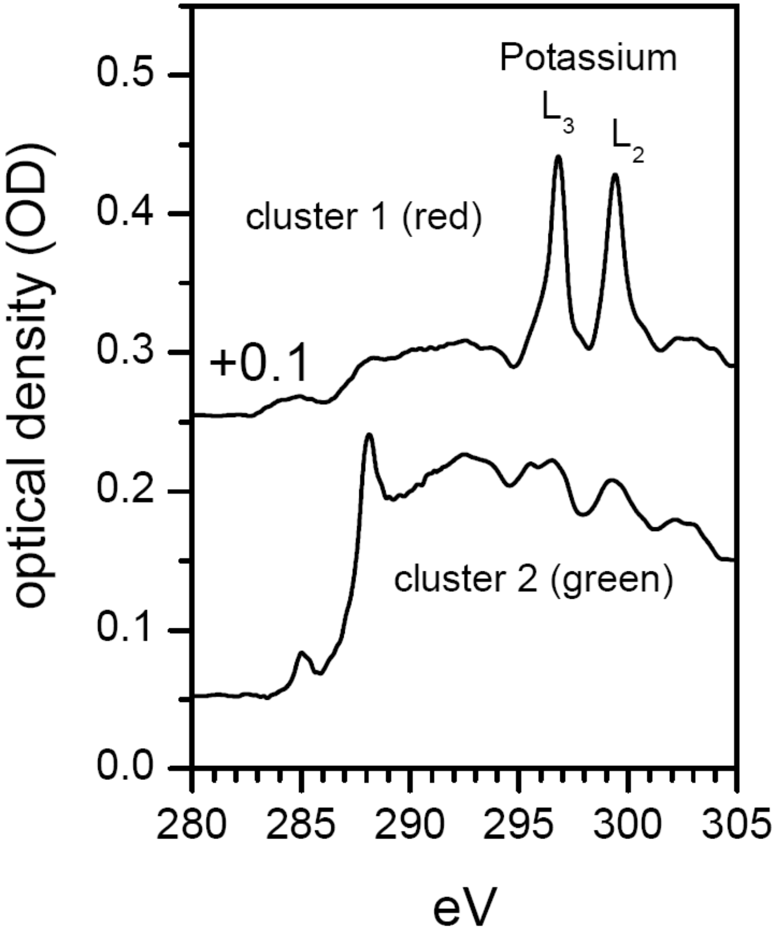
T. Schäfer, V. Chanudet, F. Claret and M. Filella, Spectromicroscopy mapping of colloidal/particulate organic matter in Lake Brienz, Switzerland. ENV. SCI. TECHNOL., **41**, 7864-7869 (2007).

STXM and C K-edge spectroscopy

Lake Brienz
1 m depth

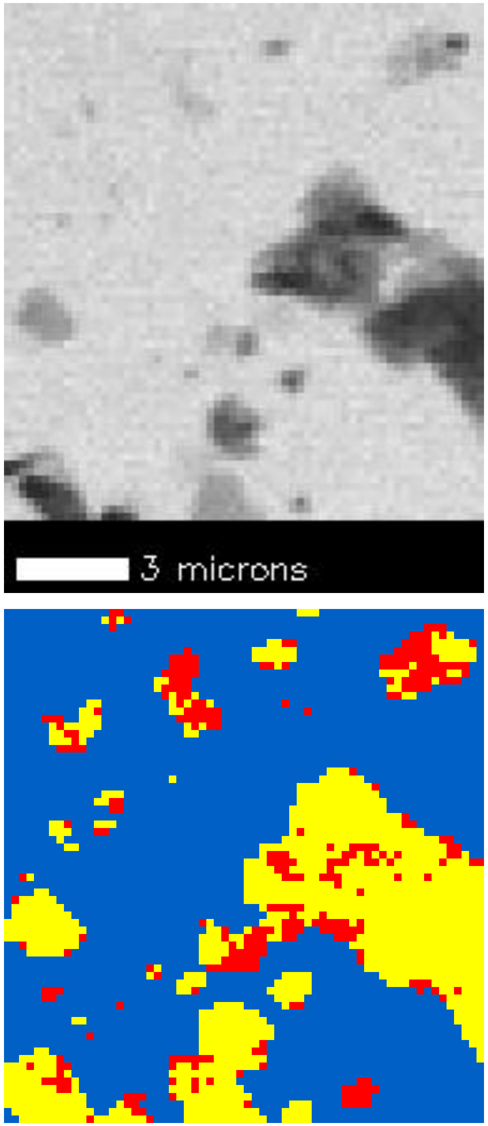


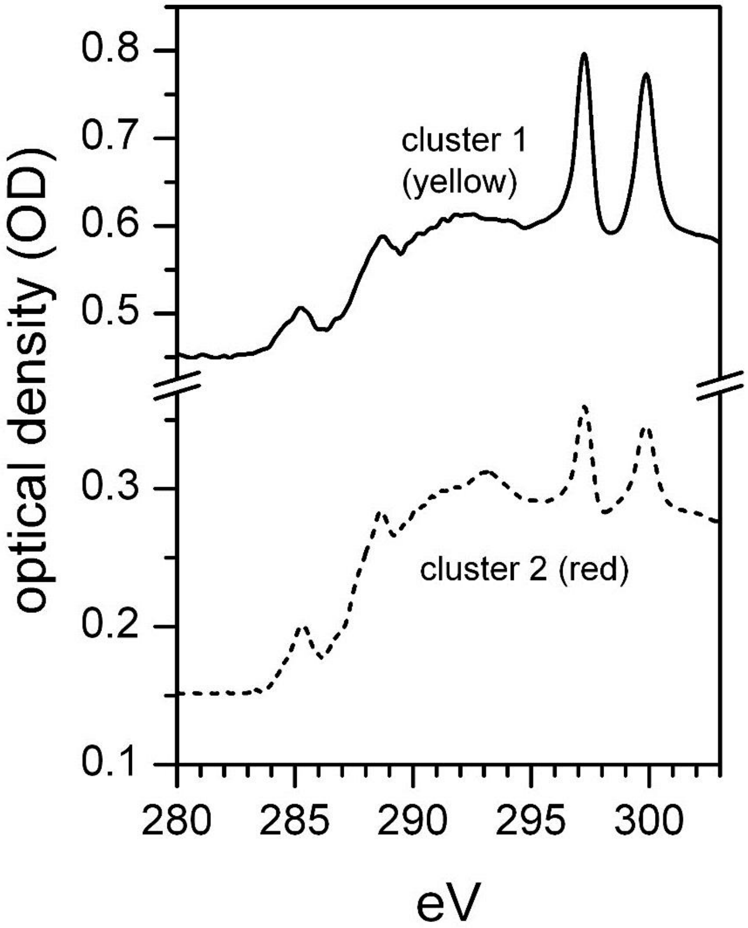




STXM and C K-edge spectroscopy

Lake Brienz
100 m depth





STXM and C K-edge spectroscopy

TABLE 2. Deconvolution Results of Lake Brienz Samples[a]

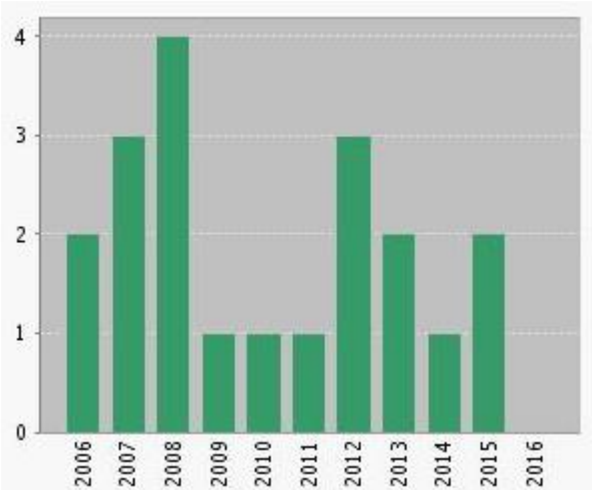
	depth: 1 m		depth: 100 m	
functional group	cluster 1	cluster 2	cluster 1	cluster 2
red shift area[b]	7	0	<1	1
C=C, C–H	11	5	17	18
phenol	5	9	2	2
aliphatic[c]	23	2	18	17
carboxyl	29	56	42	41
carbonyl	24	28	21	21

STXM (Scanning Transmission X-ray Microscope) et carbon K-edge spectroscopy
NSLS (National Synchrotron Light Source), BNL, NY, EUA

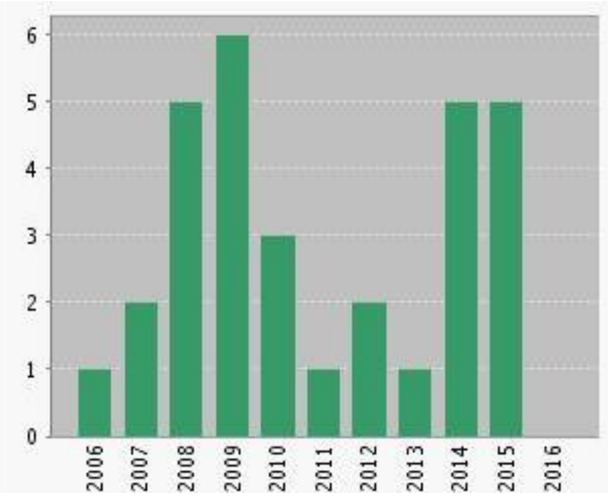
example of **environmental** study
+ **method** development

the after

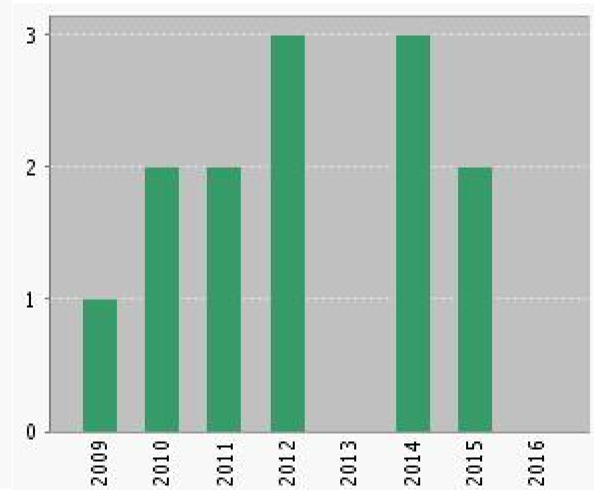
EST1 20



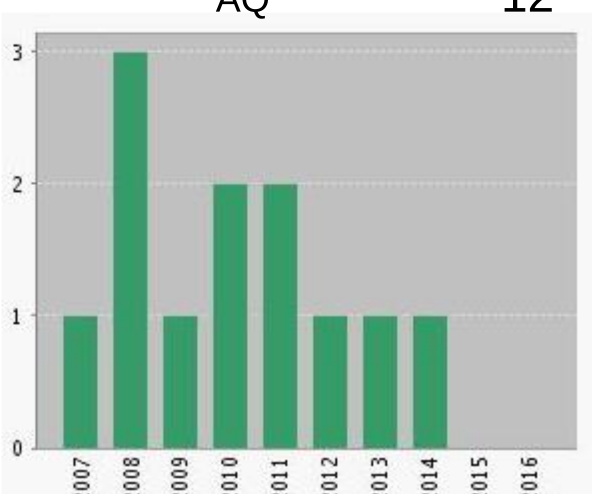
LIBD 31



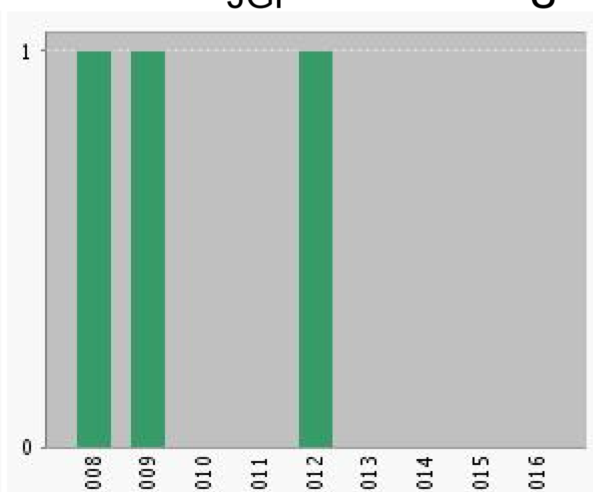
GCA 13



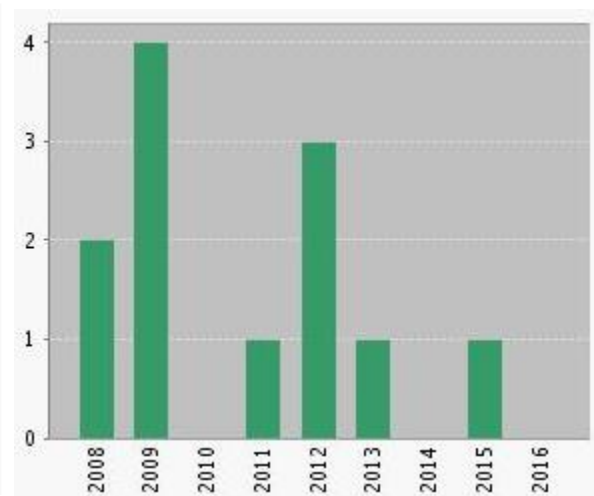
AQ 12



JGI 3

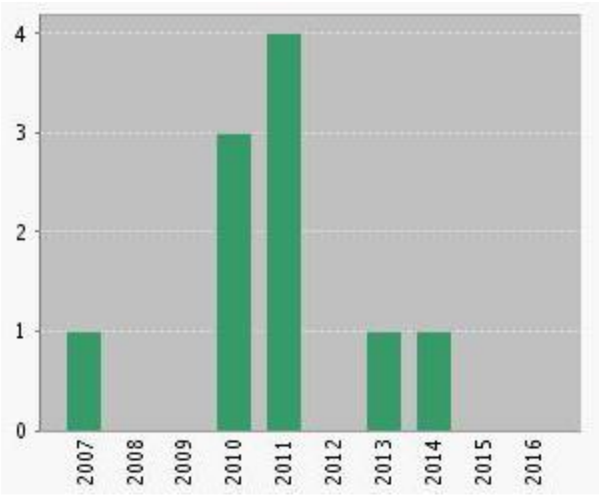


EST2 12

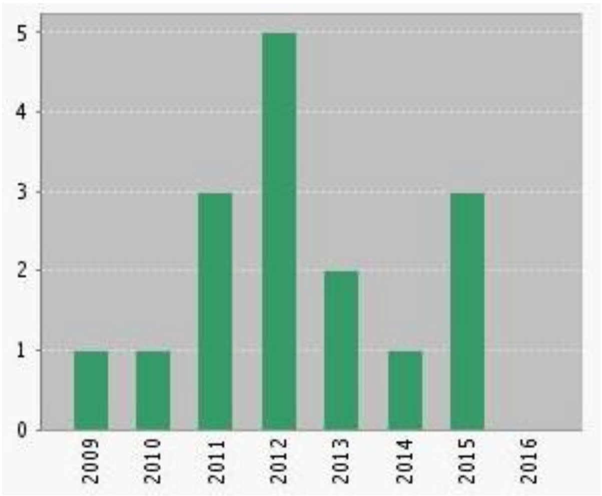


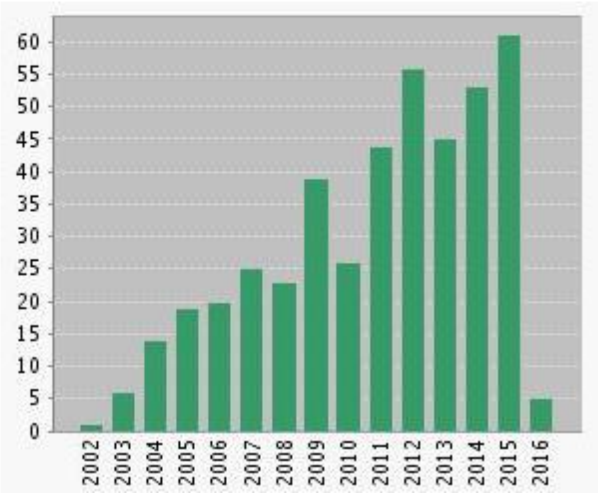
the after

WR 10



AG 16





437


LU 2443
question time...
BELBaR Berlin 2016

Benchmarking Exercise of Clay Erosion in Artificial Fracture Tests

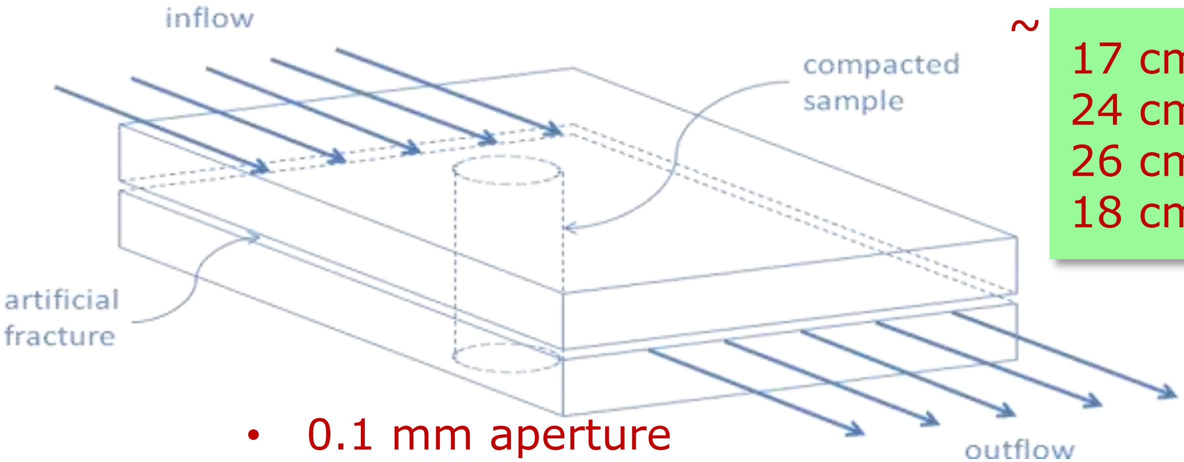
Tim Schatz, Ursula Alonso, Tiziana Missana, Christopher Reid, Frank Friedrich, Franz Rinderknecht & Kari Koskinen

BELBaR Benchmarking Participants

- **CIEMAT** *(Ursula Alonso & Tiziana Missana)*
- **B+Tech**
- **KIT/INE** *(Frank Friedrich & Franz Rinderknecht)*
- **University of Strathclyde** *(Chris Reid)*
- **Posiva** *(Kari Koskinen)*

BELBaR Benchmark Test Method

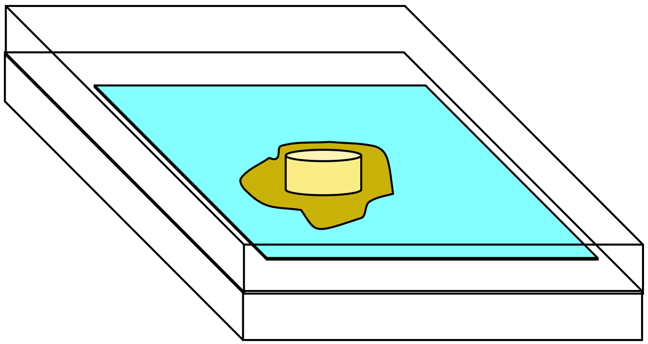
- Material
  - commercial sodium montmorillonite (Nanocor, PGN grade)
- Samples
  - dry density – 1400 kg/m^3
  - dimensions (height, diameter) ~
    - 10 mm × 19 mm (CIEMAT)
    - 20 mm × 20 mm (B+Tech)
    - 10 mm × 19 mm (UniStrath)
    - 25 mm × 80 mm (KIT/INE)
  - pre-saturated (1 mM NaCl)
- Fracture
  - custom-made, small-scale, flow-through artificial fracture cells ~
    - 17 cm × 17 cm (CIEMAT)
    - 24 cm × 24 cm (B+Tech)
    - 26 cm diameter (UniStrath)
    - 18 cm diameter (KIT/INE)



  - 0.1 mm aperture
- Solution
  - 1 mM NaCl

BELBaR Benchmark Test Protocol

Phase 1: stagnant conditions (30 days)

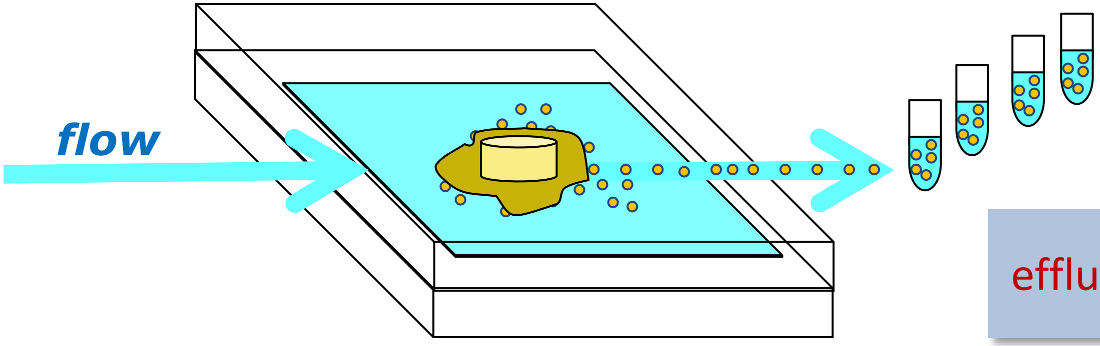


extrusion distance

Swelling pressure measurements performed by UniStrath and KIT/INE

Phase 2: <u>low flow conditions</u> (14 days at 10^{-6} m/s)

Phase 3: <u>high flow conditions</u> (14 days at 10^{-4} m/s)

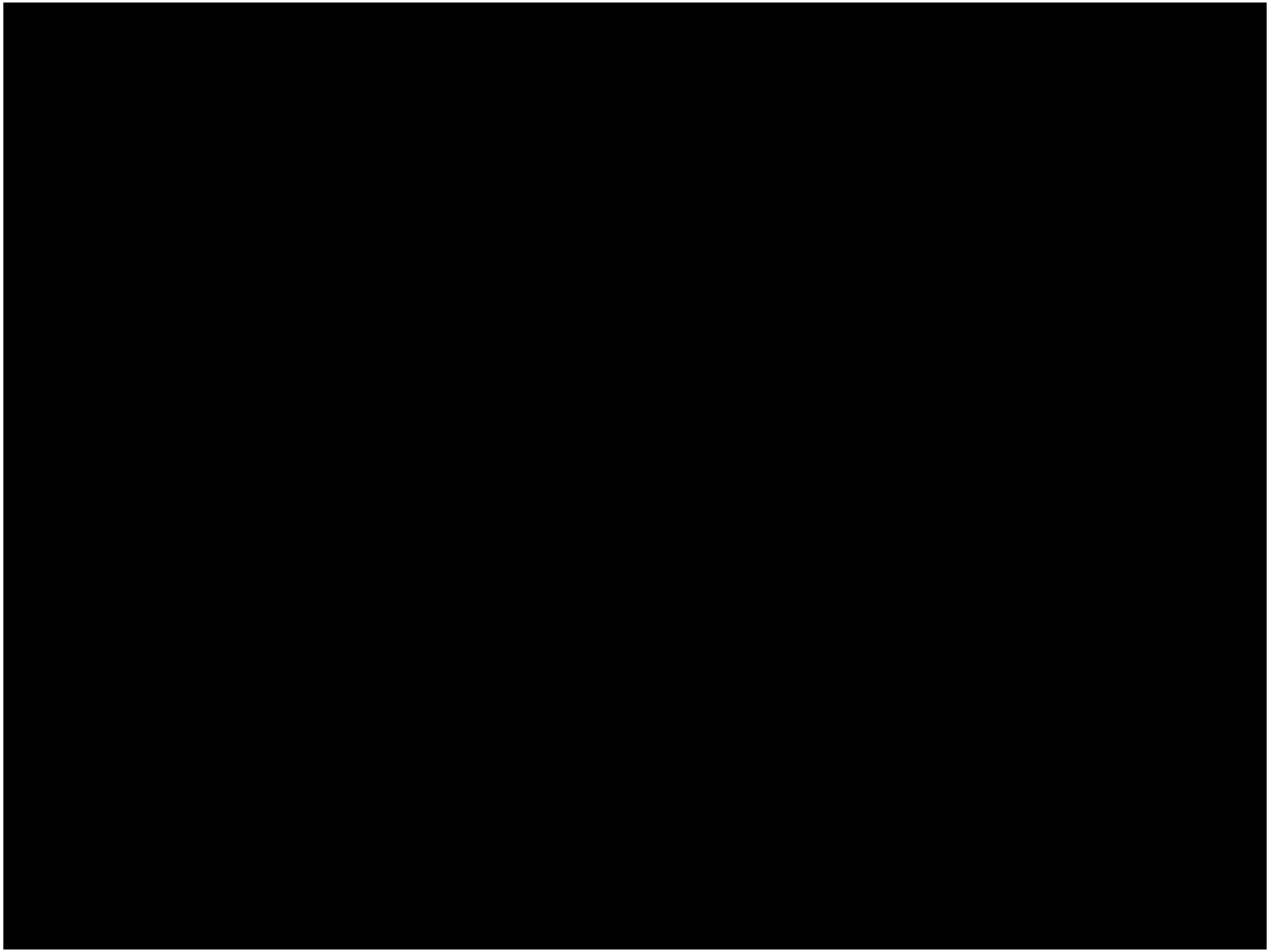


effluent solids content

BELBaR Benchmark Test Set-up

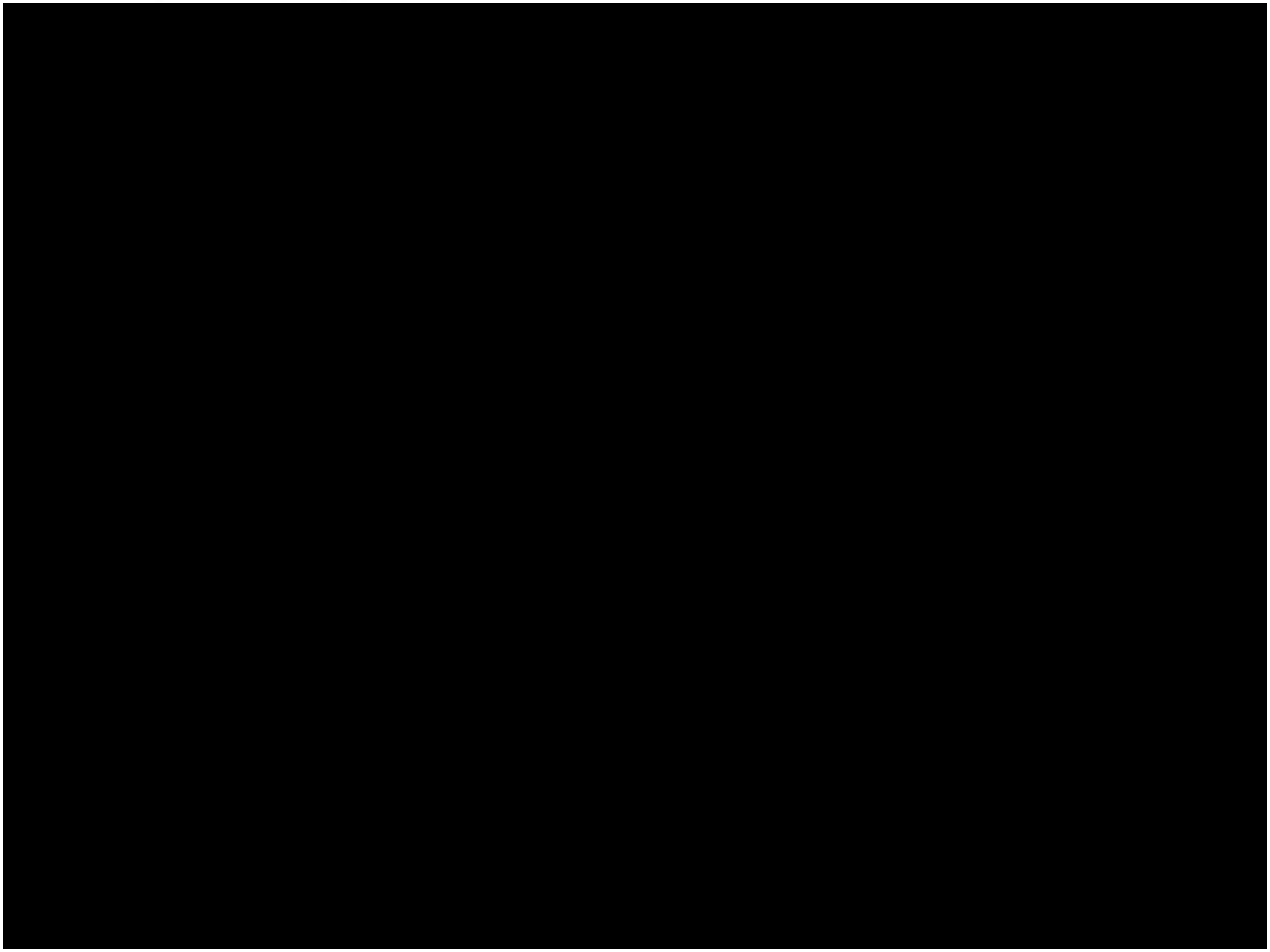
BELBaR Benchmark Test (time lapse)

B+Tech

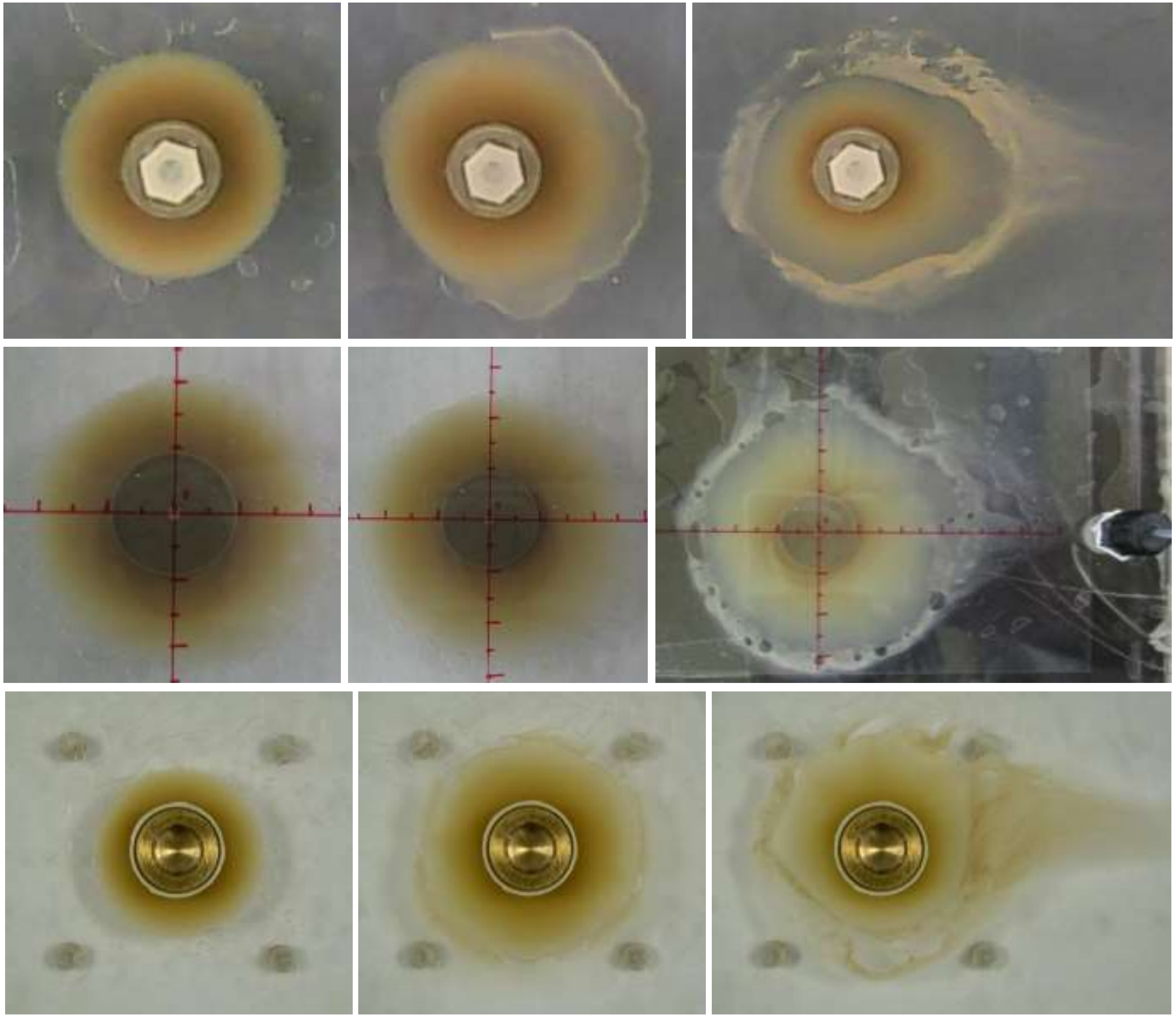


BELBaR Benchmark Test (time lapse)

University of Strathcylde



Benchmark Test Observations



Phase Characteristics

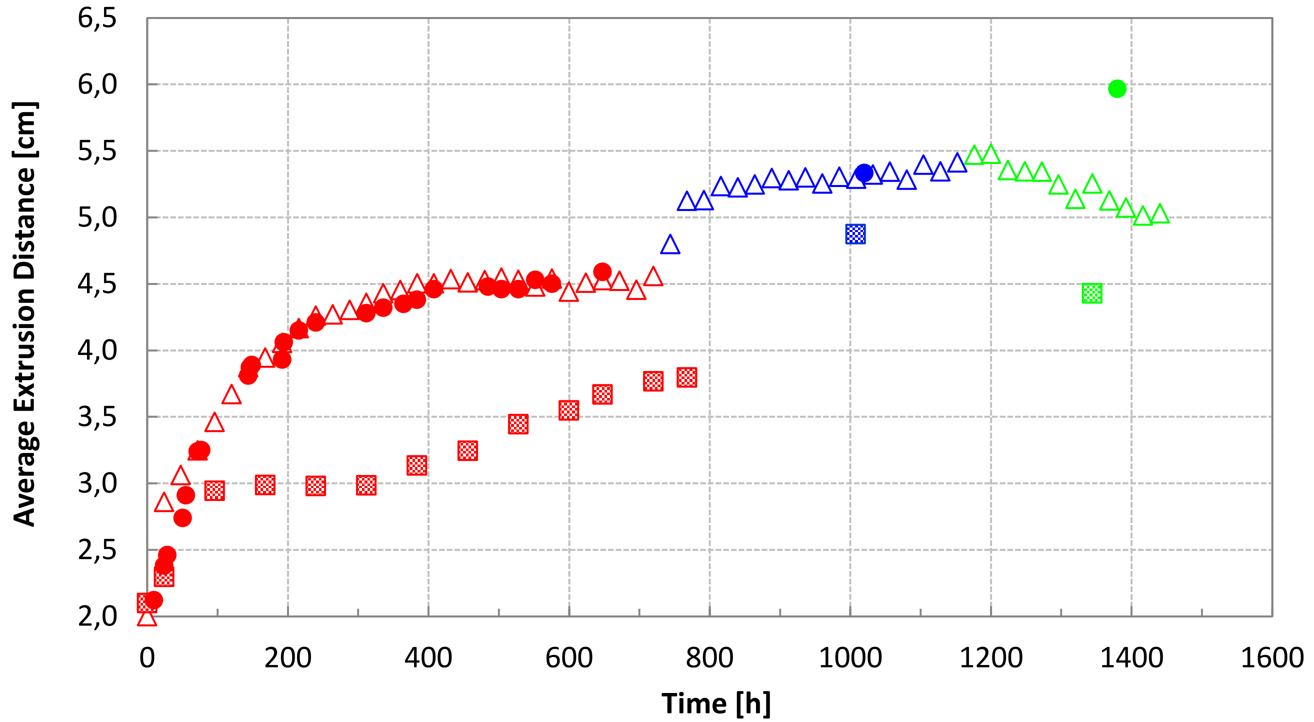
- Phase 1 of the tests (stagnant period) was characterized by symmetric extrusion of emplaced sample material to steady-state distances into the fractures.

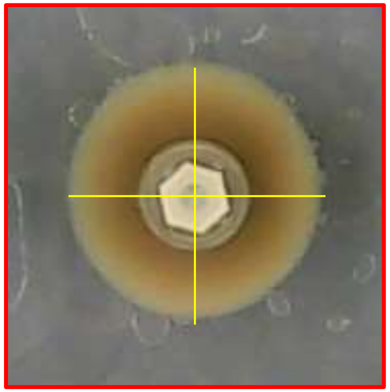
- Phase 2 of the tests (low flow velocity) was characterized by rather abrupt, asymmetric increases in extrusion and the formation of distinct solid material regions.

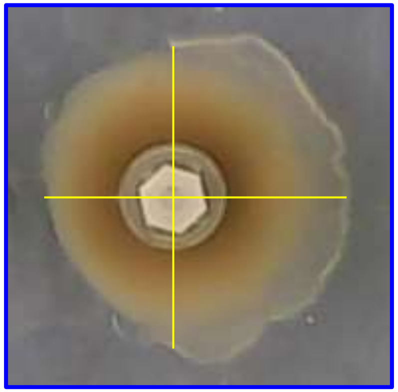
- Phase 3 of the tests (high flow velocity) was characterized by further development of the sharp boundary between the inner continuous solid material zones and the outer discontinuous particulate material zones, and, in two cases, erosive loss of the inner zone.

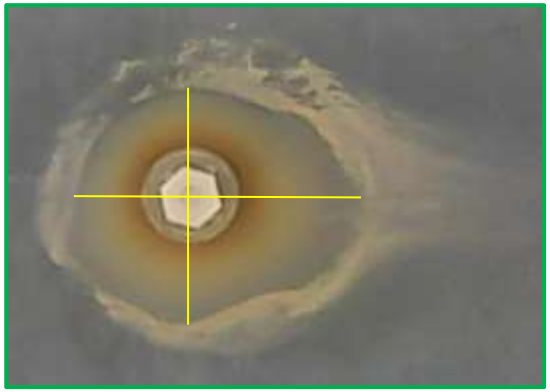
  - Clear flow patterns of entrained/dispersed eroding solid material from around the extrudates were visible during phase 3.

Extrusion Distances





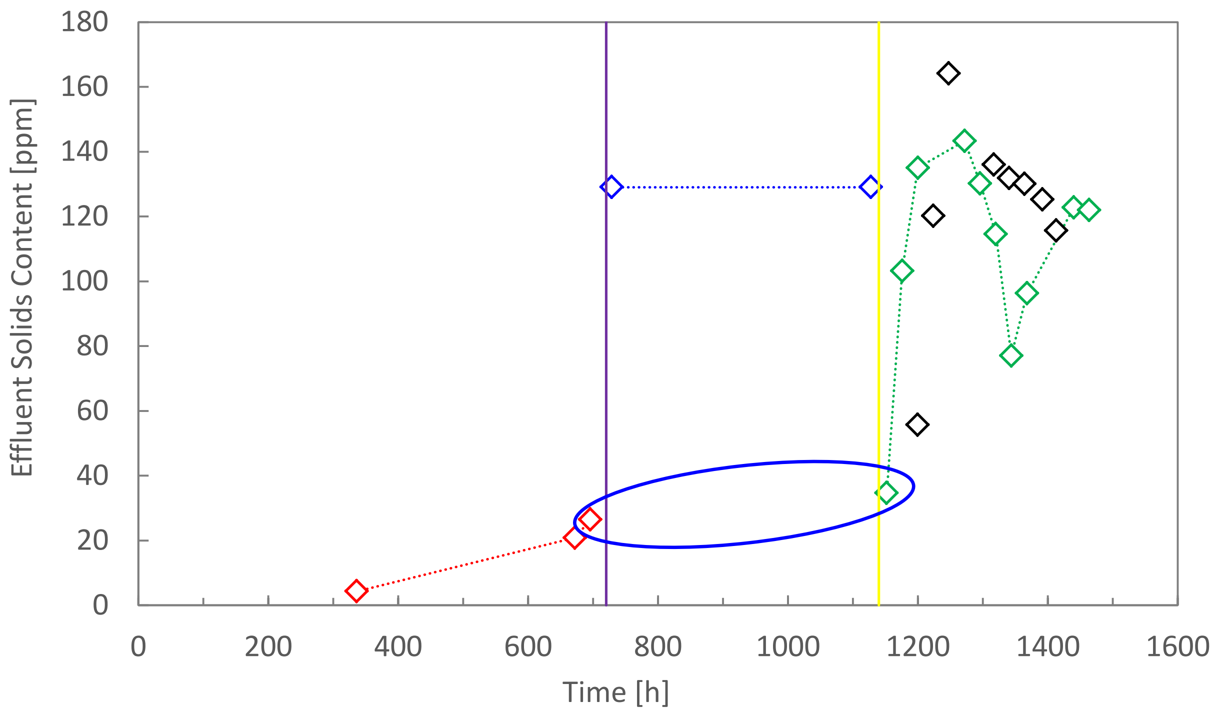




Extrusion Behaviour

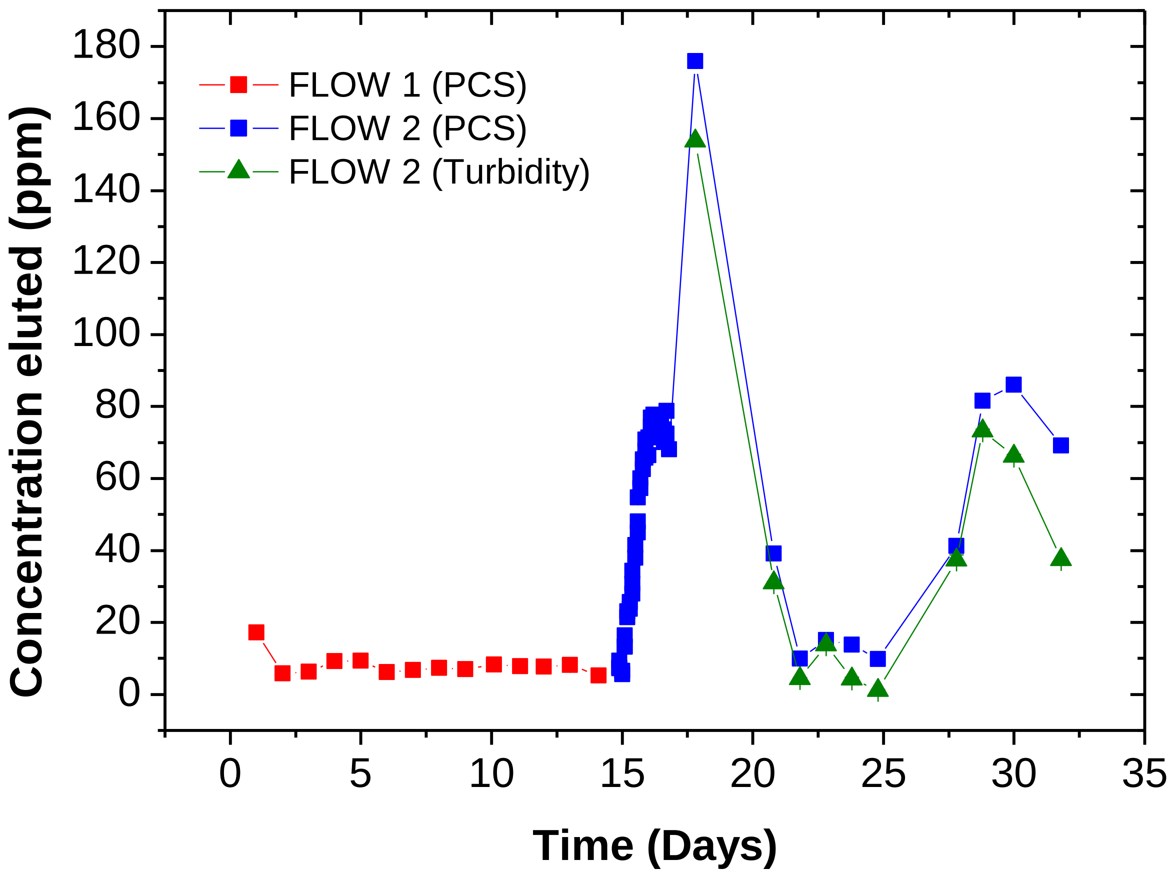
- Overall the benchmark tests showed extrusion distances, considered as averages of the horizontal and vertical lengths across the extruding, continuous phases in the fracture space, of:
  - 3.8 to 4.6 cm at the end of phase 1,
  - 4.9 to 5.3 cm at the end of phase 2,
  - 4.4 to 5.9 cm at the end of phase 3.

Effluent Solids (B+Tech)



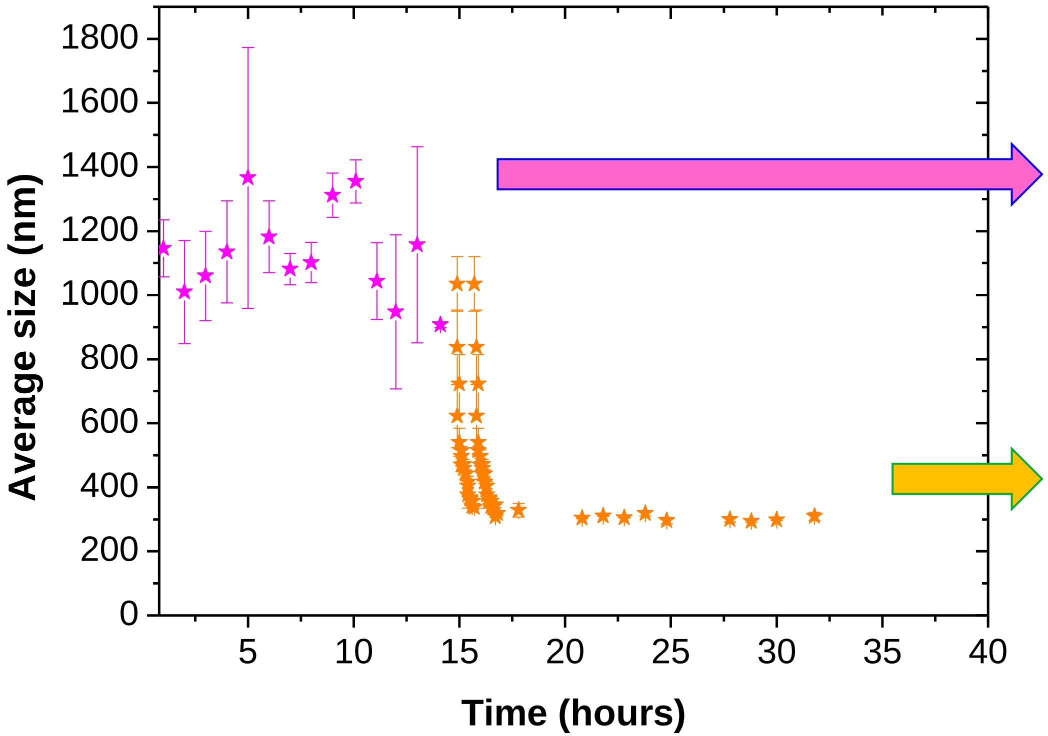
- Average effluent concentration of 30 ppm during phase 2.
- Effluent concentrations from 35 to 160 ppm during phase 3.

Effluent Solids (CIEMAT)



- Average effluent concentration of 8 ppm during phase 2.
- Effluent concentrations from 8 to 180 ppm during phase 3.

Effluent Particle Size (CIEMAT)

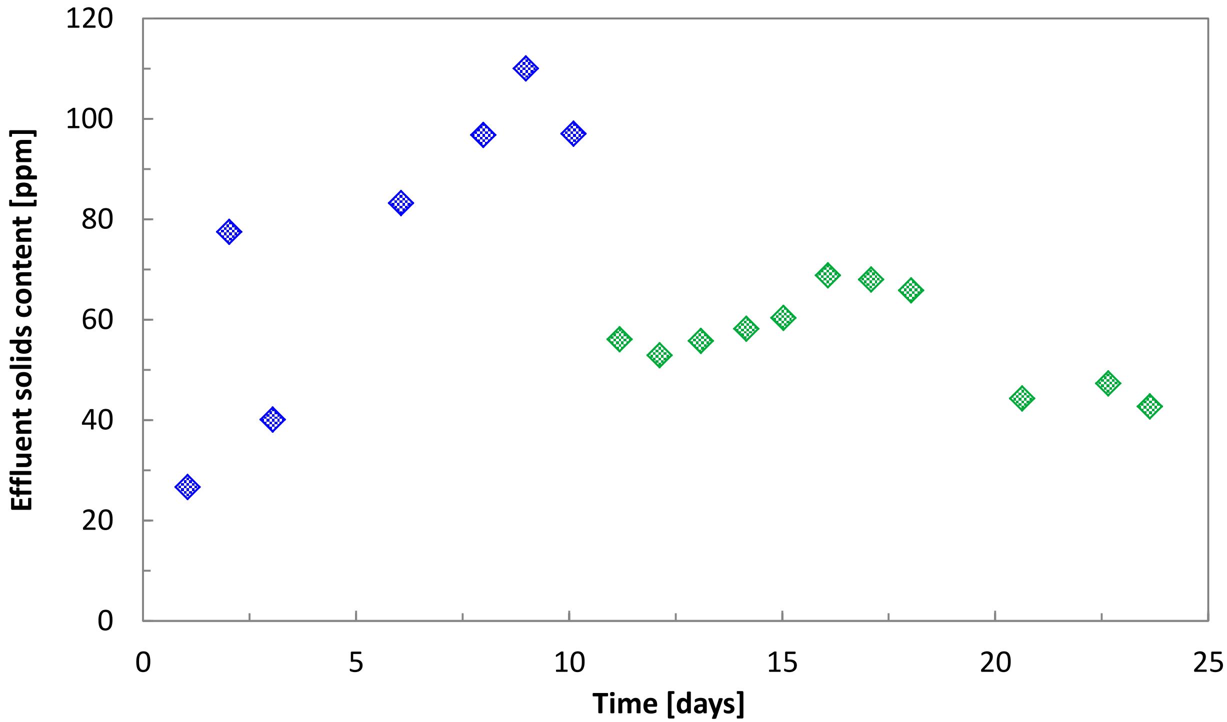


larger particles are eluted during phase 2 flow

smaller particles are removed during phase 3 flow

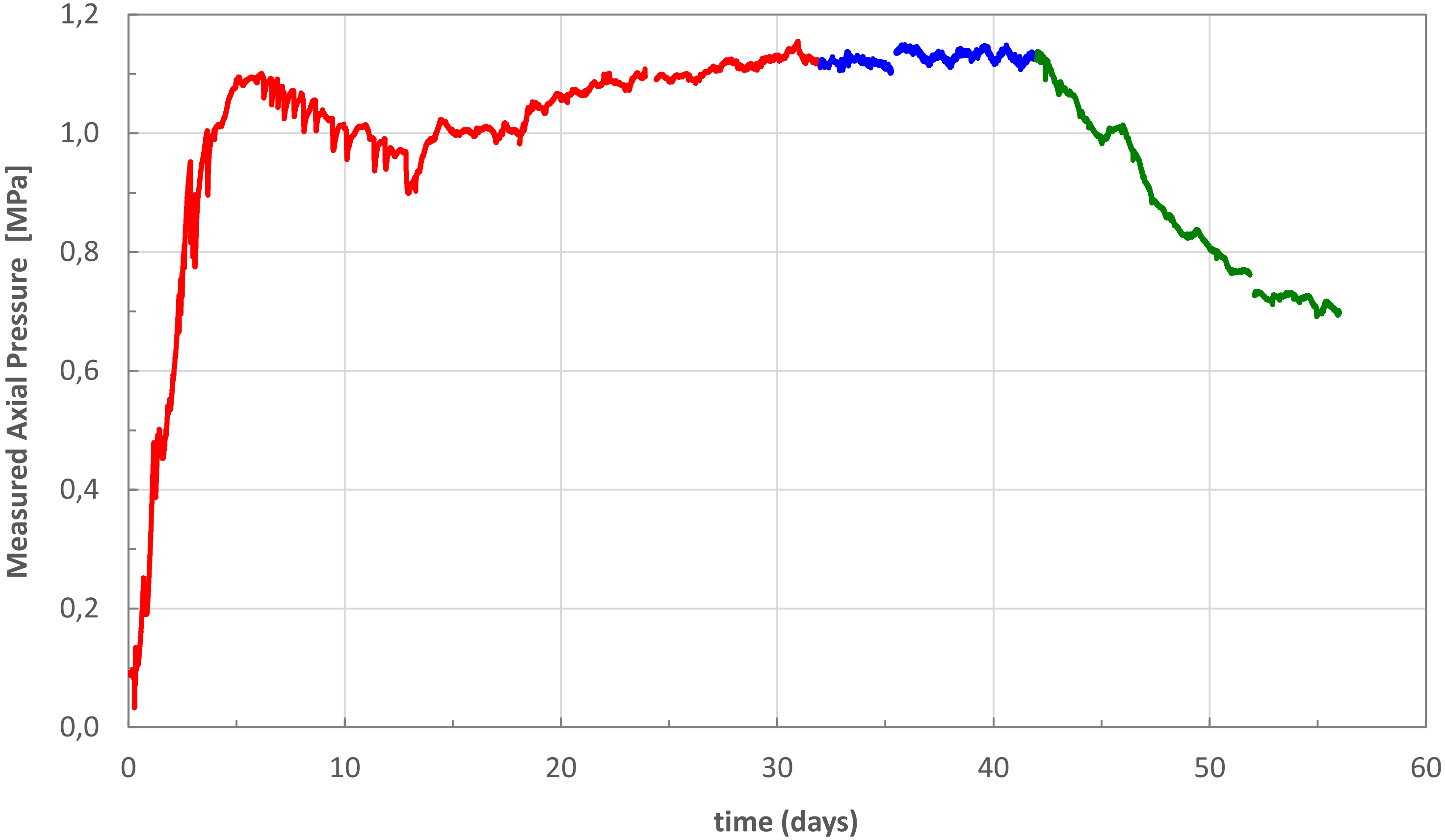
- ❑ Distinct particle size populations or disaggregation?

Effluent Solids (UniStrath)



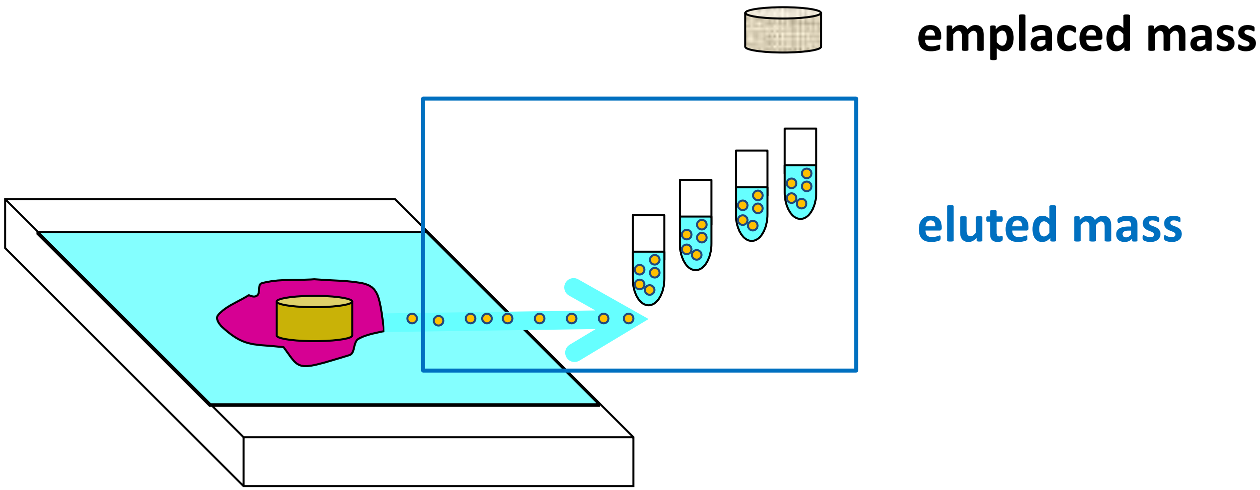
- Effluent concentrations from 27 to 110 ppm during phase 2.
- Effluent concentrations from 42 to 69 ppm during phase 3.

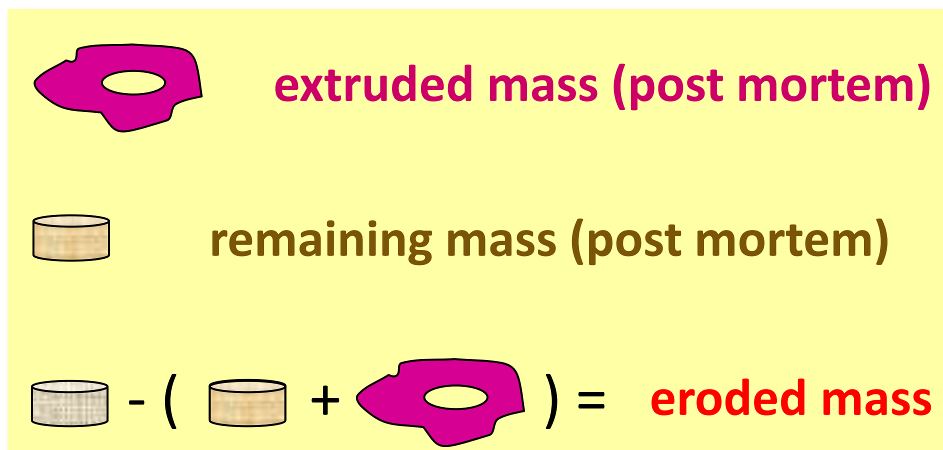
Swelling Pressure (UniStrath)



- Relatively constant pressures observed during phases 1 and 2.
- 40% drop in pressure during phase 3 (erosion).

BELBaR Benchmark Test Post-Mortem



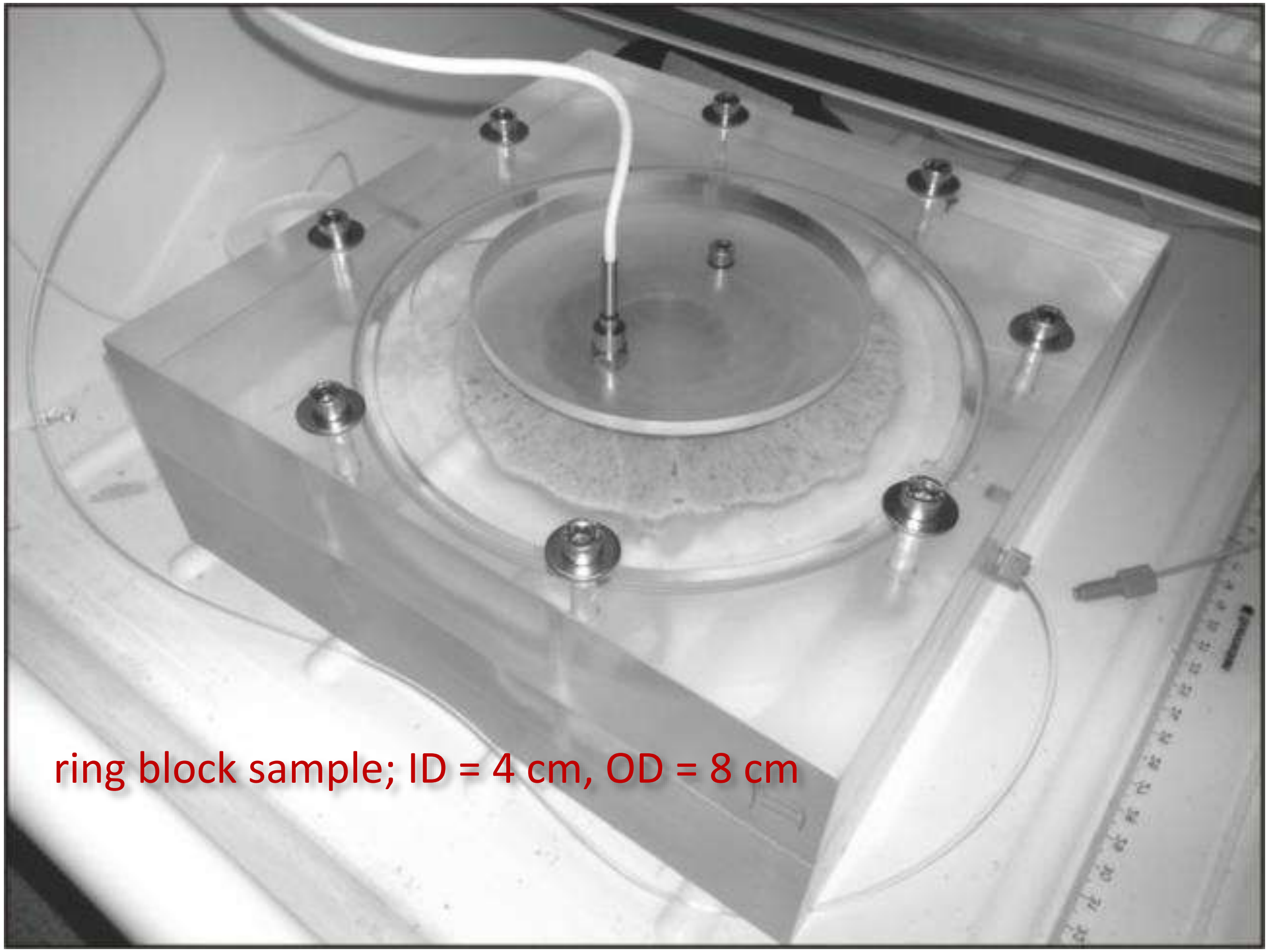


Erosion Comparison

			
Emplaced mass	3.8554	7.7023	4.3000
Extruded mass	0.3640	0.3090	0.3137
Remaining mass	3.4040	6.4977	3.2479
Eroded mass	0.0874 (2.3%)	0.8956 (11.6%)	0.7384 (17.2%)
Eluted mass	0.1180	0.5622	0.5576

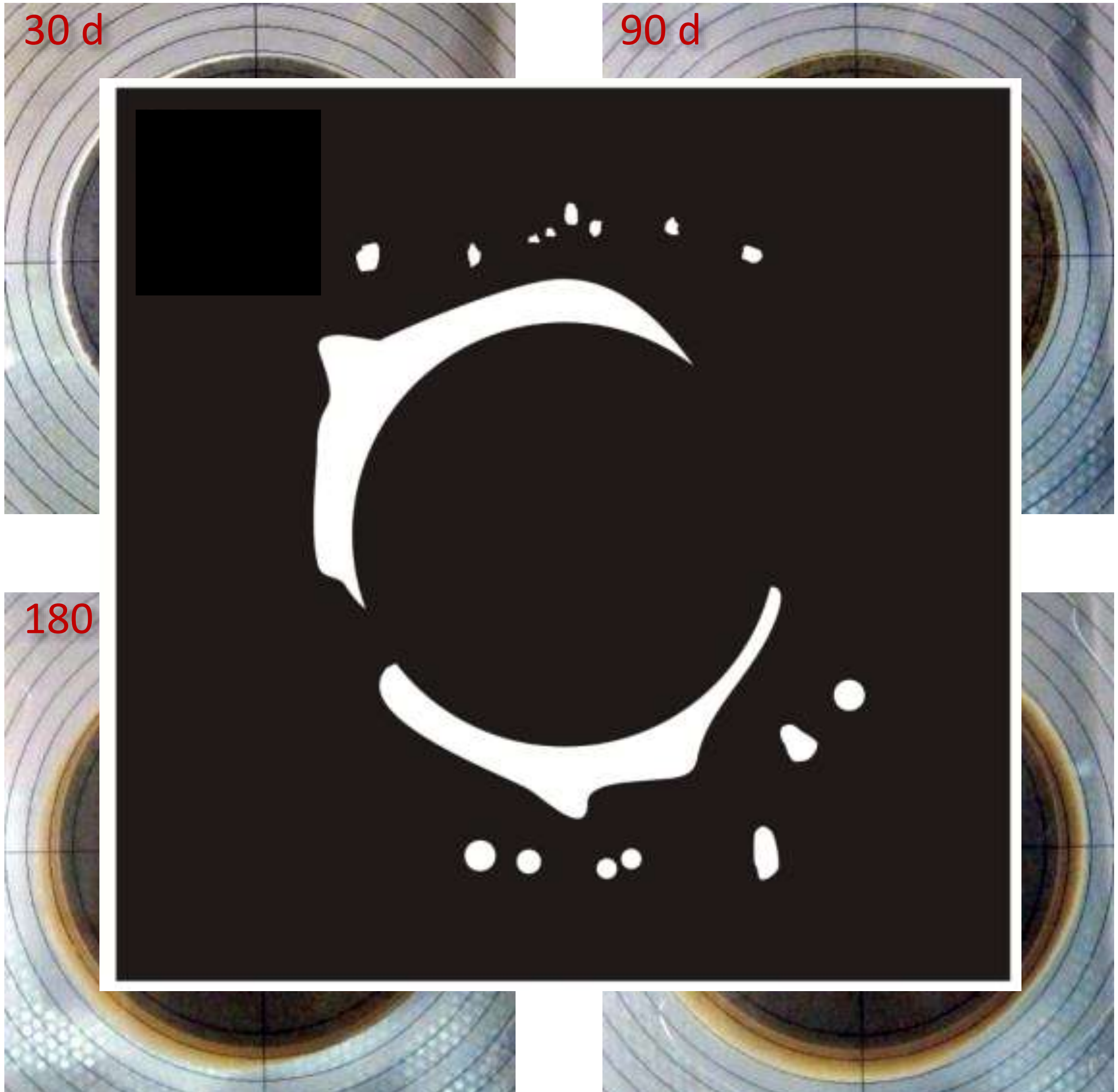
- Post-mortem analysis of remaining mass and extruded mass relative to emplaced mass indicates total losses of 2 to 17%.

BELBaR Benchmark Test at KIT/INE

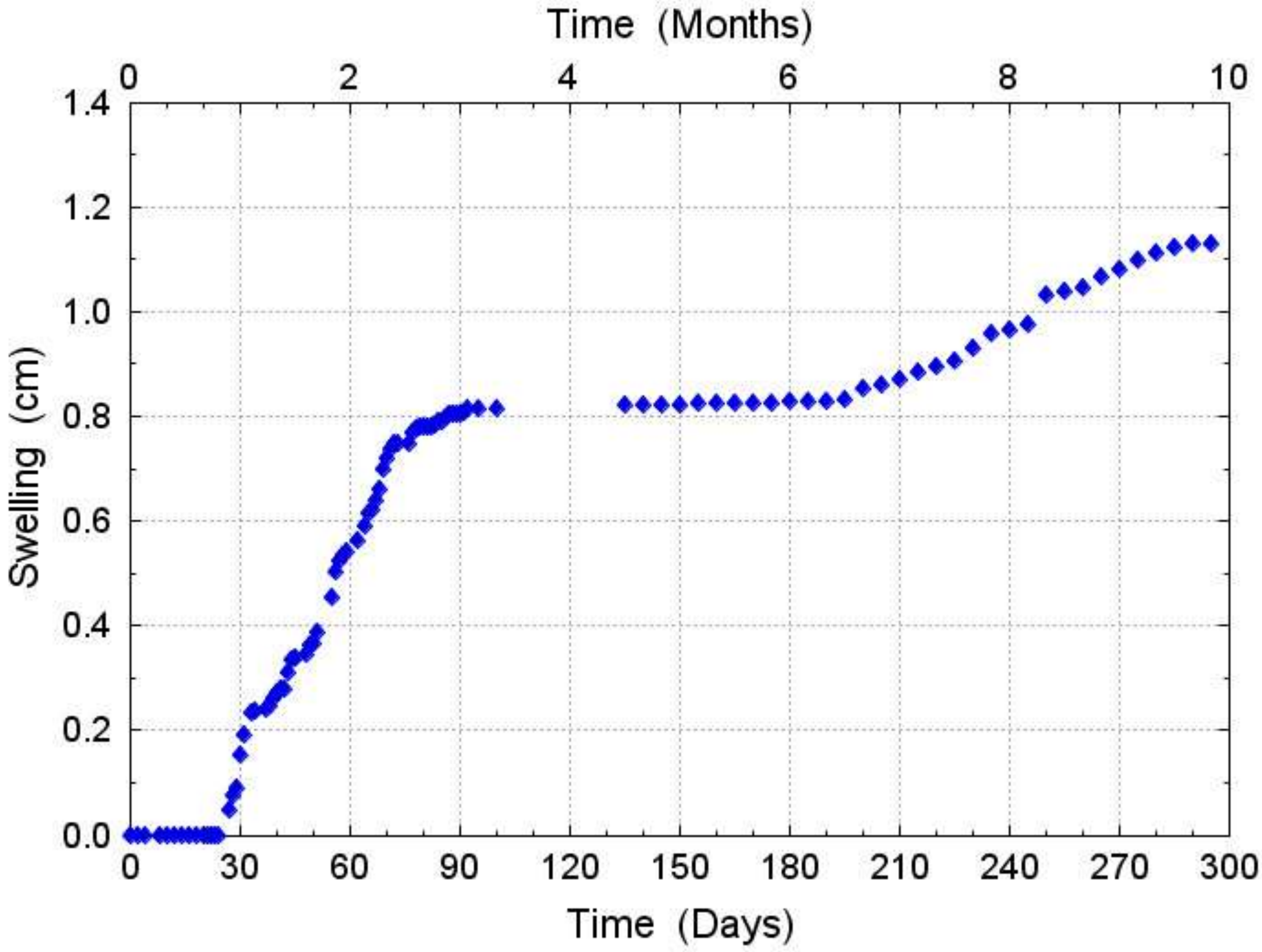


- Fracture volume could not be filled with solution; phases 2 and 3 of the benchmark tests protocol were not initiated.

Extrusion Observations (KIT/INE)

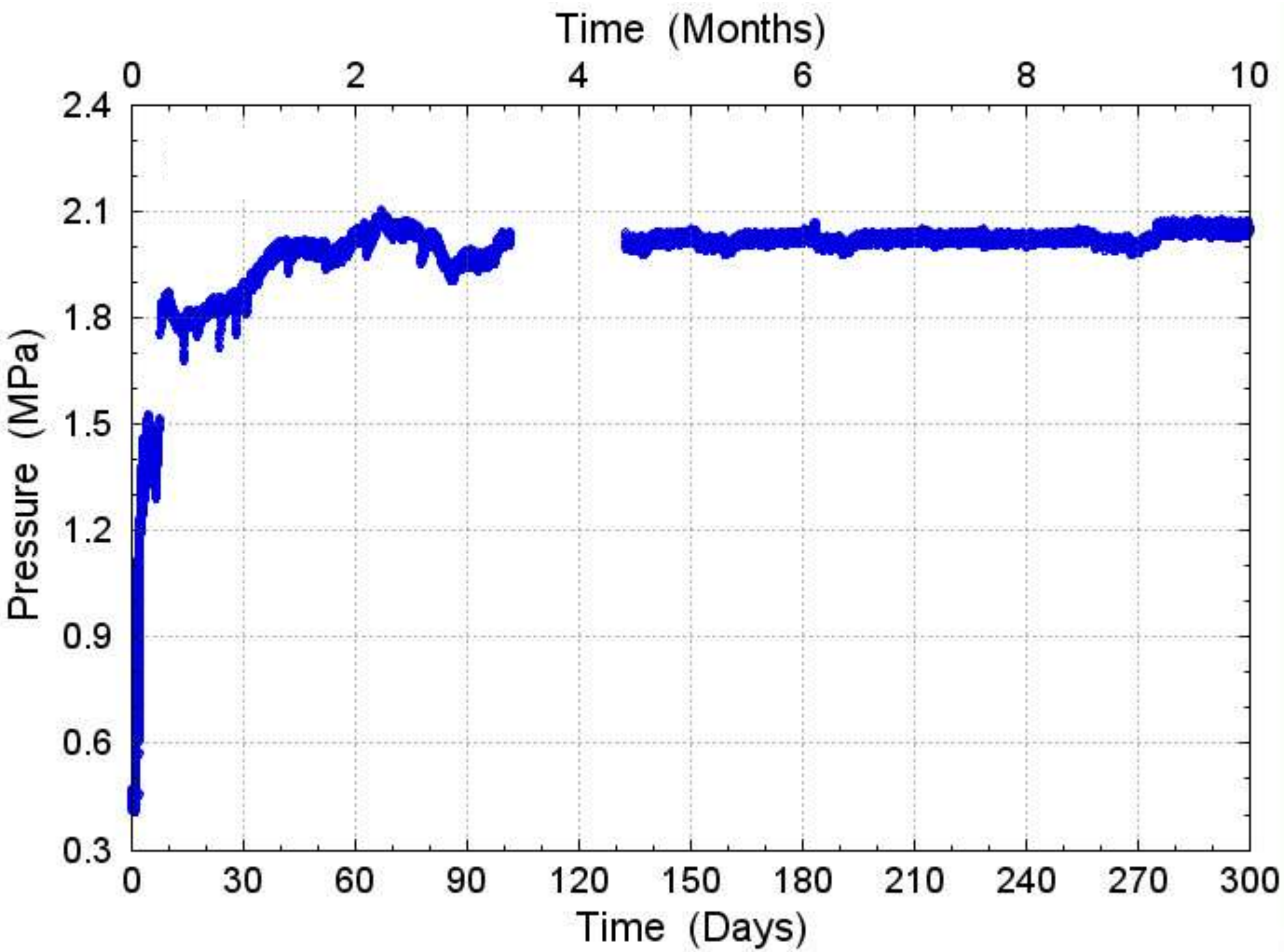


Extrusion Distance (KIT/INE)



- Limited extrusion in time and distance relative to smaller sample tests.

Swelling Pressure (KIT/INE)



- Relatively constant pressures observed after 60 days.

Summary

- In general, the results of the benchmark tests performed on similarly sized samples are relatively consistent with one another.
  - Extrusion distances were in agreement to within 15% over all three tests phases.
  - Minimum to maximum eluted solids concentration ranges measured during phase 3 were found to be favorably overlapped
  - Relative erosion was determined to be from 2 to 17%
- With a more rigorously detailed protocol, artificial fracture tests could be more tightly benchmarkable.
- The behaviour of the larger test system (and elsewhere) indicates that comparison between tests even at these modest scaling increases may not be straightforward.

Size of Clay Platelets, pH and Temperature Matter

M. Segad
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BERKELEY LAB
LAWRENCE BERKELEY NATIONAL LABORATORY

ALS
ADVANCED LIGHT SOURCE

Outline of Presentation

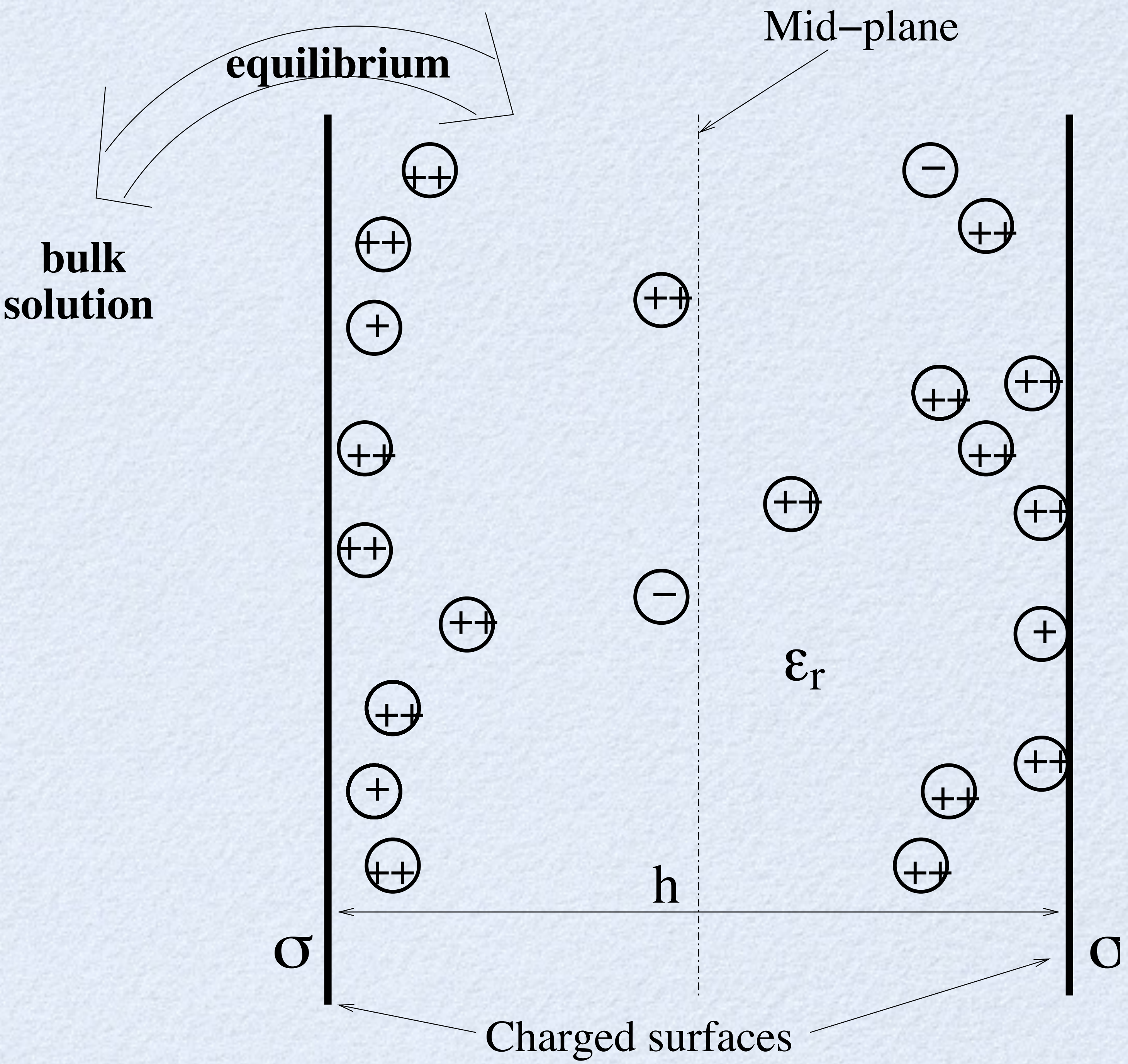
- Platelet-Water-Salt Interactions
- The Role of pH
- The Role of Temperature

Platelet-Water Interactions

- Theoretical Model

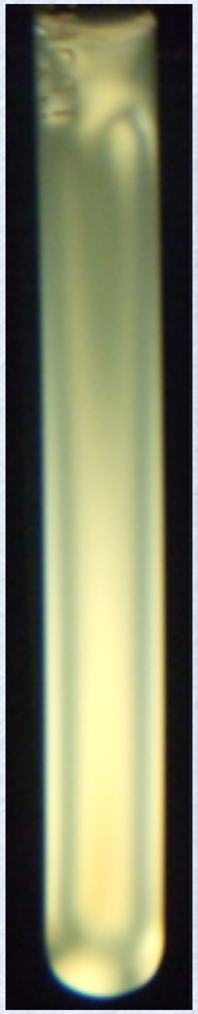
$$P_{el} = k_B T \sum c_i(0) + p^{corr} - p^{bulk}$$

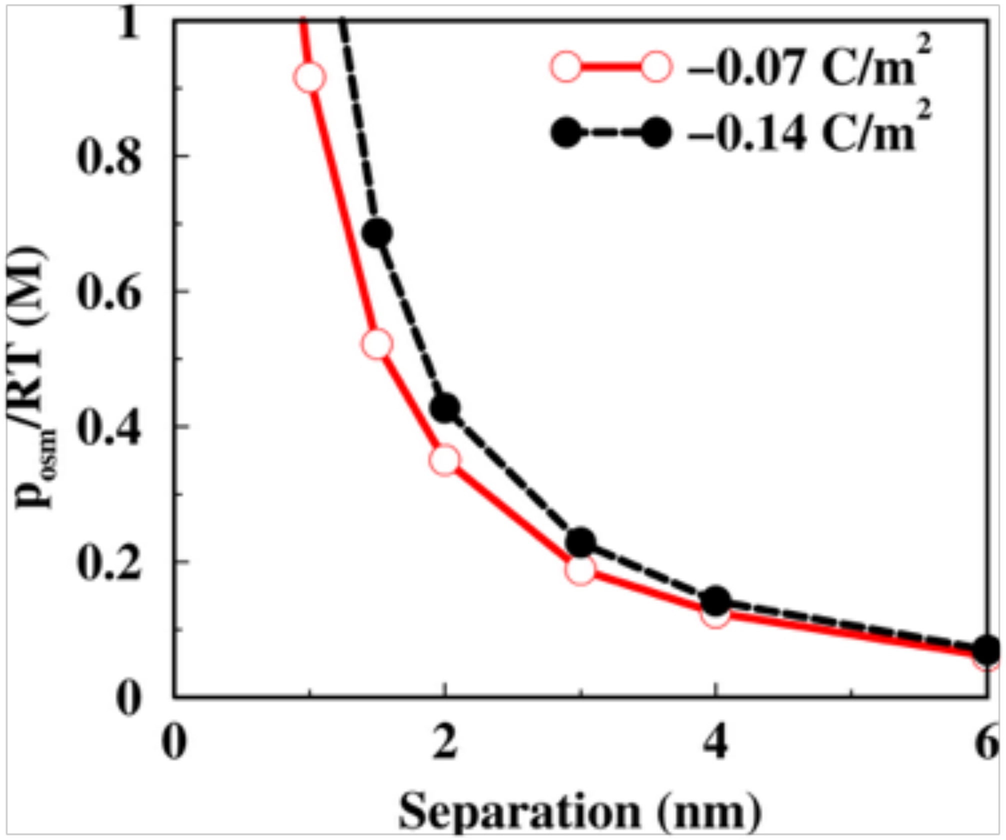
$$P_{tot} = P_{el} + P_{vdw}$$

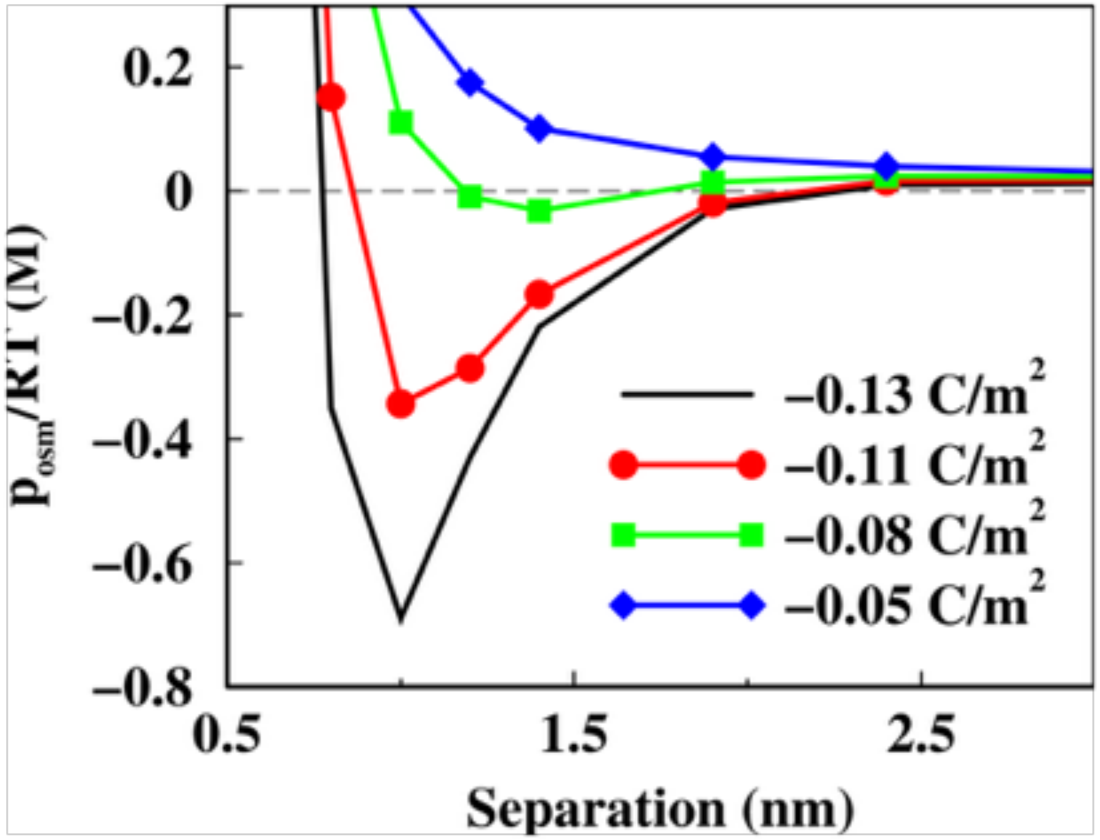


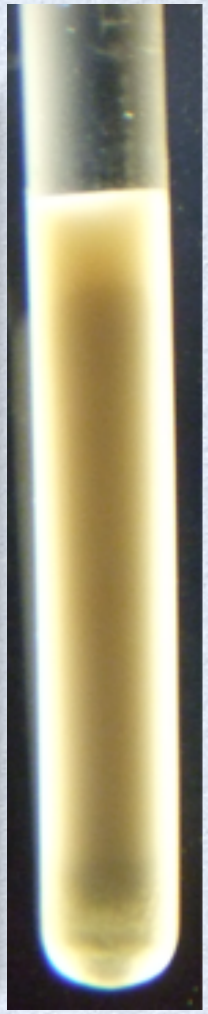
Platelet-Water Interactions

- MC simulation results (salt free)







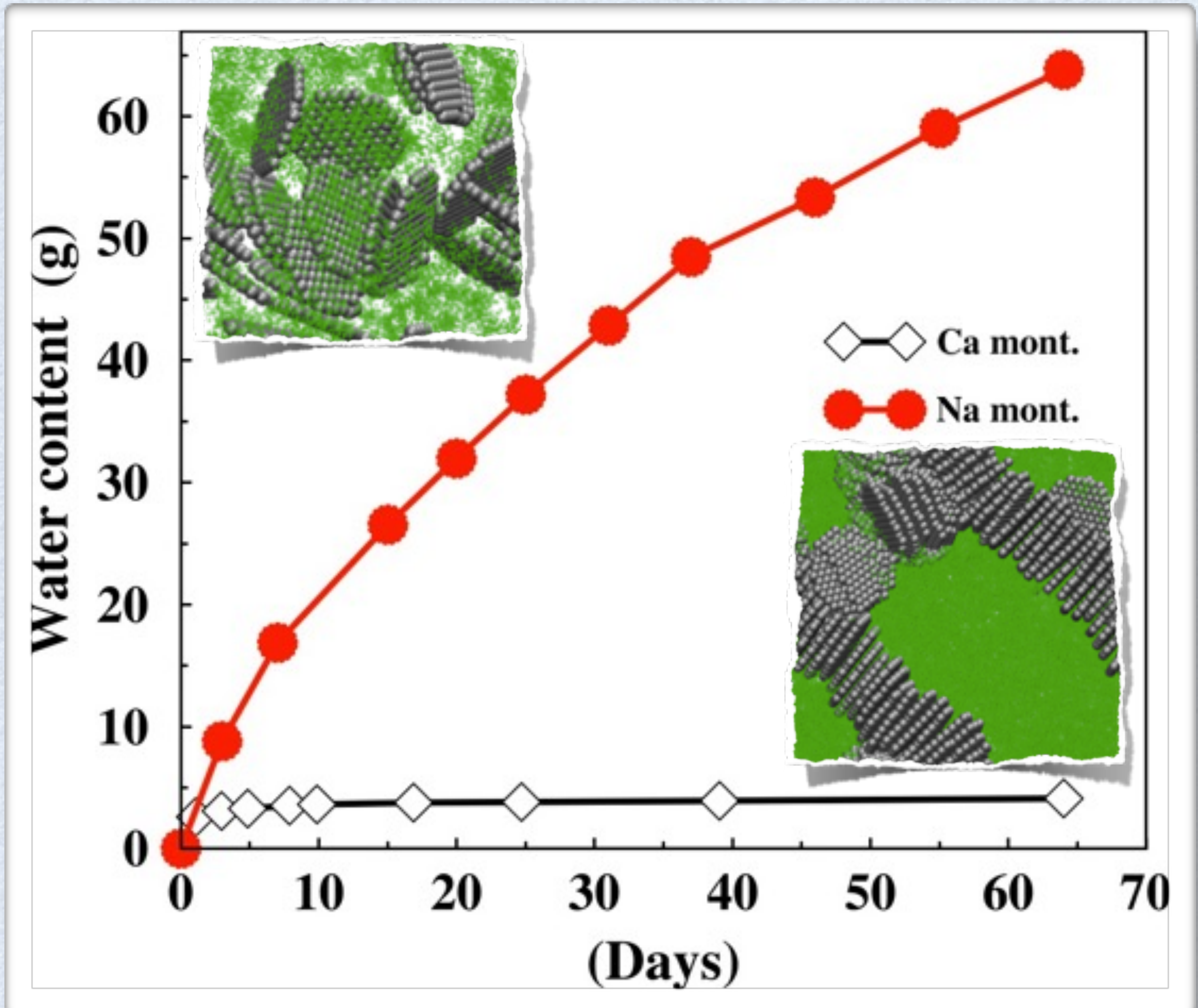


Na mont.

Ca mont.

Platelet-Water Interactions

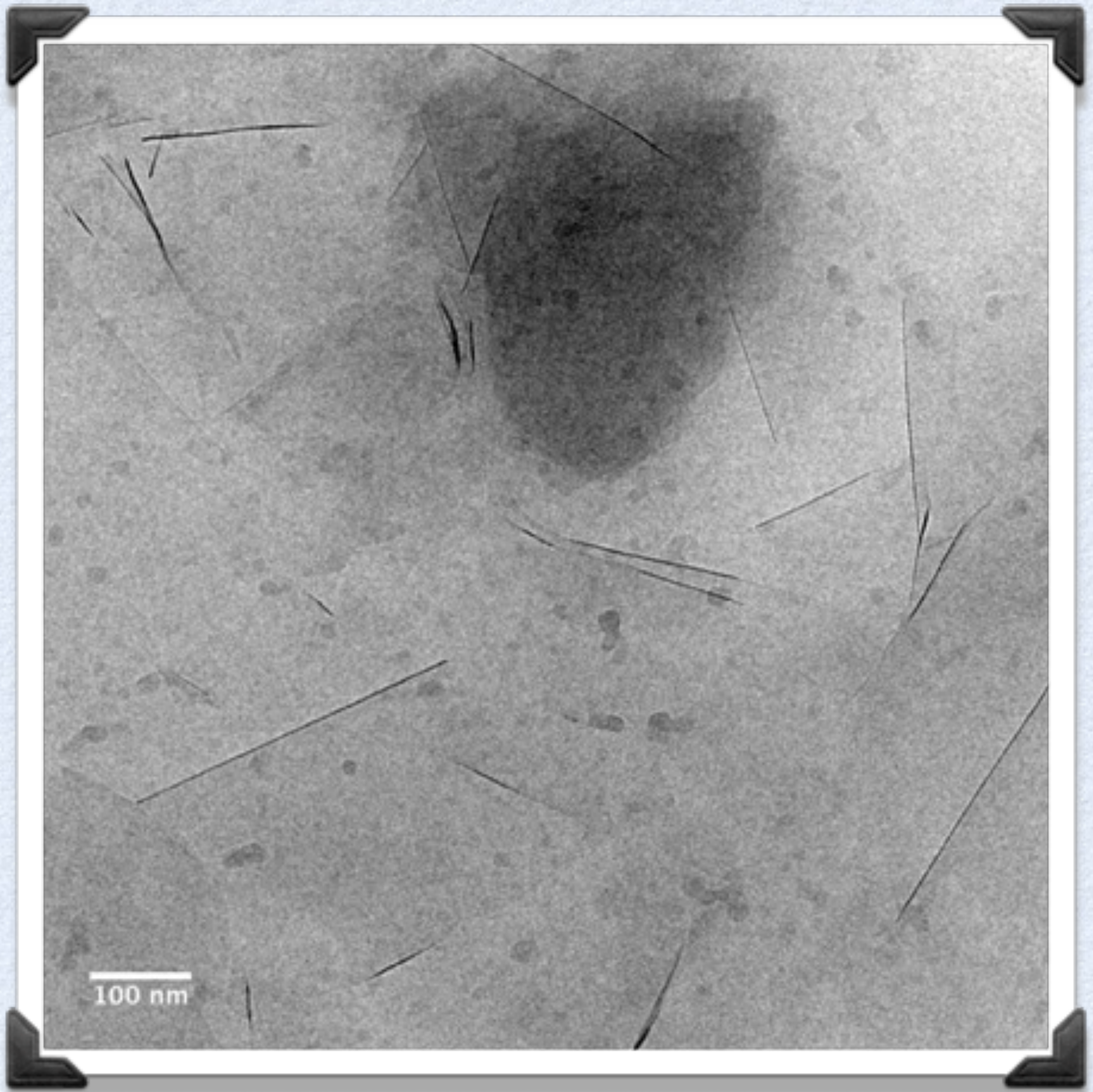
- Dialysis experiments (swelling behavior)



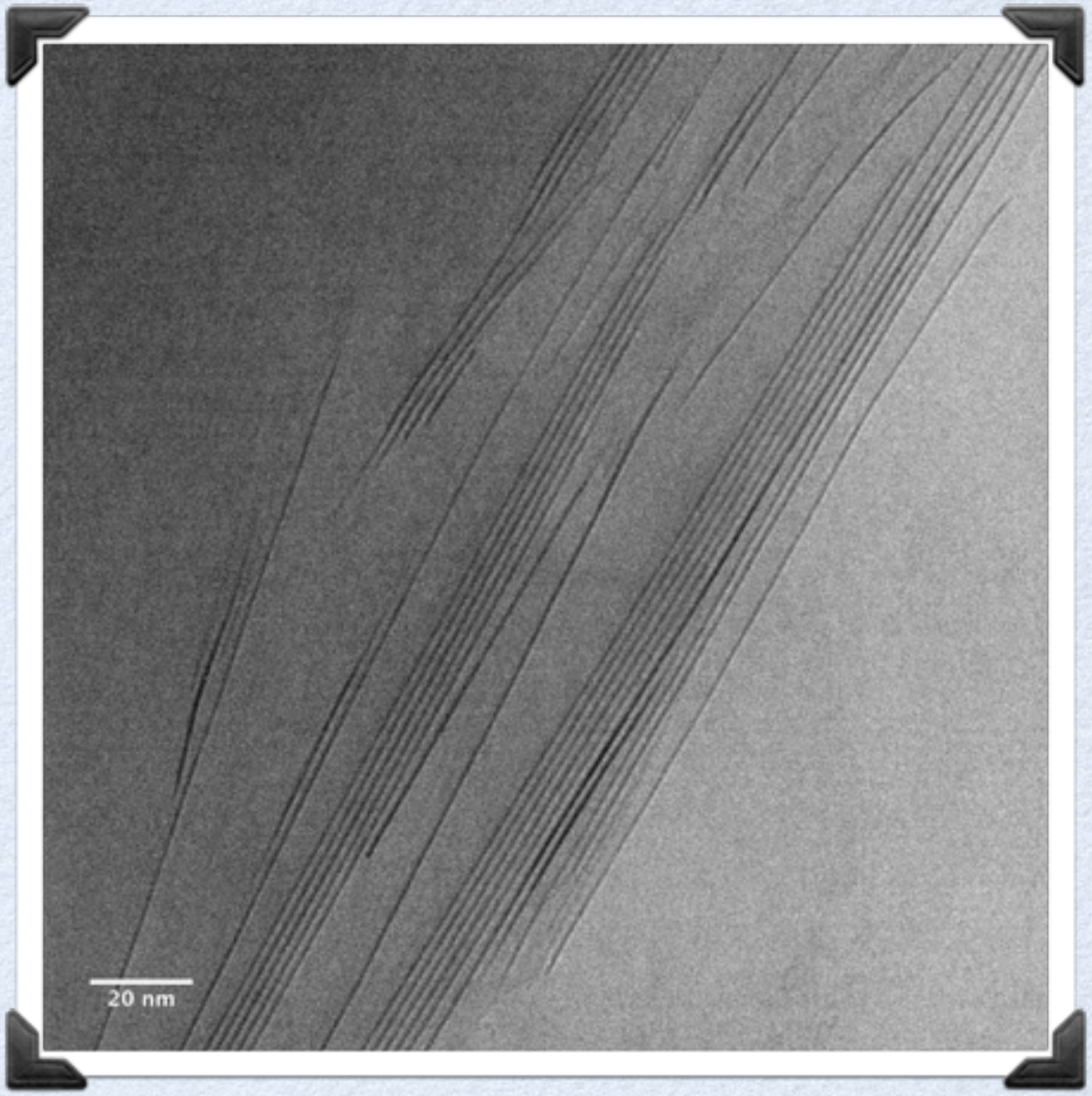
Time (Days)

Platelet-Water Interactions

- Imaging experiments



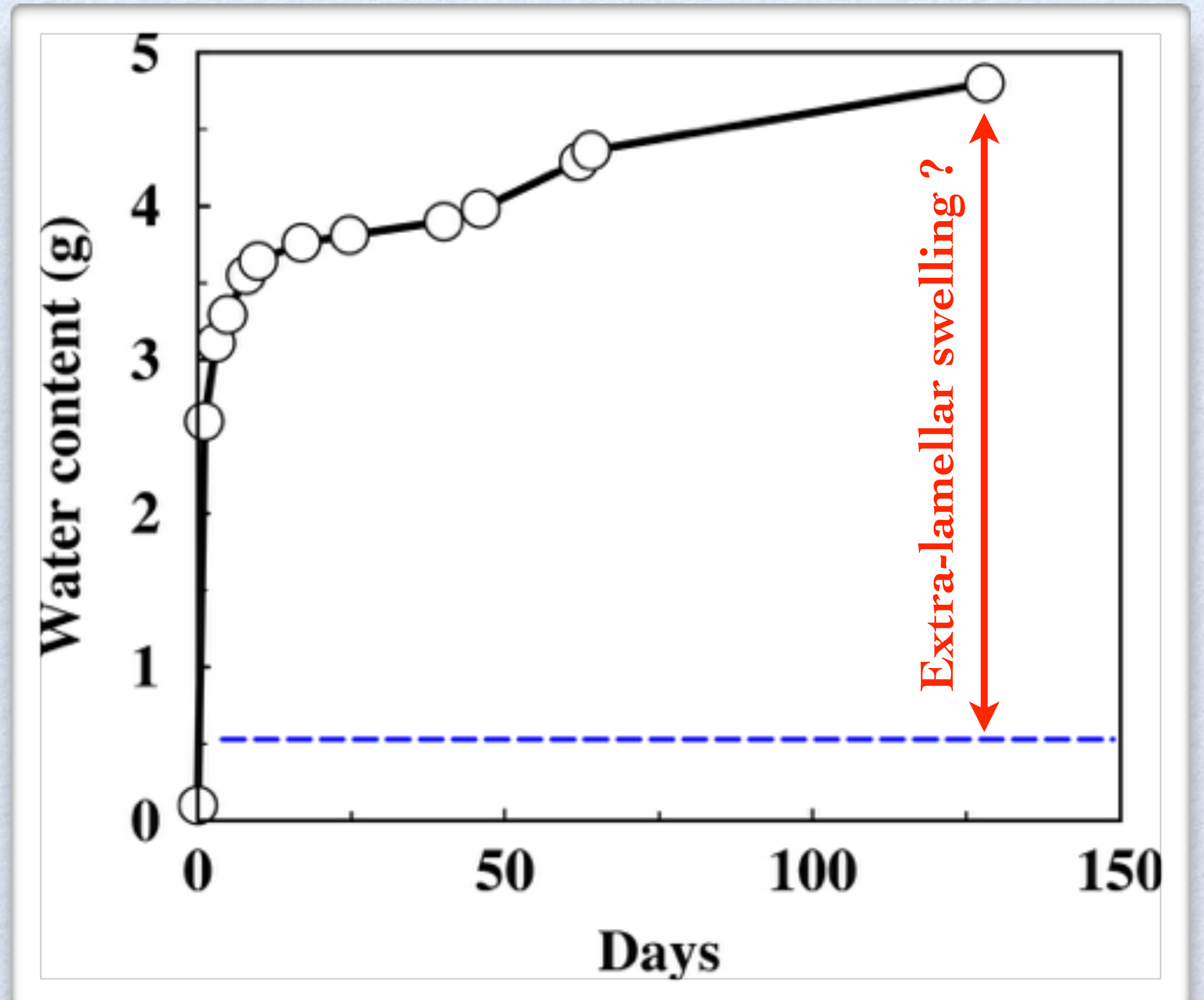
Na montmorillonite in millipore water



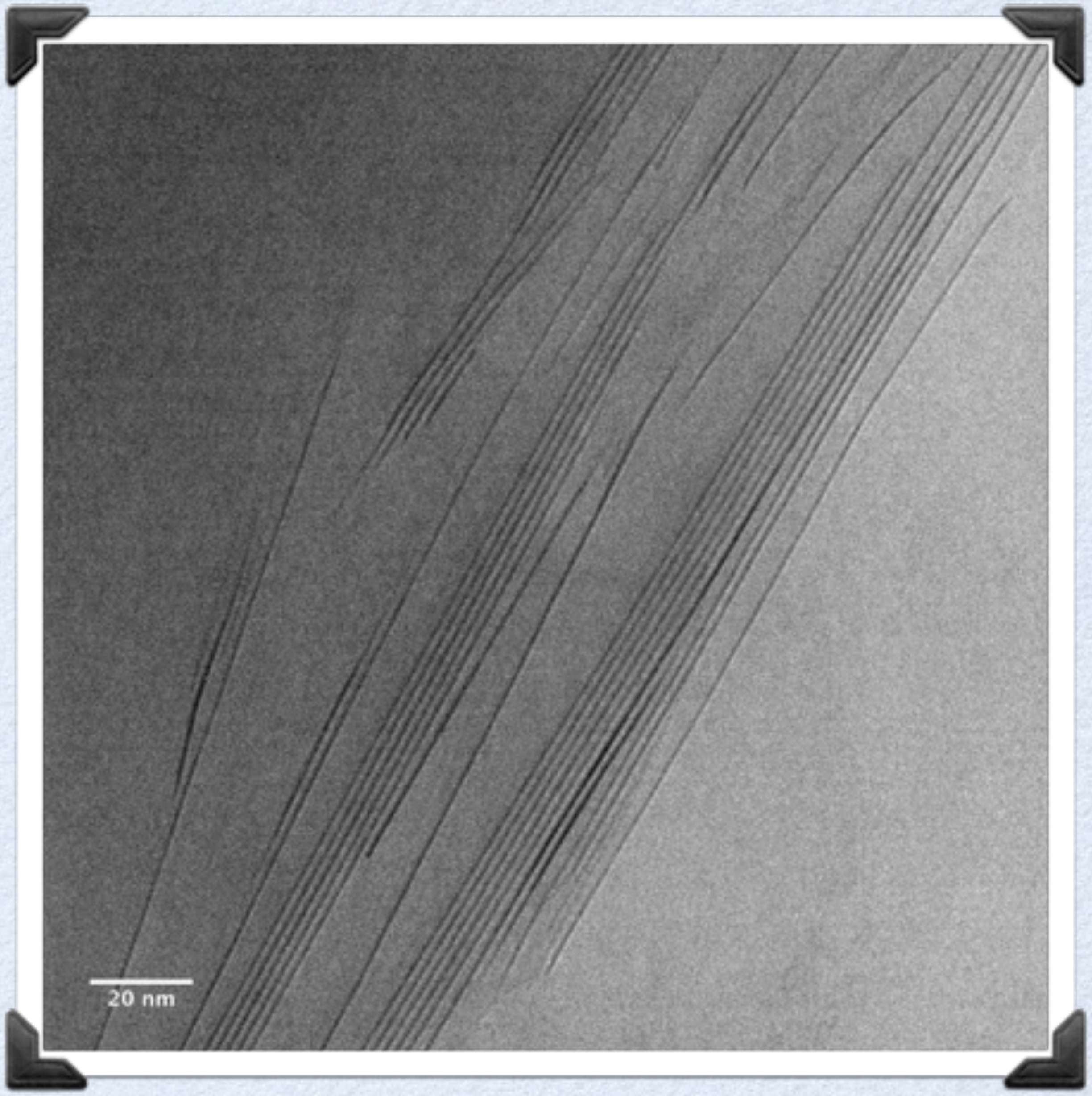
Ca montmorillonite in millipore water

Platelet-Water Interactions

- Imaging experiments



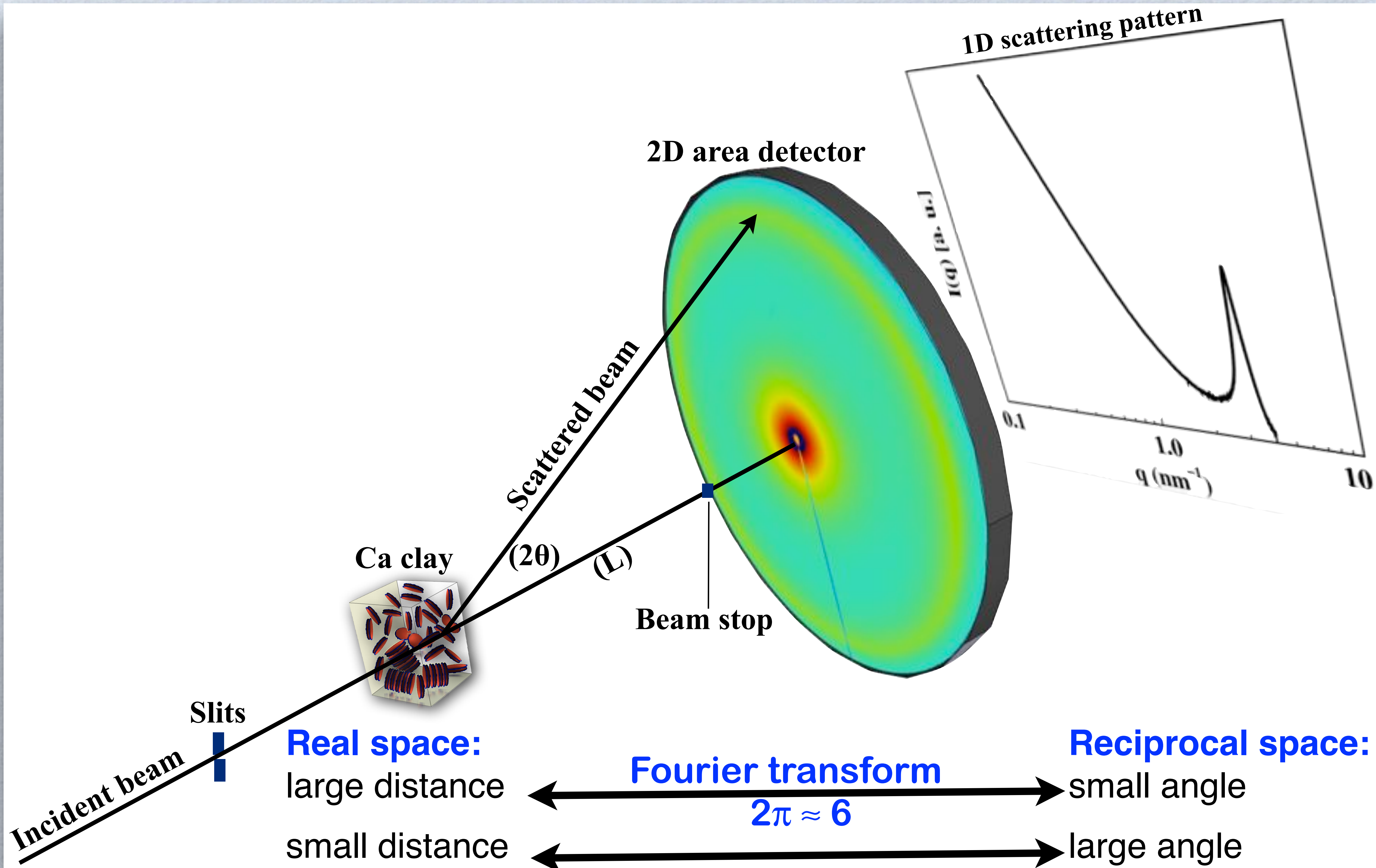
Ca montmorillonite in millipore water



Ca montmorillonite in millipore water

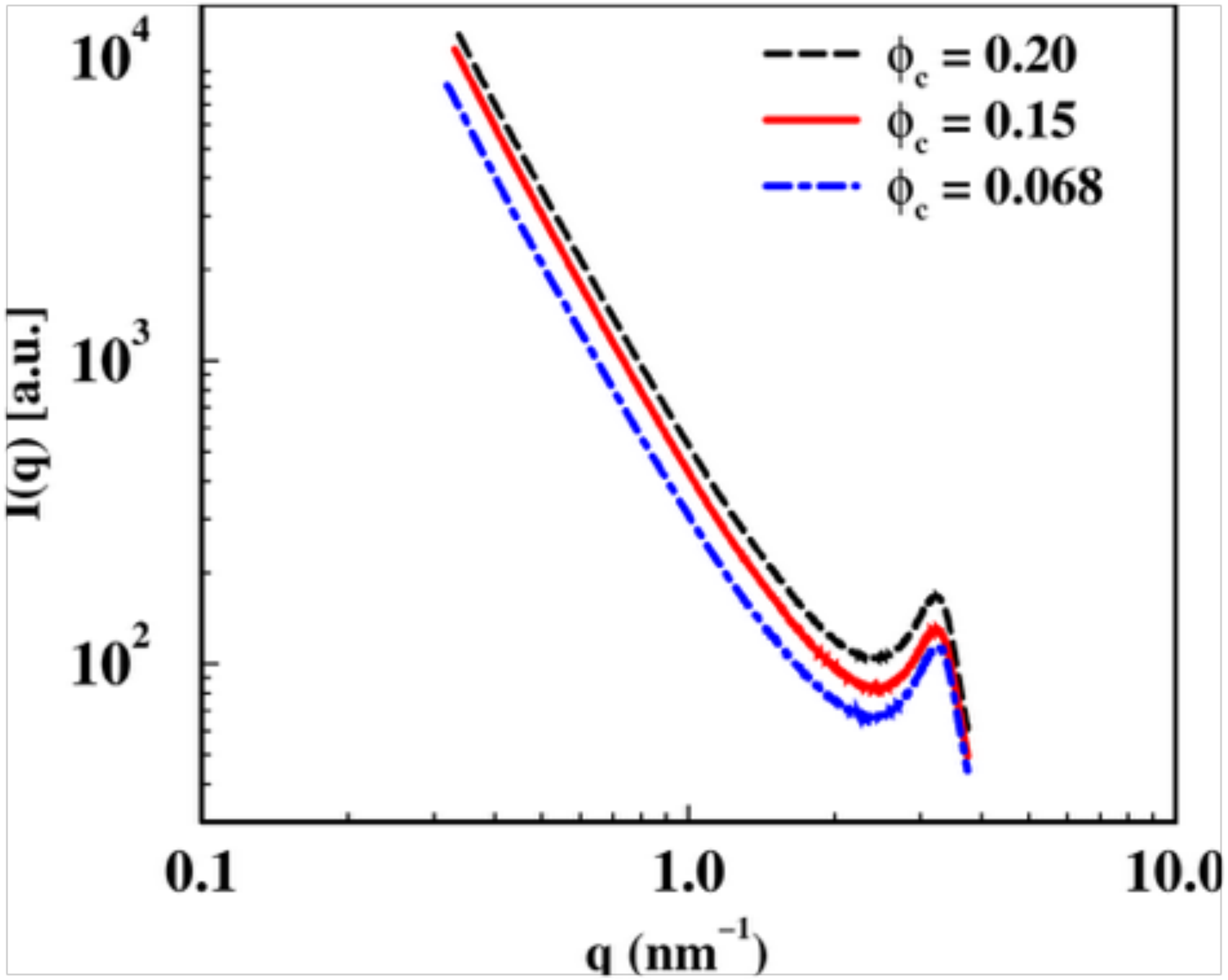
Platelet-Water Interactions

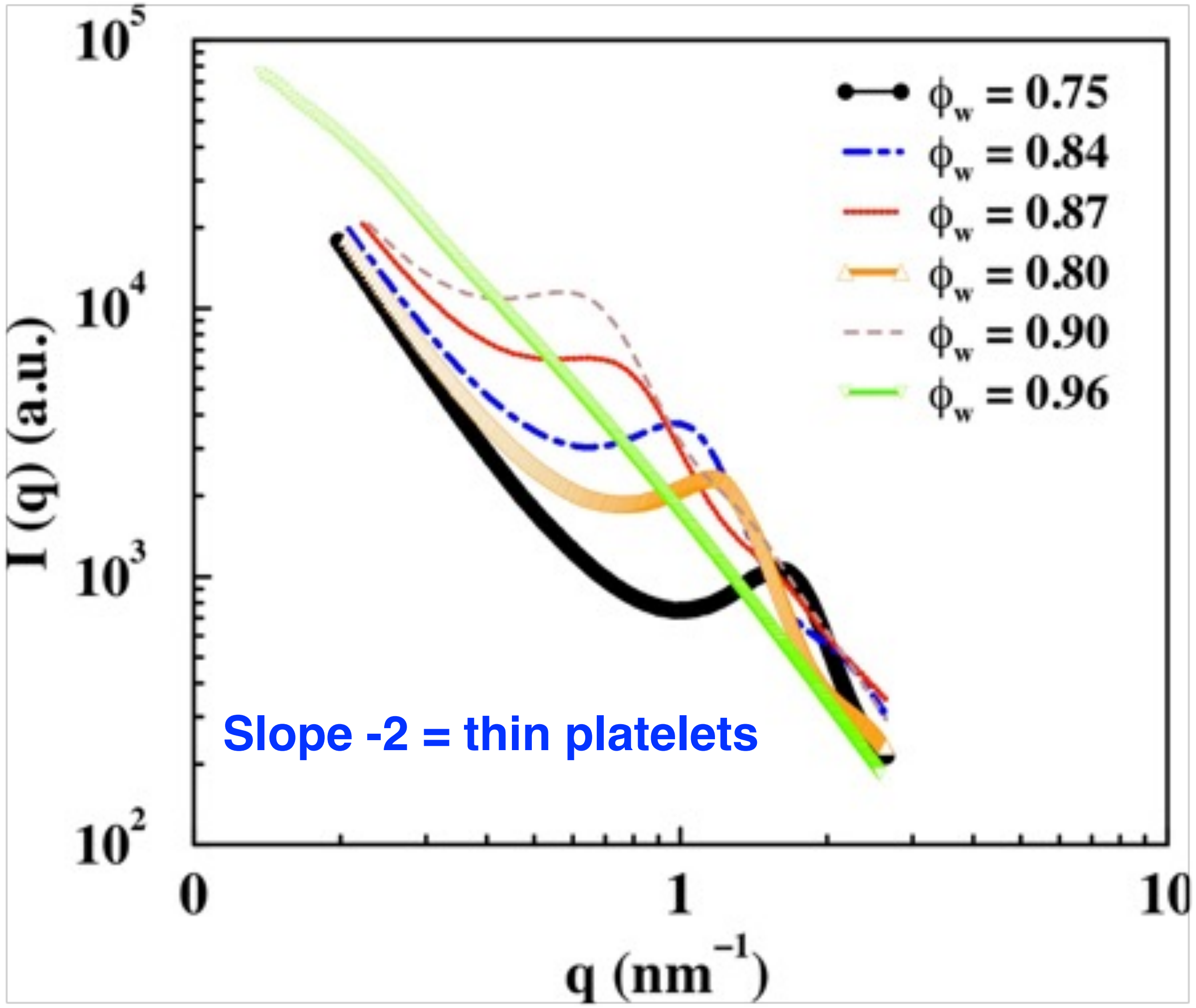
- Main technique: WAXS/SAXS/USAXS



Platelet-Water Interactions

- WAXS/SAXS results of mono- and divalent systems (salt free)





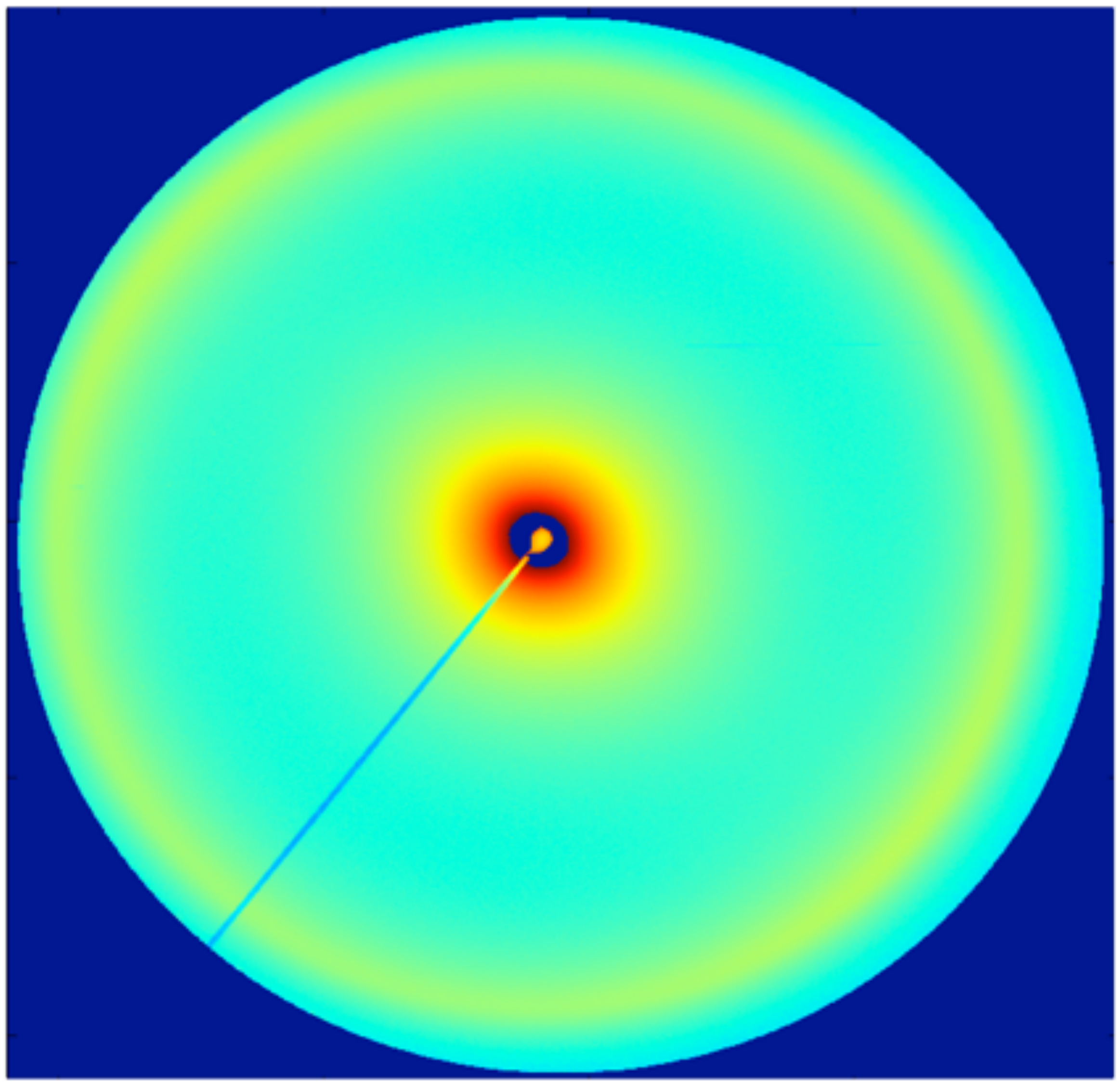
Ca montmorillonite in millipore water

Na montmorillonite in millipore water

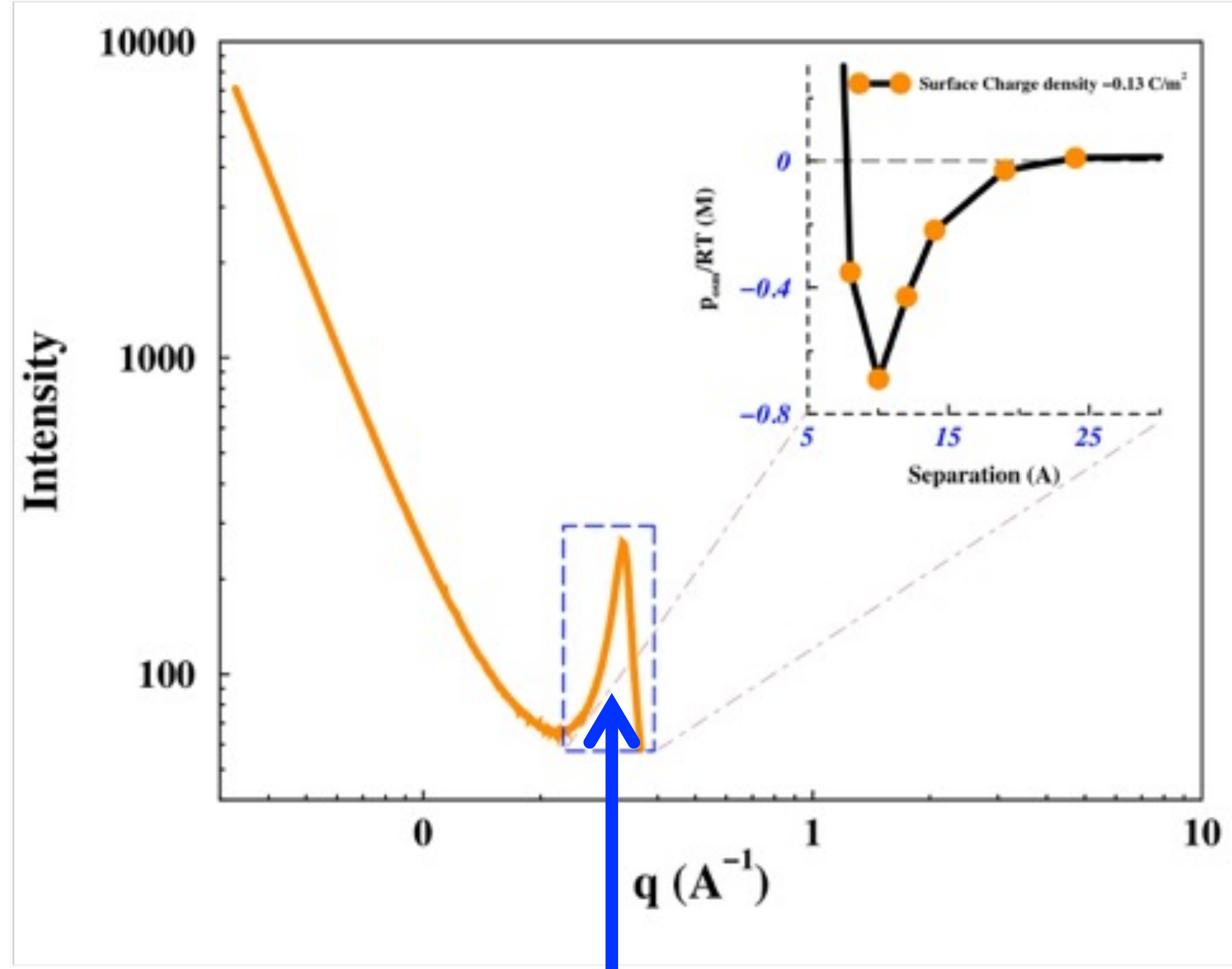
© *M. Segad et al. J. Phys. Chem. C, 116, 7596-7601 (2012).*

Platelet-Water Interactions

- WAXS/SAXS and MC results of divalent systems (salt free)



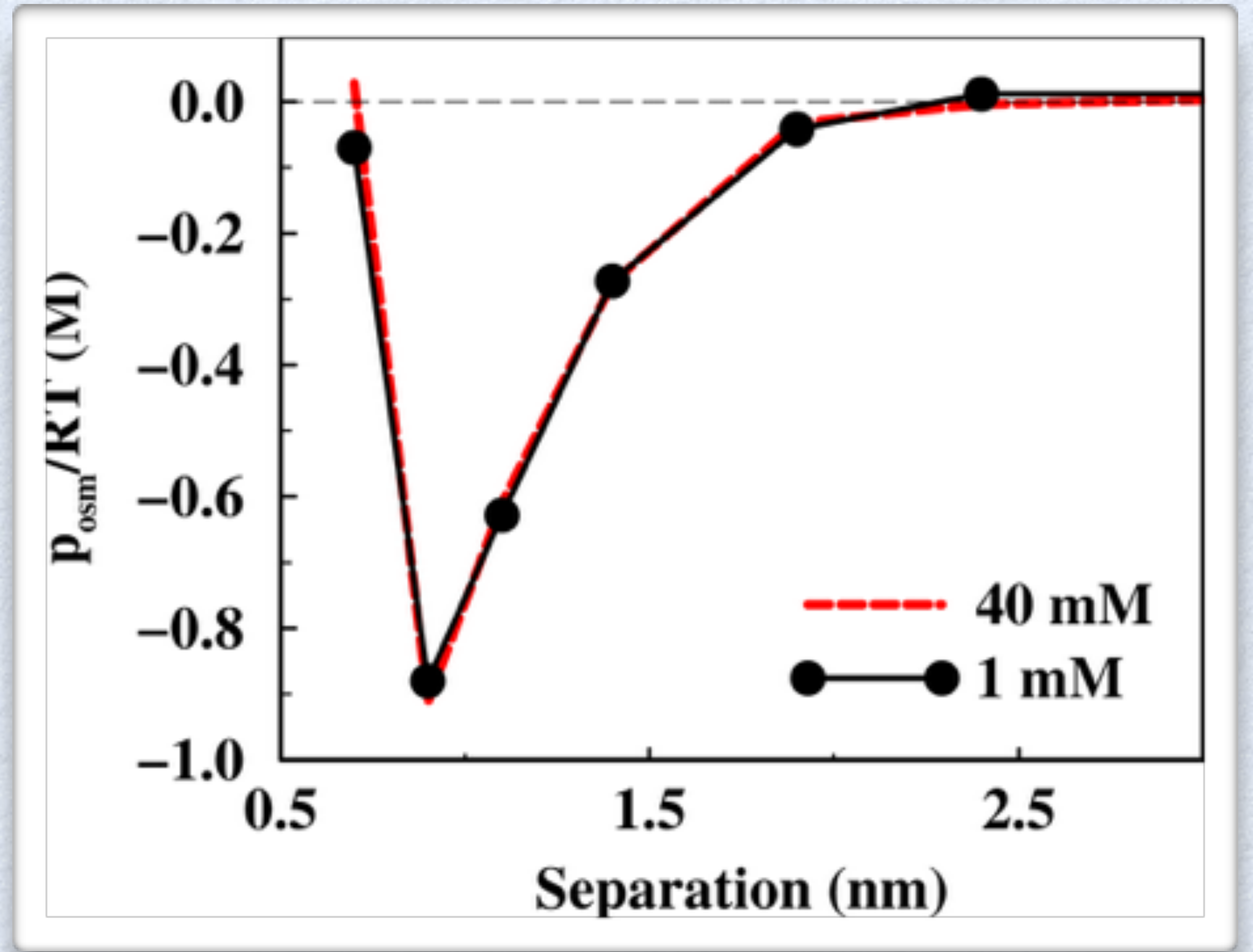
2D SAXS pattern of Ca montmorillonite with millipore water

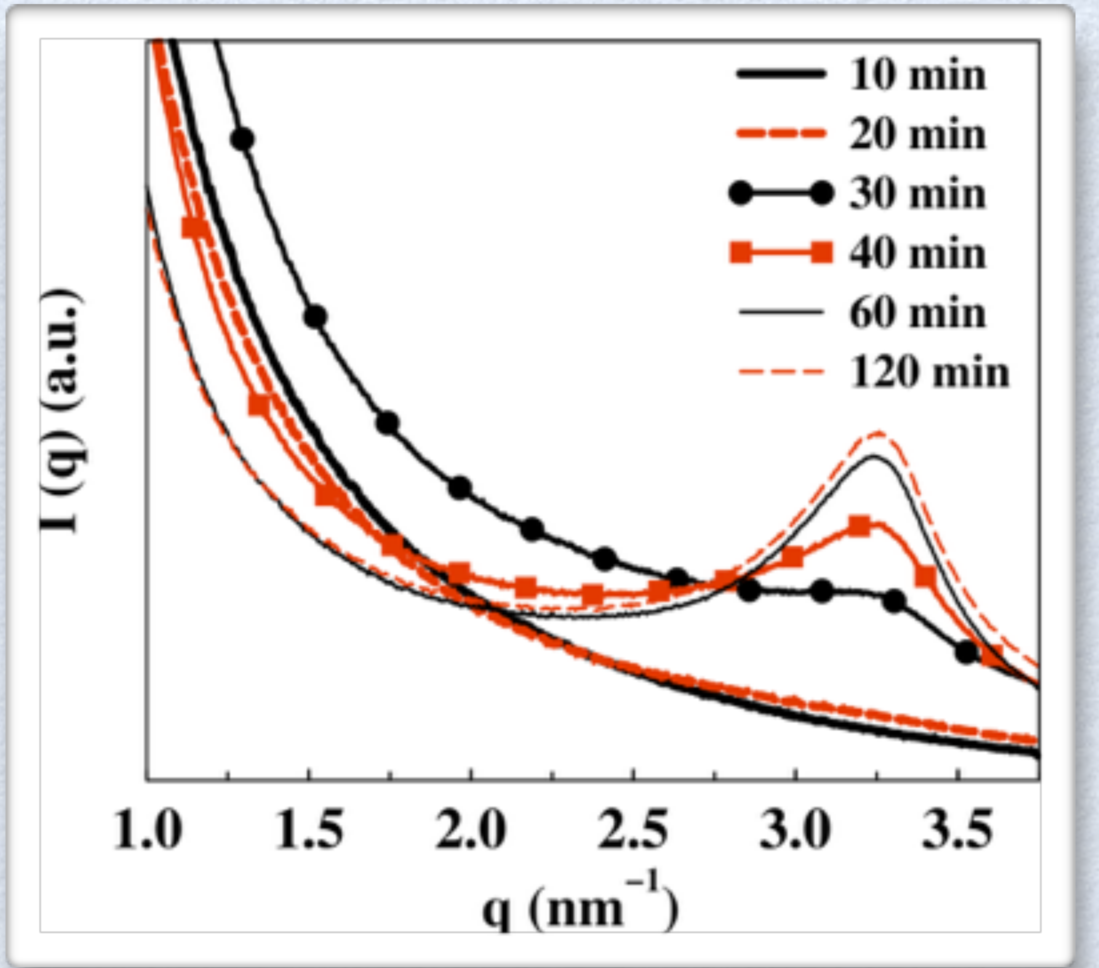


Peak in reciprocal space gives repeat distance 2π/q ≈ 2 nm in real space

Platelet-Water Interactions

- Aggregation process (tactoid formation) in salt solution





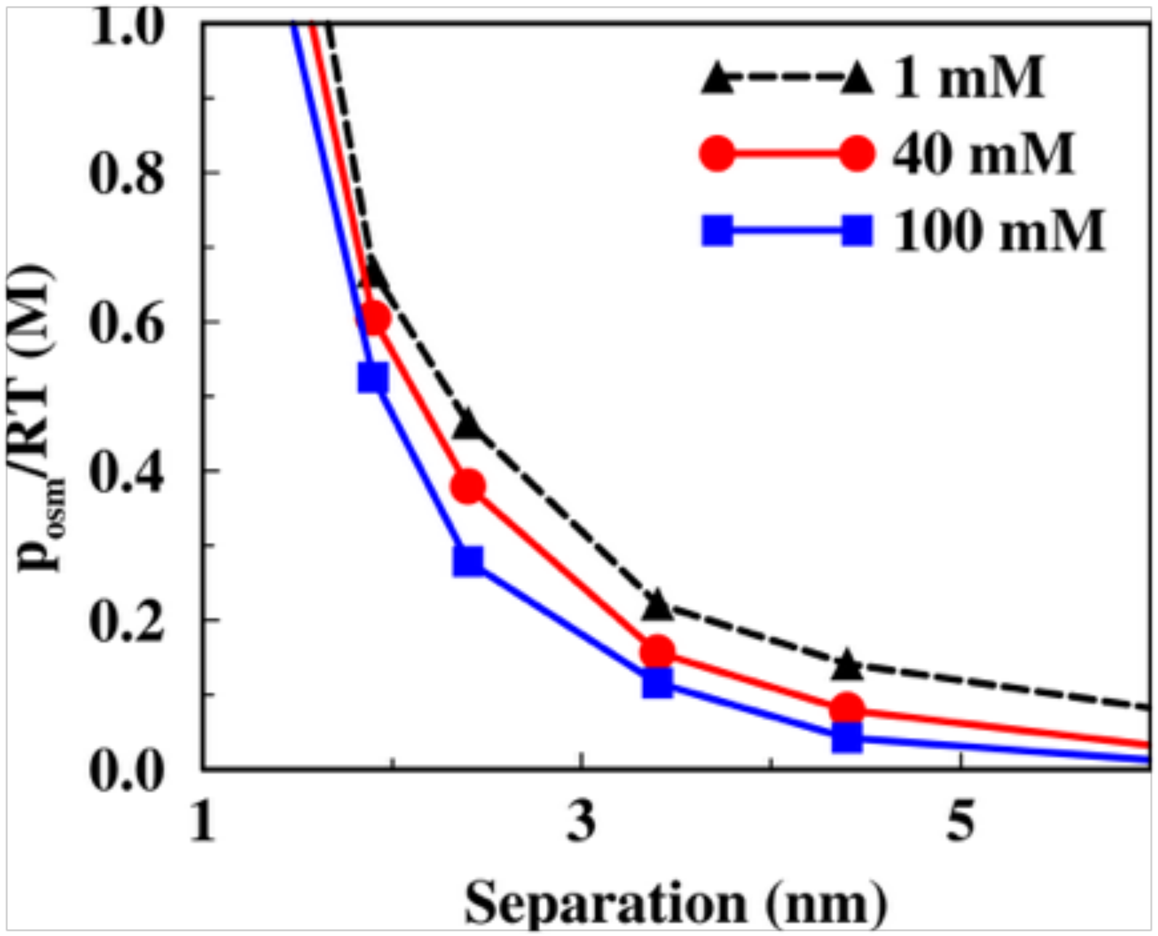
MC results show salt effect on the net osmotic pressure. The slit is in equilibrium with a bulk solution containing a 2:1 salt

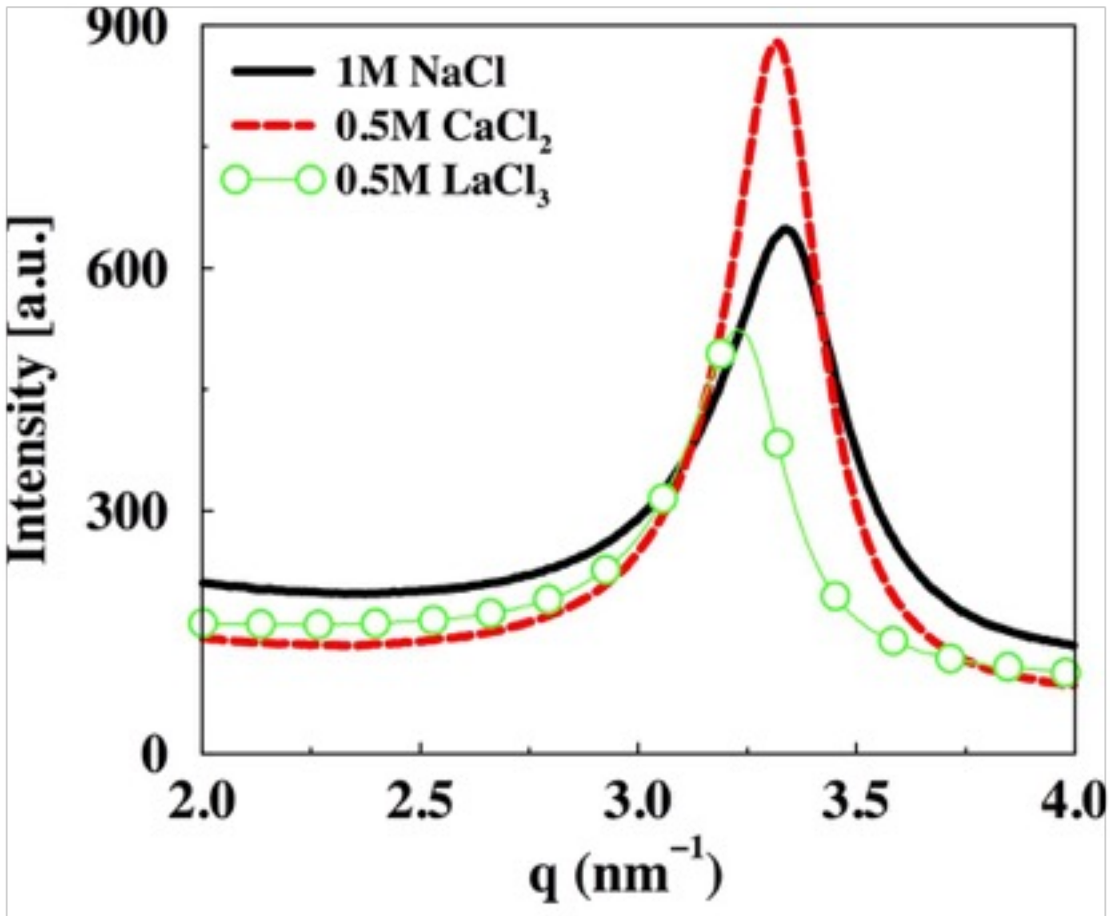
SAXS spectra show the influence of adding 5mM $CaCl_2$ on the microstructure of Na montmorillonite dispersions

© M. Segad et al. J. Phys. Chem. C 2012, 116, 25425-25433.

Platelet-Water Interactions

- Aggregation process (tactoid formation) in salt solution



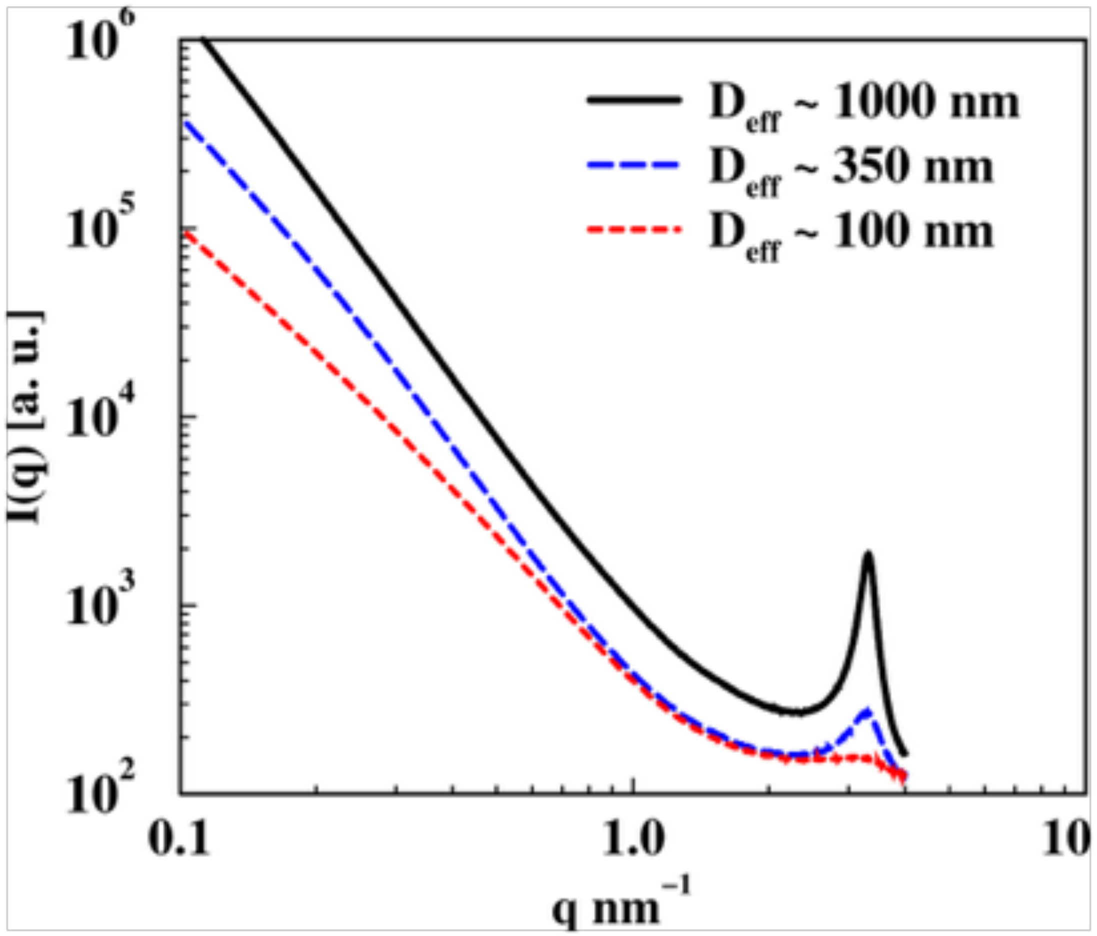


MC results show salt effect on the net osmotic pressure. The slit is in equilibrium with a bulk solution containing a NaCl salt

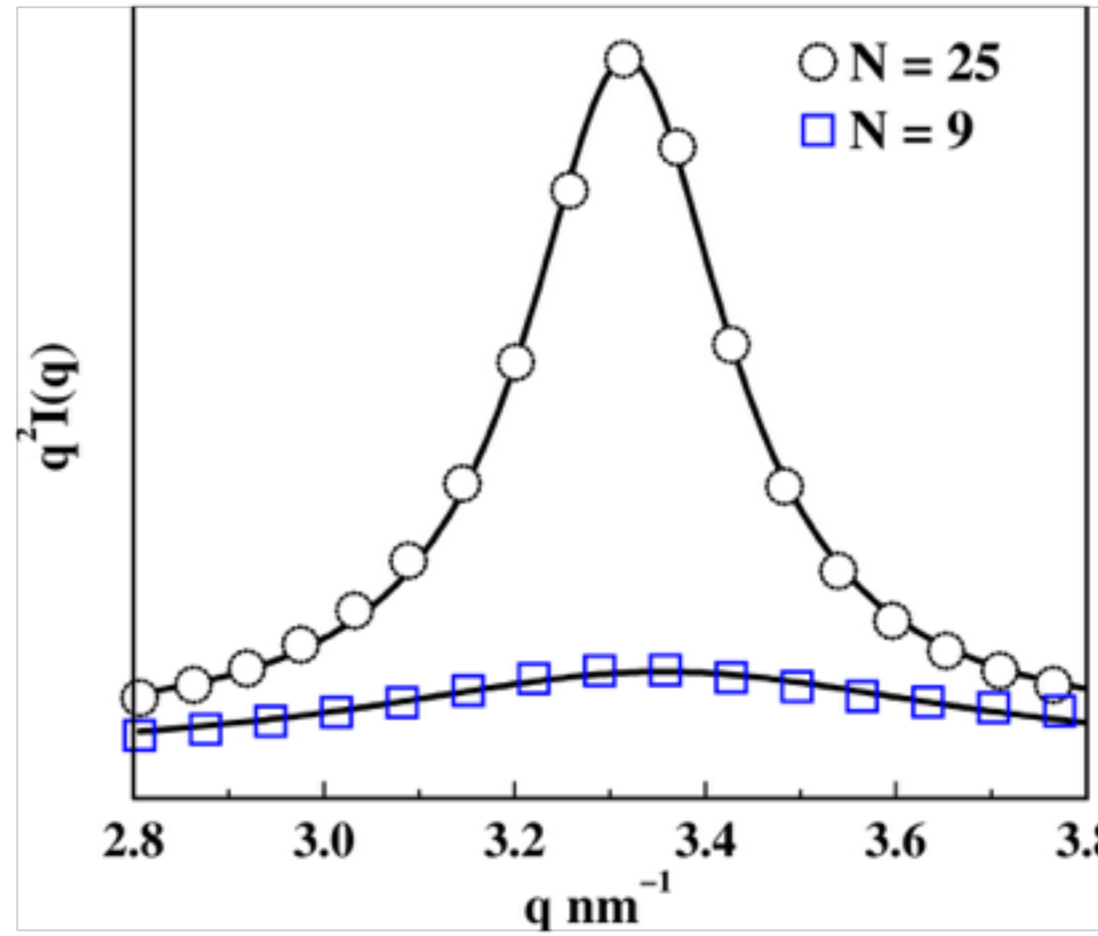
WAXS/SAXS peaks of montmorillonite dispersions in the presence of various salt solutions

Platelet-Water Interactions

- Aggregation number and size of platelets



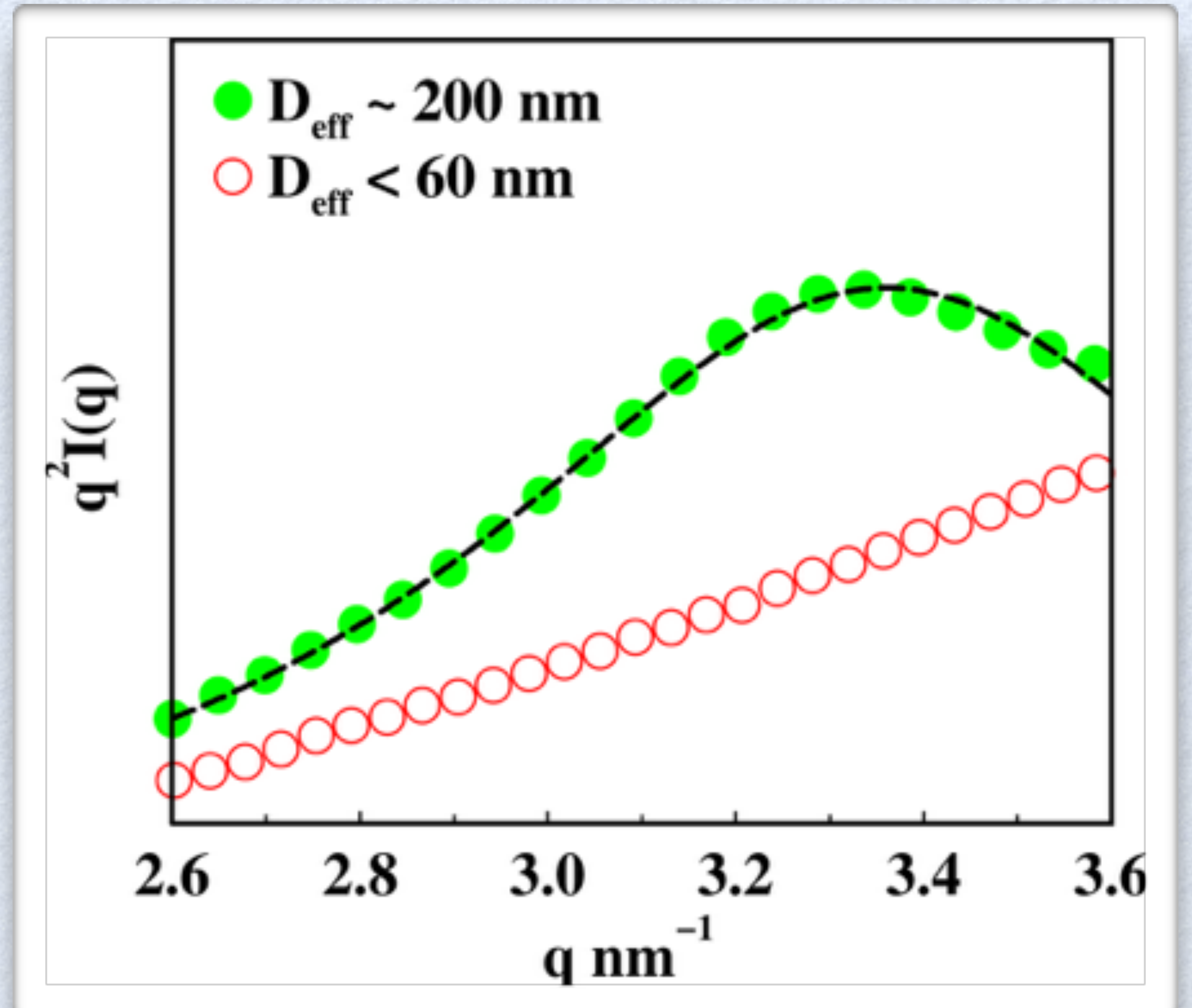
Ca montmorillonite in millipore water



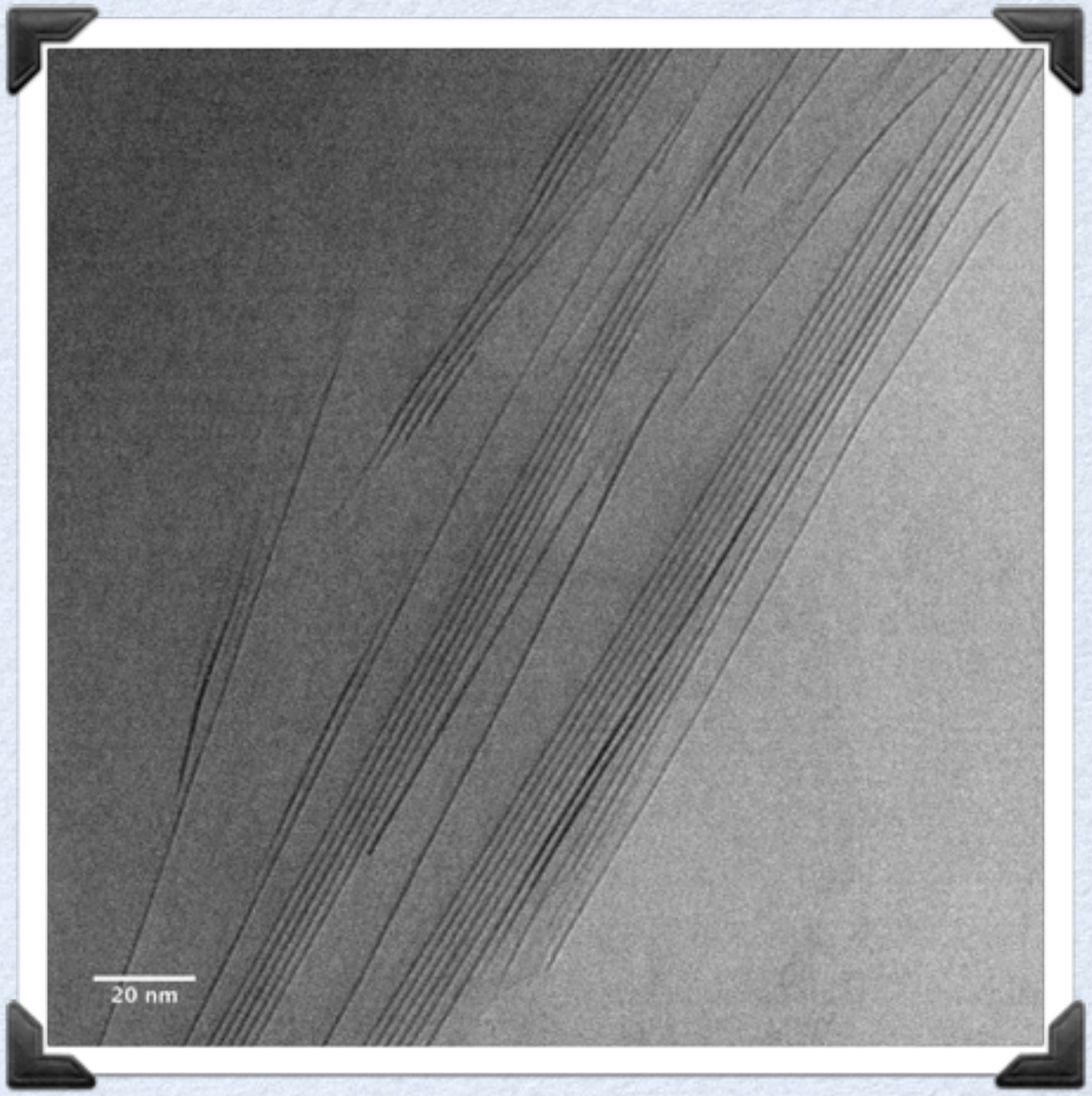
The reason behind the limited number of platelets per a tactoid (i.e. N<<100) is yet a mystery!

Platelet-Water Interactions

- Aggregation number and size of platelets



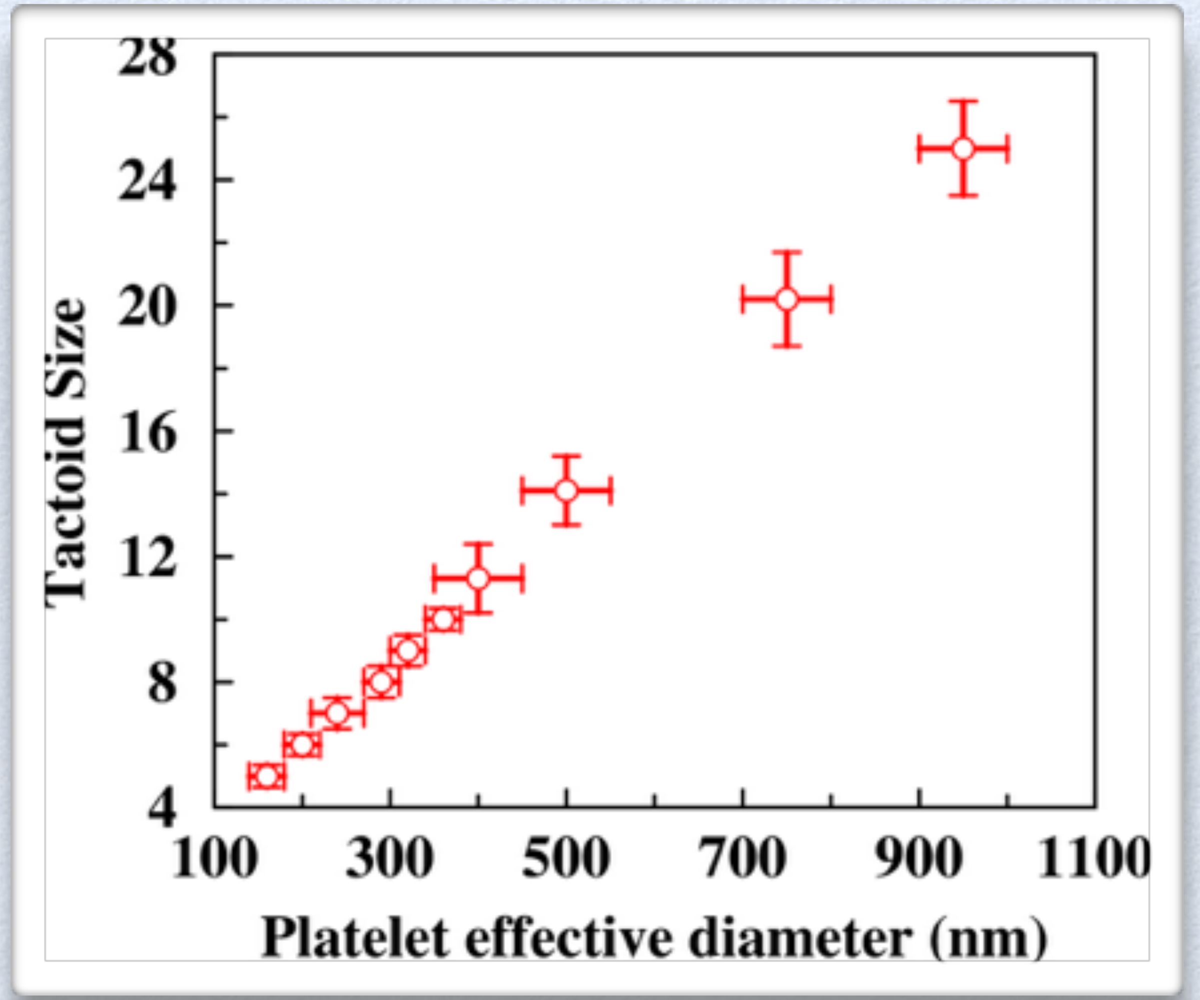
Montmorillonite platelets equilibrated in 500mM $CaCl_2$

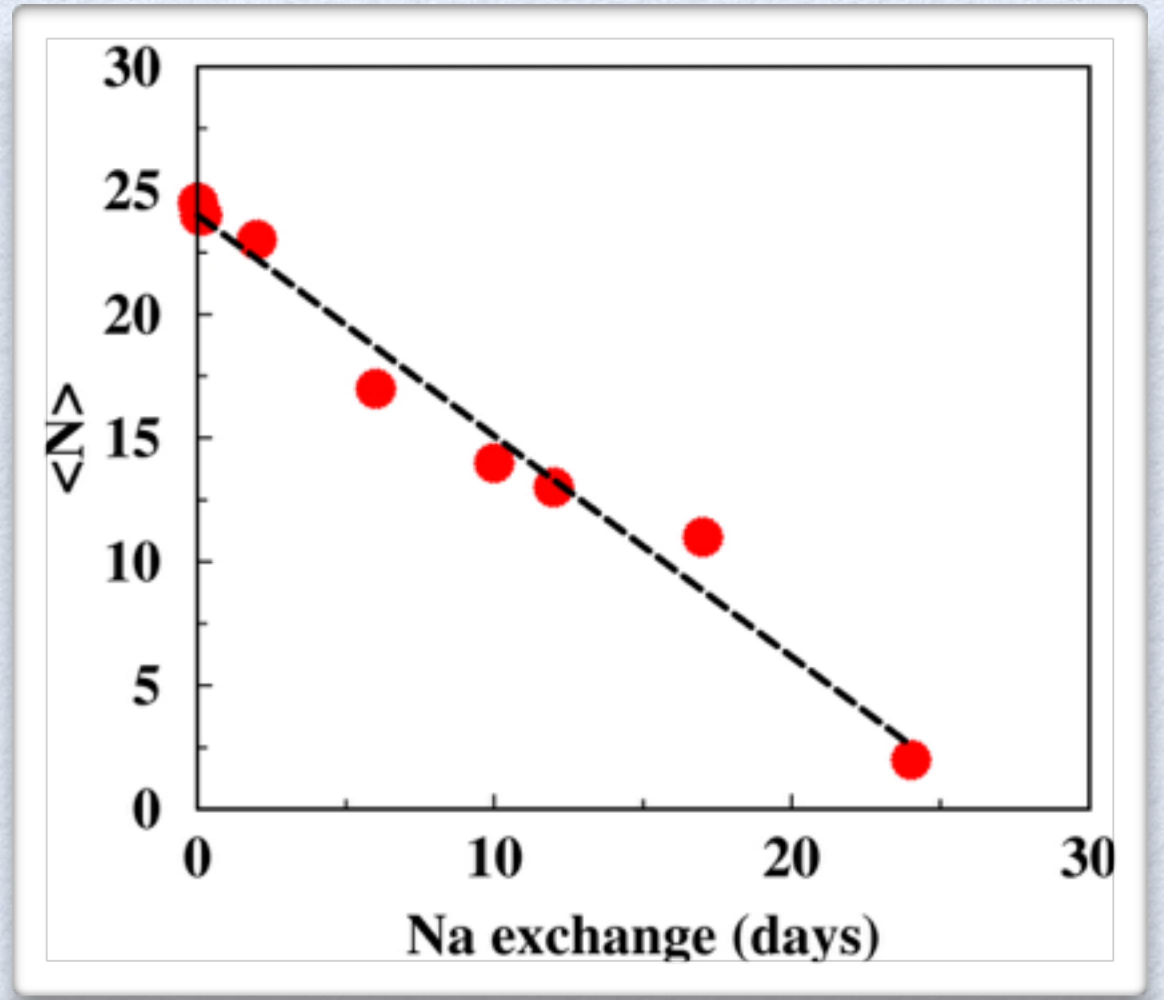


For aggregated system of charged platelets, excellent agreement regarding tactoid size was found between Cryo-TEM observations and scattering experiments

Platelet-Water Interactions

- "New" empirical relation between tactoid and platelet sizes



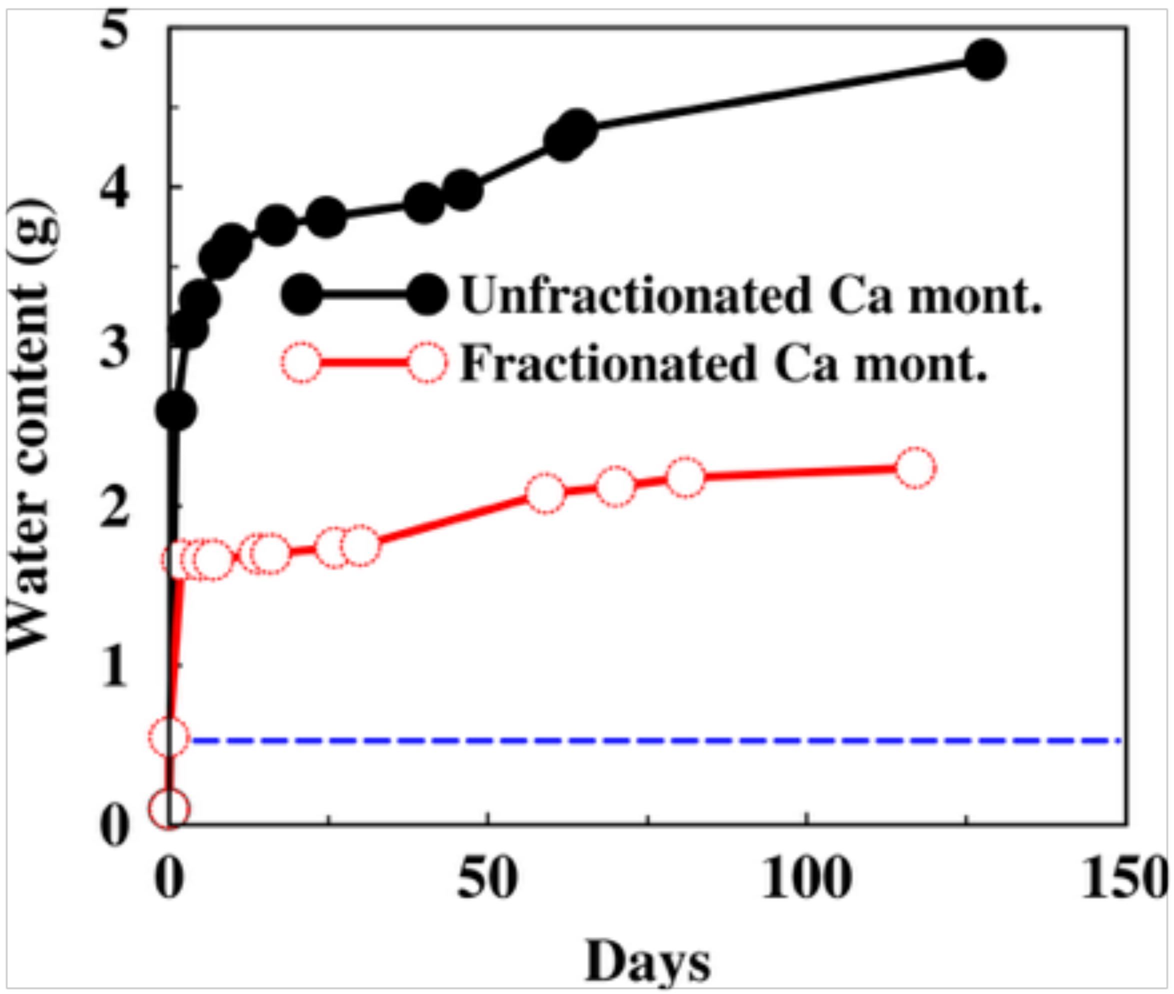


$$\langle N \rangle \approx \delta + \alpha \langle D \rangle$$

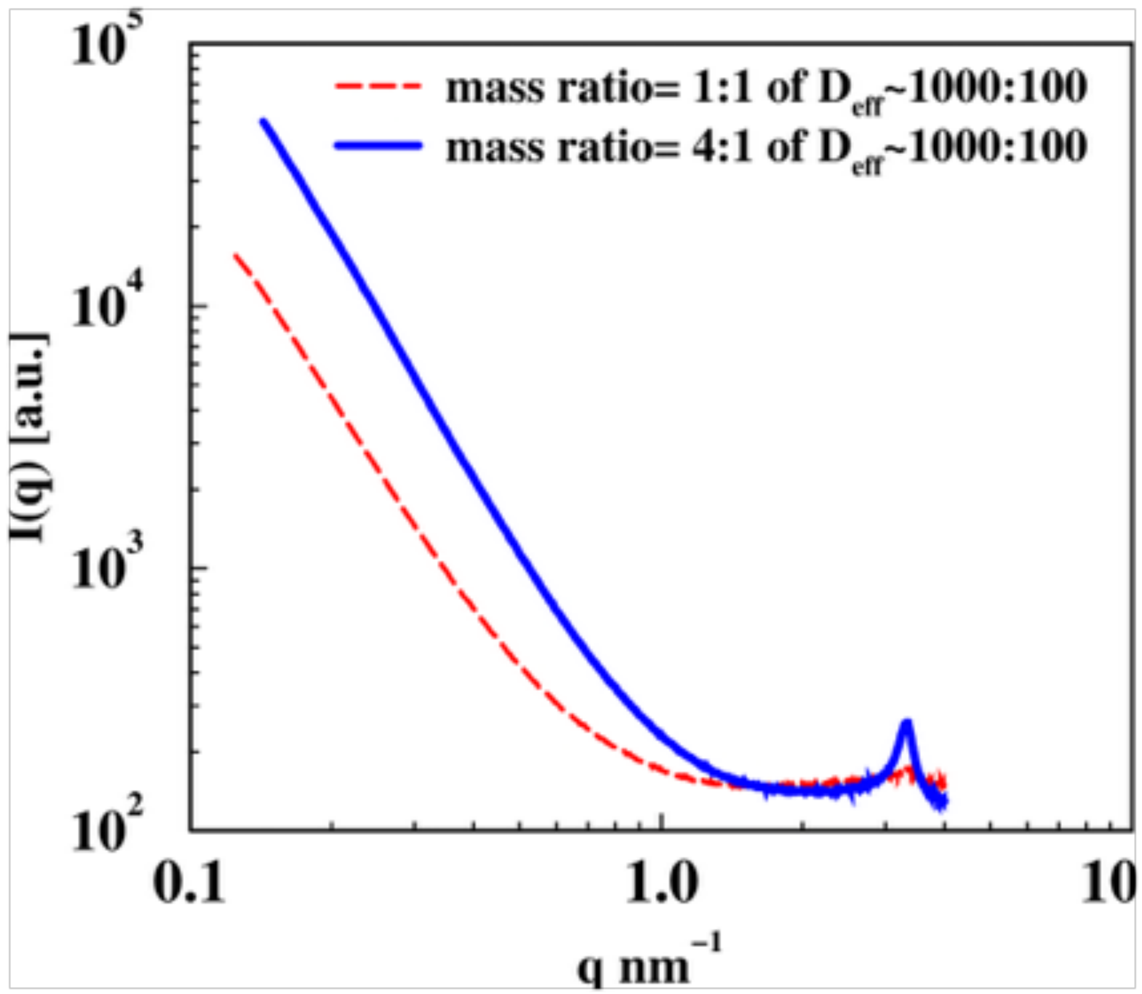
© M. Segad J. Applied Crystallography, 46, 1316-1322 (2013).

Platelet-Water Interactions

- The origin of extra-lamellar swelling



Swelling of fractionated & unfractionated Ca mont



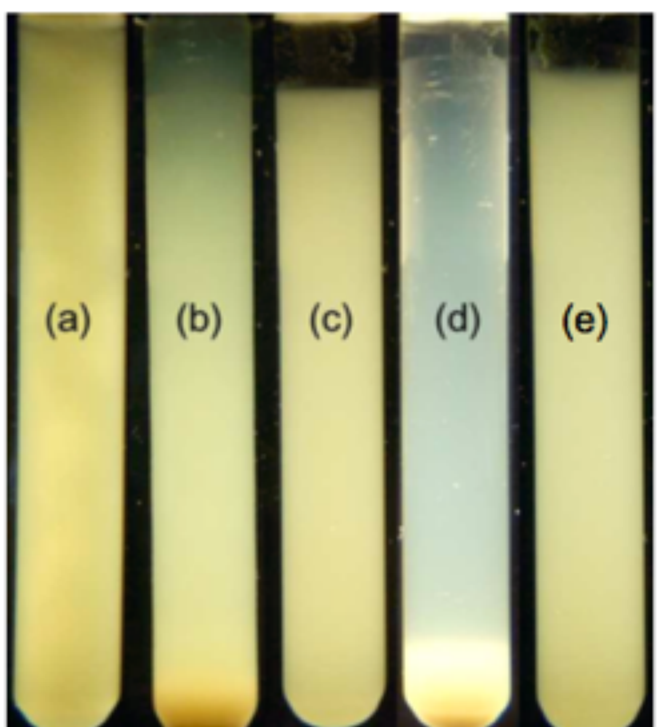
SAXS of mixed-size platelets

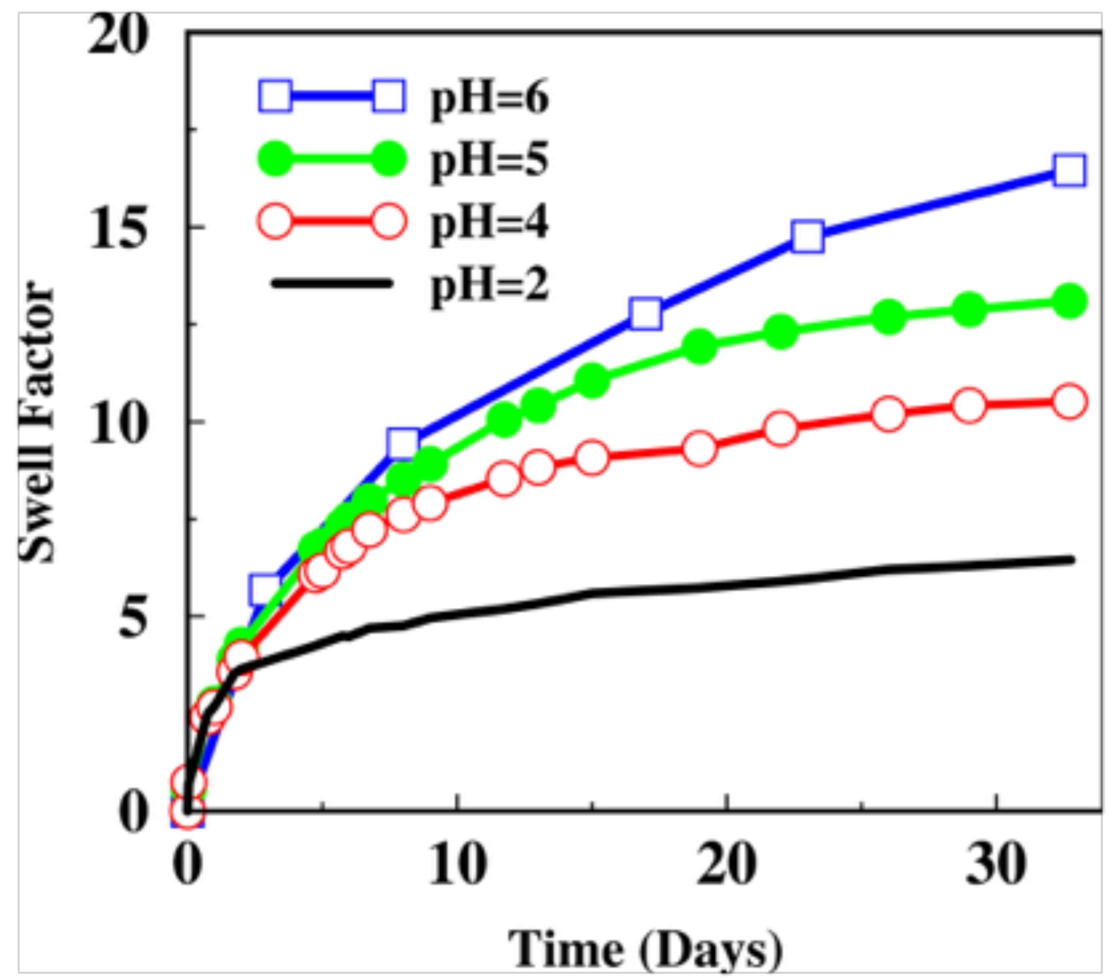
© M. Segad et al. Nanoscale, 7,16290-16297 (2015).

The Role of pH

Clay Dispersions	Si μM	Al μM	Fe μM	Mg μM
Na Mont at pH=4	280	0	3	3
Na Mont at pH=2	950	180	40	63

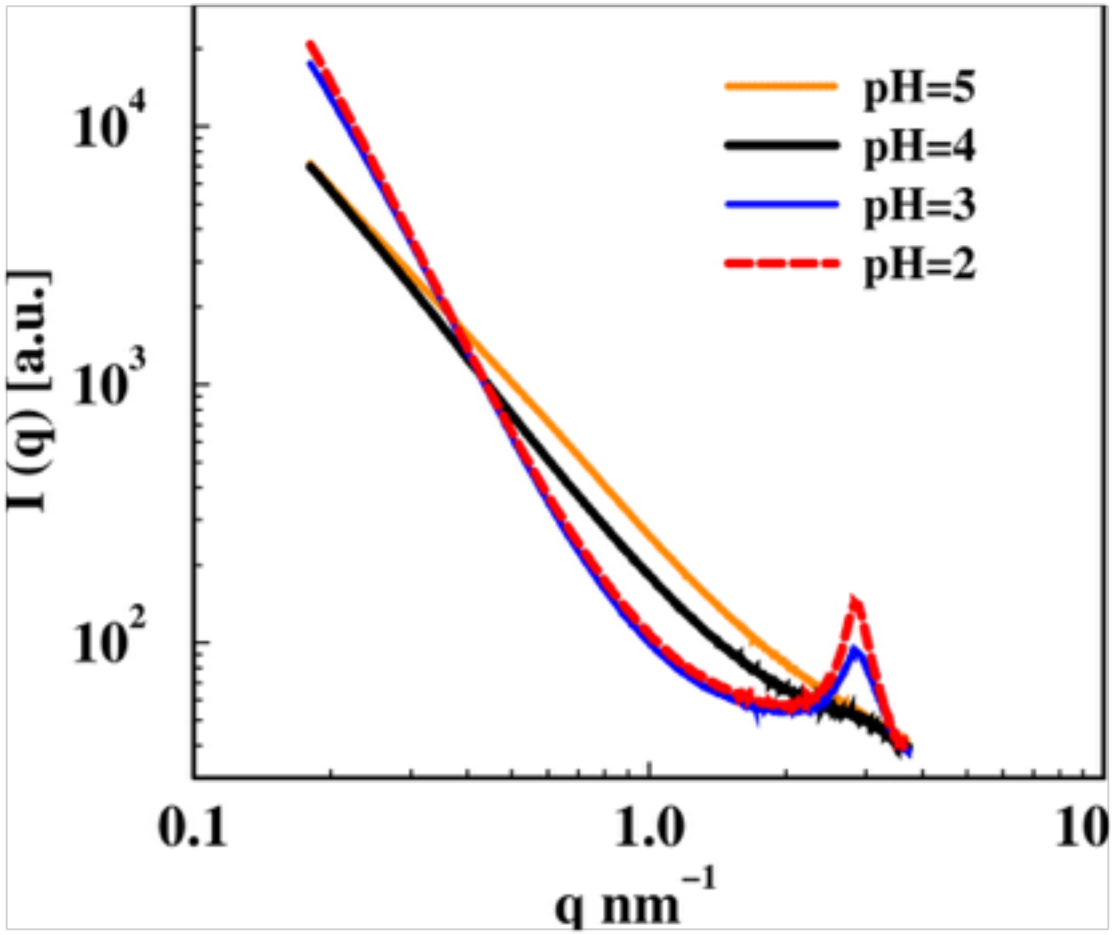
Parameter	(a)	(b)	(c)	(d)	(e)
pH	6	4	4	4	6
c_s (mM)	25	0	25	0	25
ϕ_c (%)	1	1	0.3	0.3	0.3



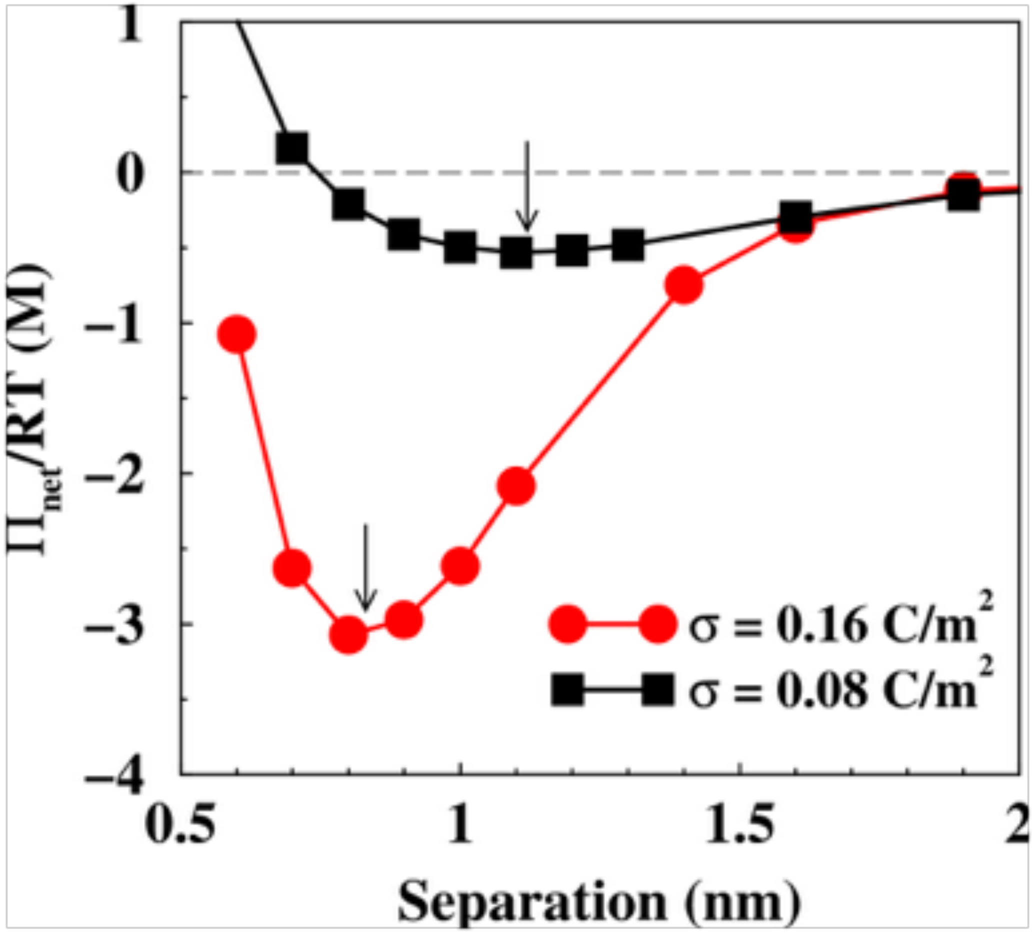


(Na) montmorillonite at different pH

The Role of pH



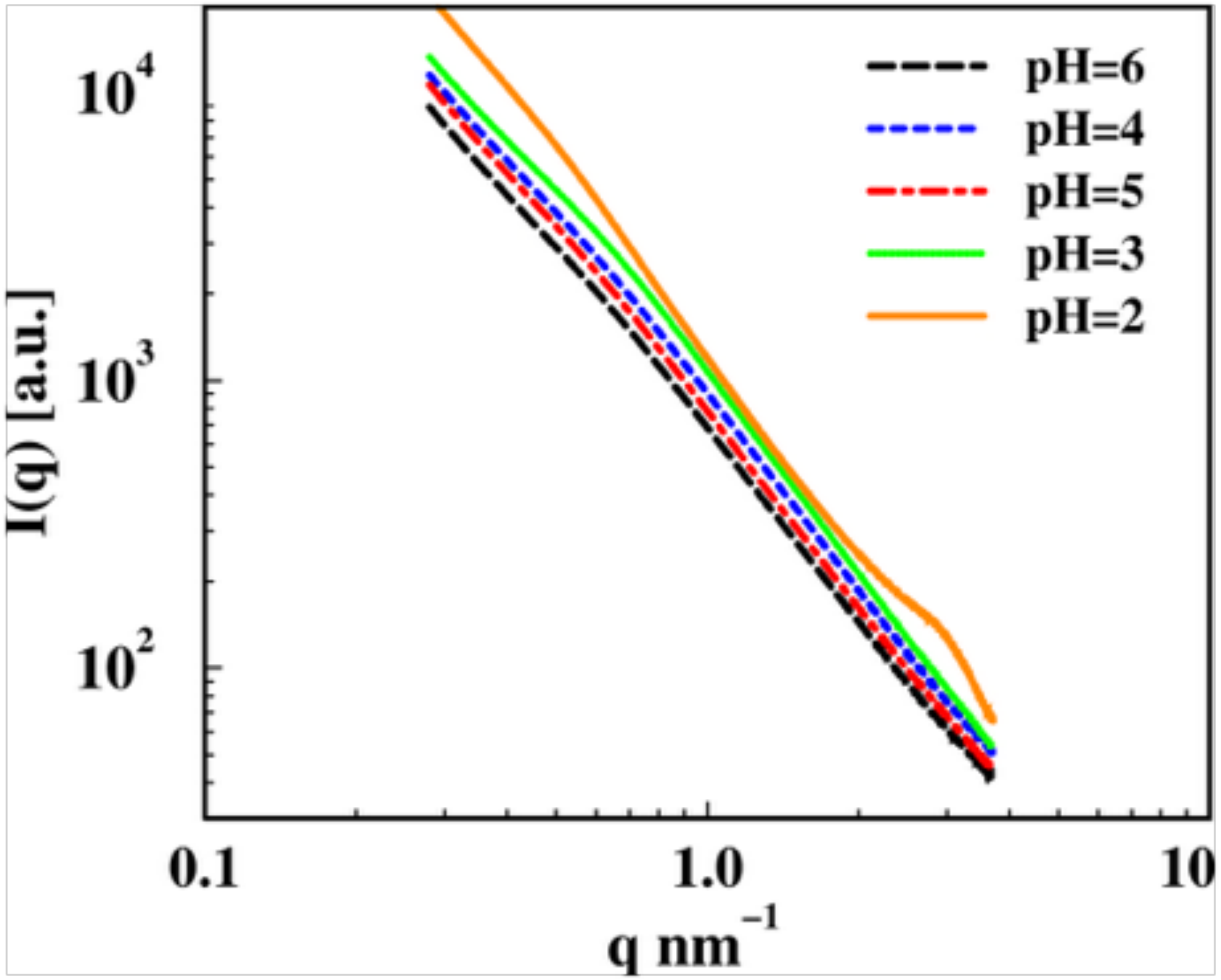
(Na) montmorillonite at different pH

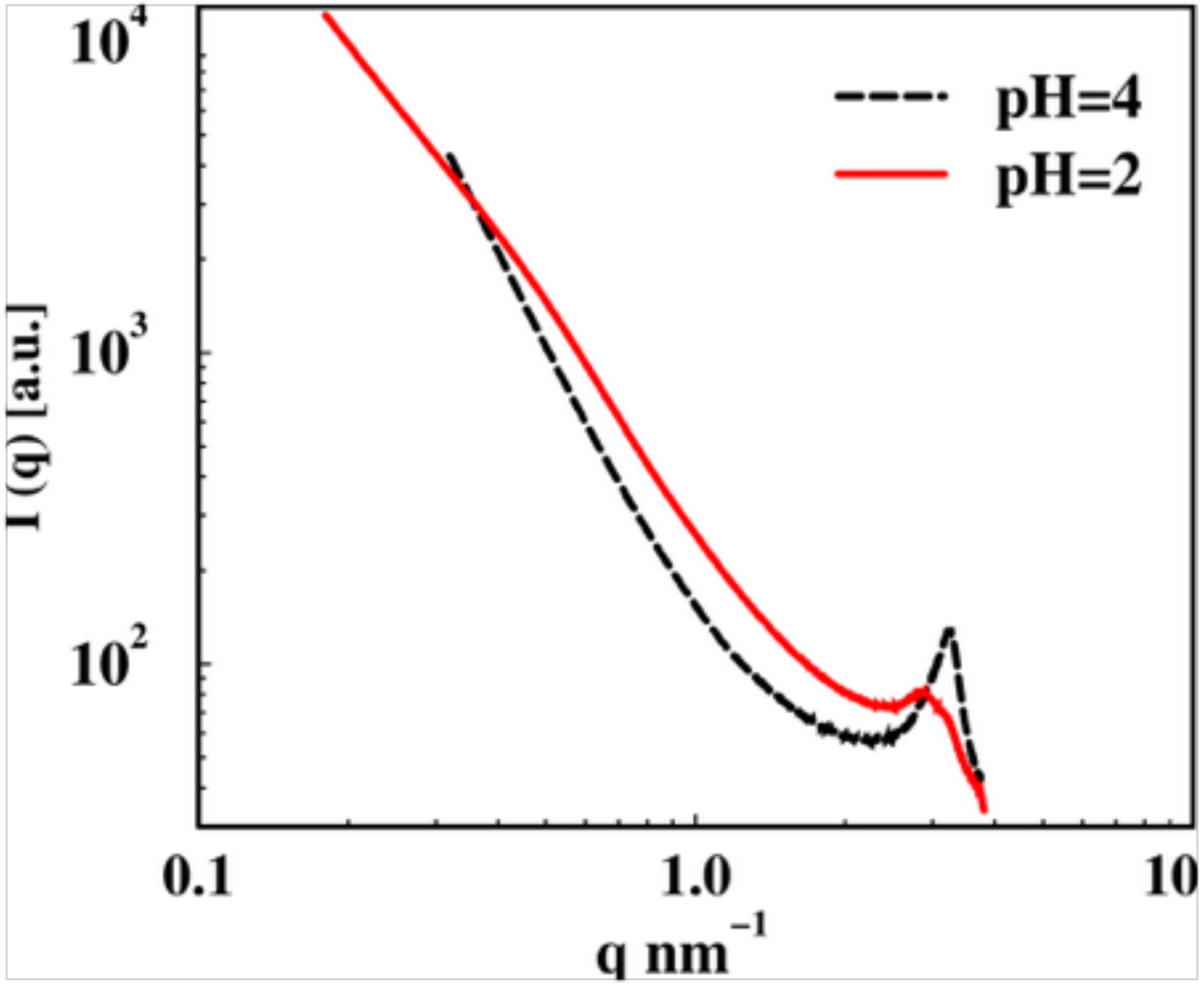


(Na) montmorillonite at different pH

© M. Segad et al. PCCP, 17, 29608-29615 (2015).

The Role of pH

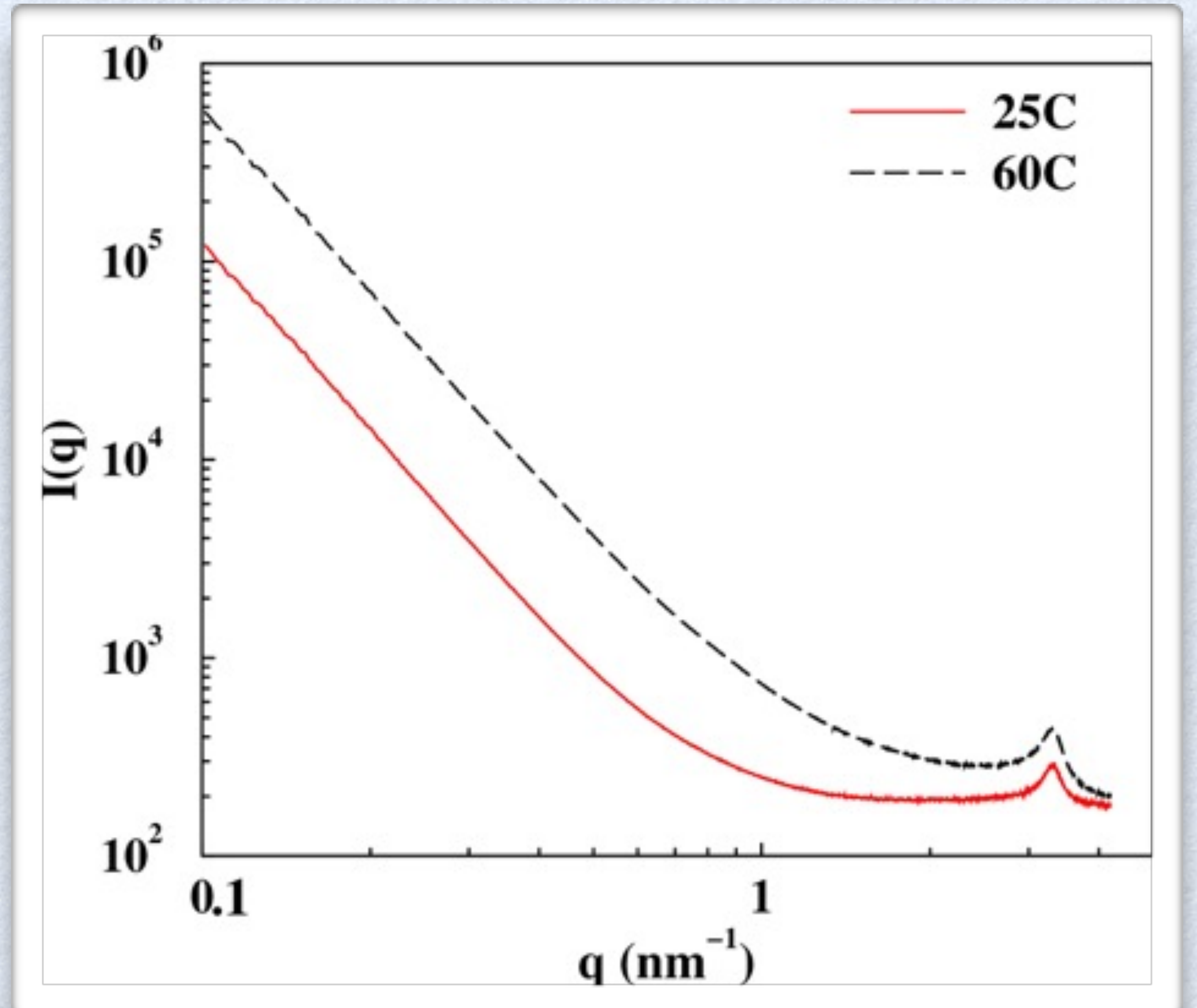




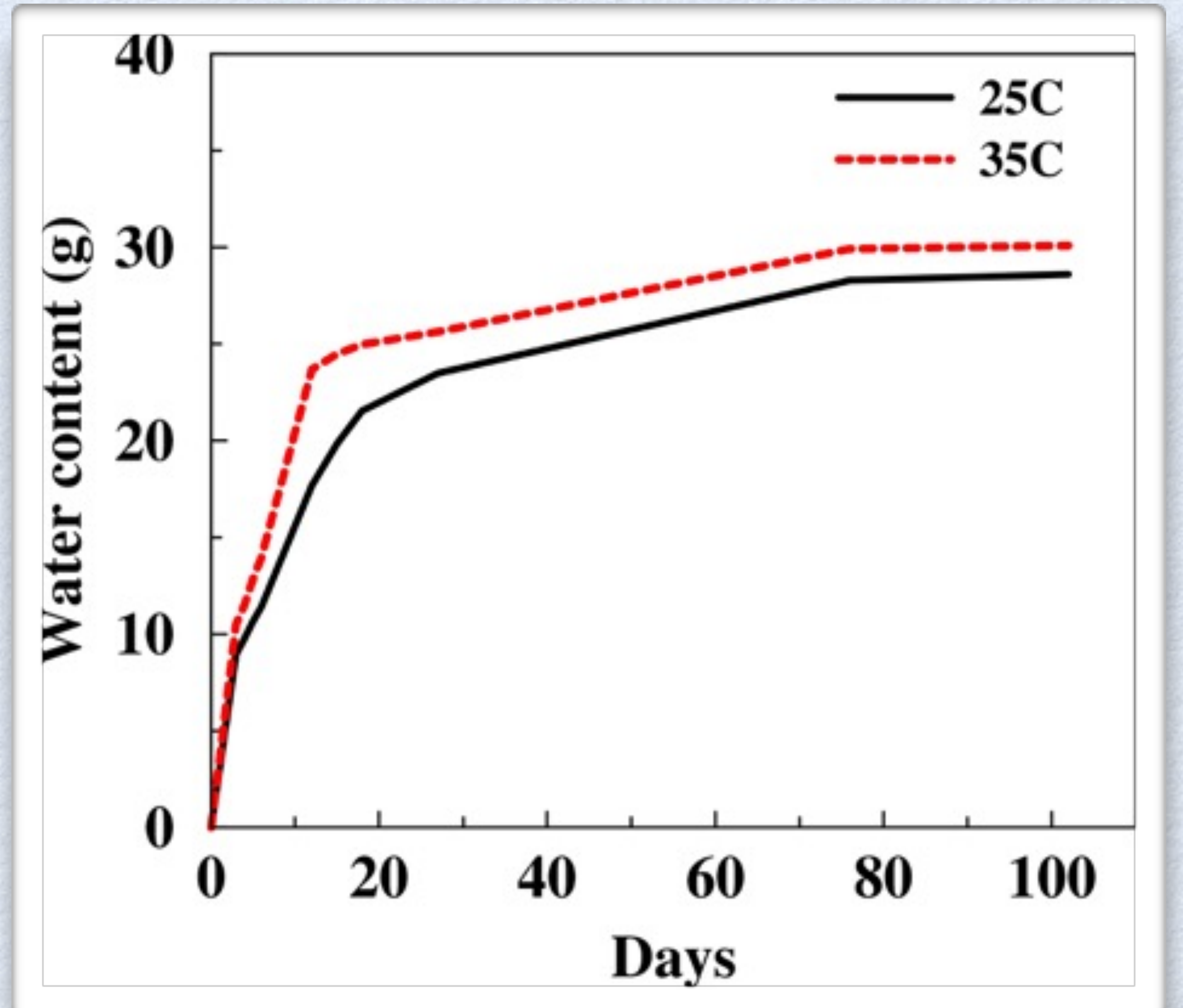
Na montmorillonite in 30 mM NaCl

Ca montmorillonite at different pH

The Role of Temperature



(Na) montmorillonite equilibrated in 500mM $CaCl_2$ at different temperatures



Na montmorillonite in Millipore water at different temperatures

Take Home Messages

Size of Clay Platelets, pH and Temperature Matter

And, more ? remaining than answered

Acknowledgements

Alexander Hexemer (ALS)
Peter Zwart (BCCB)
&
The Financial Support of
LDRD

UNDERSTANDING THE MECHANISMS OF CHEMICAL EROSION OF BENTONITE – NEED FOR A HOLISTIC APPROACH

Heini Reijonen, Nuria Marcos, Saanio & Riekkola Oy,

Barbara Pastina, Posiva Oy

Contents

- Background
- Sources of information & examples
- Conclusions

Background

- Chemical erosion and its implications need to be assessed in performance assessments (PA)
- To do this, a conceptual model(s) is needed
- Conceptual model is a basis for PA modelling
- Conceptual model can include, in addition to the process chemical erosion, also other relevant and interconnected processes (such as colloidal behaviour, sedimentation etc.)

Background

- Additional to this discussion (this presentation), also modelling development as well as groundwater evolution considerations are needed to fully assess chemical erosion in PA

Sources of information

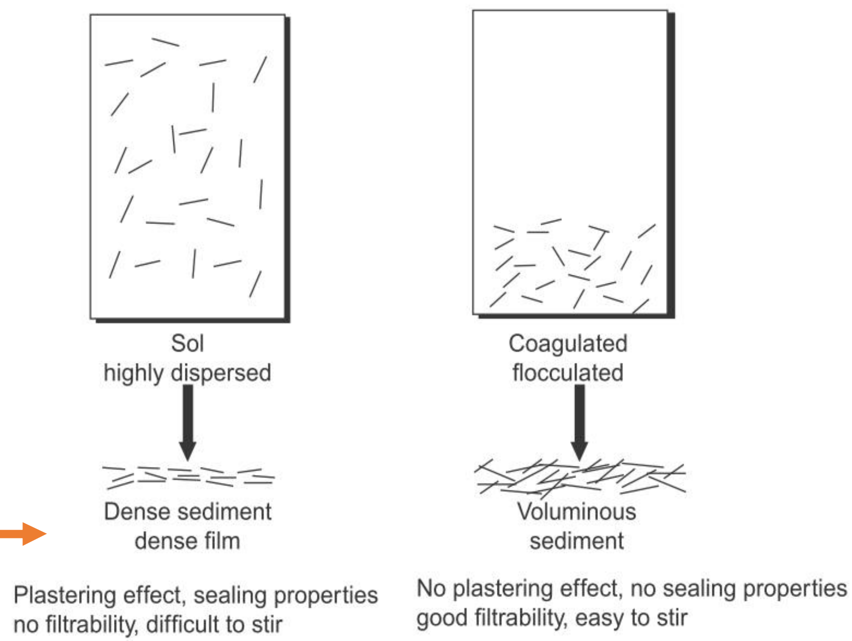
- Currently we use knowledge based on:
  - Limited amount of small scale experiments
  - Modelling based on the experimental results
- What is missing:
  - State-of-the-art review on chemical erosion in repository environment (past, present and future)
  - Review on chemical erosion considering also simultaneous processes – coupling!
  - Additional experiments to fill the gap between simplified systems and the expected system in the repository
  - URL results – will we get anything from CFM?
  - Detailed knowledge on the natural smectite stability at repository (or scenario) relevant environments

Sources of information

FEW EXAMPLES

1. Sedimentation

- Bentonite behavior has been extensively studied within geotechnical sciences and colloid sciences
  - Colloid science combined the concepts of dispersion, stability of dispersions, aggregation and sedimentation
  - What type of filter cakes are expected in repository environment?



Two types of sedimentation defined for well dispersed clay colloids (left) and aggregates (right) (Lagaly and Dékány 2013).

Sources of information - mechanisms

2. Gravity and available volume

- Gravity has a profound effect for erosion in vertical or inclined fractures (cf. lab experiments)
- Gravity also helps sedimentation
- The fracture volume in natural rock is not infinite → sedimentation will occur – fractures becomes more sparse with depth and their apertures are smaller
- Salinity also increases with depth → colloids destabilisation
- Aim for a conservative approach, but not unrealistic!

Sources of information - mechanisms

3. Filter cake formation

- Geotechnical sciences use the properties of bentonites
    - Filter cakes formation is basis for bentonite drilling slurries performance
    - This information should be reviewed from the safety case point of view

4. Water compositions – natural vs. simulant

- The experimental set ups currently used to study chemical erosion are overly simplified (cf. Na/Ca Cl solutions).
- Natural waters are more complex and buffered by the host rock
- Can we describe smectite stability in dilute conditions only using cation concentration?
- Few examples of ground and Allard waters:

Parameter	Unit	RO (min)[1]	RO (max)[1]	KI (min)[1]	KI (max)[1]	Grimsel[2]	Allard-MO[3]	Allard-MR[3]
TDS	mg/L	61.7	189.9	133.2	240.2	83.0	~220	~220
pH	field	6.8	9.3	7.2	8.5	9.6	8.4	8.8
Eh	mV	-330.0	230	-350.0	400.0	-200.0		
O2	mg/L	0.0	1.1	0.0	0.4			
Na	mg/L	4.3	43.2	4.7	27.0	15.9	52.5	52.5
K	mg/L	0.7	3.0	0.2	2.4	0.2	3.9	3.9
Ca	mg/L	2.7	23.0	11.2	33.0	5.2	10.2	5.1
Mg	mg/L	0.1	5.3	0.9	8.6	0.015	2.8	0.7
Fe(tot)	mg/L	0.0	3.0	0.0	1.4	0.0002		
Cl	mg/L	0.9	7.4	1.0	5.8	5.7	47.5	48.8
HCO3	mg/L	0.0	123.3	82.4	158.6	27.45	90.7	65.0
SO4	mg/L	1.0	6.5	0.1	3.5	5.9	9.6	9.6
SiO2	mg/L					15.0	2.9	1.7
Sr	mg/L					0.18		
Mn	mg/L					0.0003		
F	mg/L					7.2		

1) McEwen & Äikäs 2004

2) as given in Hellä et al. 2014

3) Vuorinen & Snellman 1998

Sources of information - mechanisms

4. Water compositions – natural vs. simulant

- Effect of other cations?
- Effects of anions, esp. HCO_3 and sulphate?

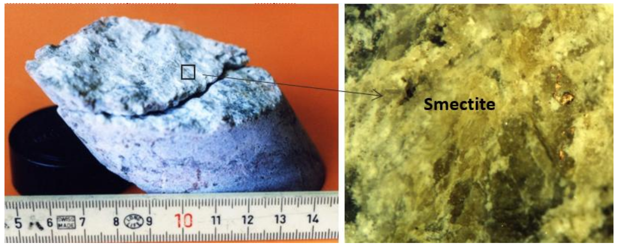
Parameter	Unit	RO (min)[1]	RO (max)[1]	KI (min)[1]	KI (max)[1]	Grimsel[2]	Allard-MO[3]	Allard-MR[3]
TDS	mg/L	61.7	189.9	133.2	240.2	83.0	~220	~220
pH	field	6.8	9.3	7.2	8.5	9.6	8.4	8.8
Eh	mV	-330.0	230	-350.0	400.0	-200.0		
O2	mg/L	0.0	1.1	0.0	0.4			
Na	mg/L	4.3	43.2	4.7	27.0	15.9	52.5	52.5
K	mg/L	0.7	3.0	0.2	2.4	0.2	3.9	3.9
Ca	mg/L	2.7	23.0	11.2	33.0	5.2	10.2	5.1
Mg	mg/L	0.1	5.3	0.9	8.6	0.015	2.8	0.7
Fe(tot)	mg/L	0.0	3.0	0.0	1.4	0.0002		
Cl	mg/L	0.9	7.4	1.0	5.8	5.7	47.5	48.8
HCO3	mg/L	0.0	123.3	82.4	158.6	27.45	90.7	65.0
SO4	mg/L	1.0	6.5	0.1	3.5	5.9	9.6	9.6
SiO2	mg/L					15.0	2.9	1.7
Sr	mg/L					0.18		
Mn	mg/L					0.0003		
F	mg/L					7.2		

1) McEwen & Äikäs 2004
2) as given in Hellä et al. 2014
3) Vuorinen & Snellman 1998

Sources of information - mechanisms

5. Fracture smectites

- Why do we find smectites in dilute conditions?
- Natural smectites could at least tell about:
  - How old thay are? (in situ?)
  - How do they occur? Differences depending on parageneses, smectite+kaolinite, smectite + calcite etc.
  - Are they all exchanged/originally Ca-form?
    - Samples from open and closed fractures
  - Isotopic signatures of groundwater-rock interaction?

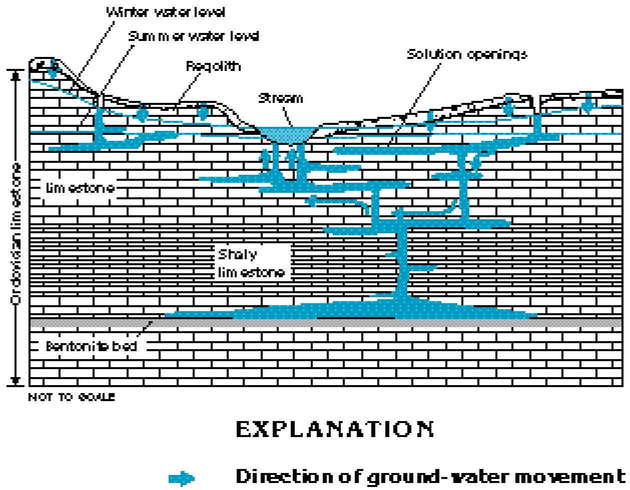


Sources of information - mechanisms

6. Bentonites

- Bentonite deposits located adjacent to water-conducting sedimentary rocks (limestone, sandstone etc.) could provide an answer to the question:
    - what changes are seen in bentonite when fresh water flows next to it?
        - Cation exchange reactions in bentonite deposits
        - Rate of exchange (when local hydrogeological history is known)
        - Do bentonites intrude in the adjacent sediments/fractures in any circumstances?

An example how bentonites function in limestone aquifers:



Modified from Zurawski, Ann, 1978, Summary appraisals of the Nation's ground-water resources—Tennessee region: U.S. Geological Survey Professional Paper 813–L, 35 p.

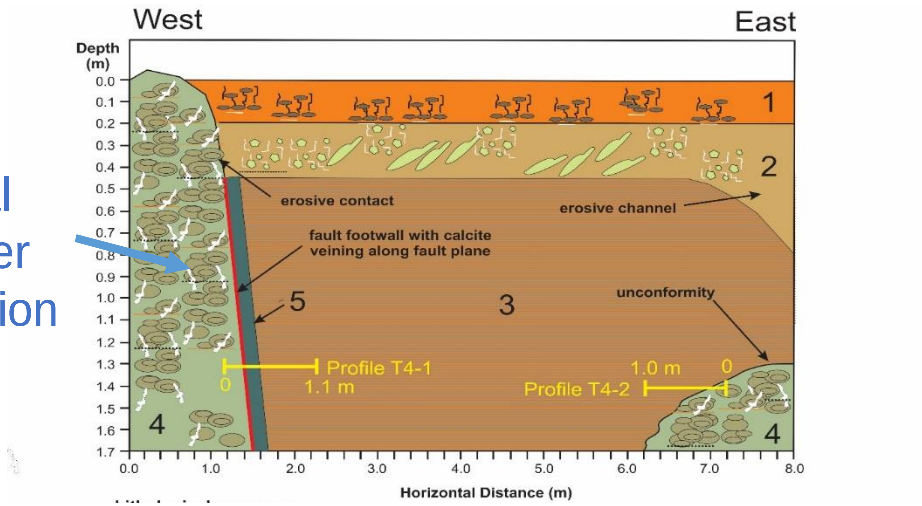
Figure 97. The limestone and dolomite aquifers contain small quantities of insoluble material and, therefore, produce only a thin layer of residuum when weathered. Recharge water percolates through the thin layer of surface material, called regolith, and subsequent-ly moves through vertical frac-tures and horizontal bedding planes in the rocks. The slightly acidic water dissolves some of the limestone and dolomite as it moves to streams and other areas of discharge, such as springs and wells. The vertical movement of the recharge water and, therefore, the depth of de-velopment of solution openings, are restricted by zones of low permeability.

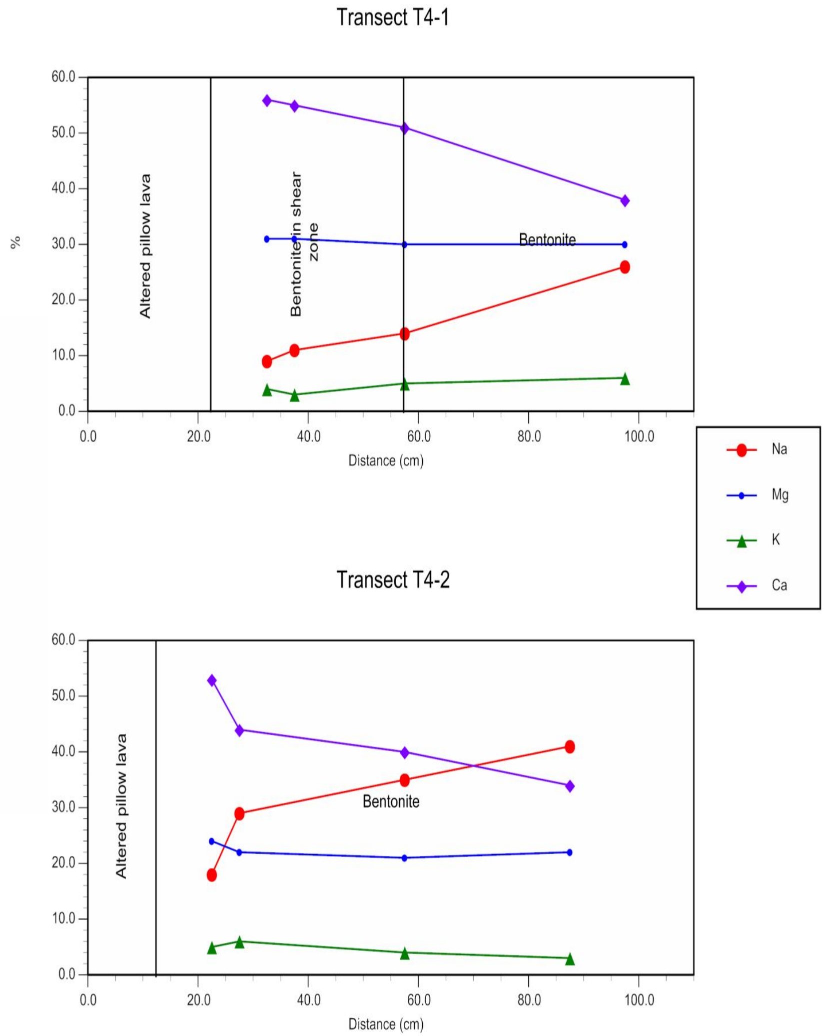
Sources of information - mechanisms

6. Bentonites

An example of cation exchange at a bentonite pillow lava contact surface:

Local aquifer formation





- chlorine concentration 2.4mM and the total charge equivalent of main cations is about 7mM

POSIVA 2014, WR 2014-02

Conclusions

- A more holistic approach is needed to perform a reliable assessment of the bentonite stability in repository conditions.
- The mismatch between laboratory experiments and observations in nature is due to a lack of understanding on the overall parameters and processes affecting the erodability of smectite and how these interact with each other.

Main implications:

1. The information in the already existing scientific literature should be considered more thoroughly
2. The experimental set ups to study chemical erosion should cover also more complex groundwater compositions (accounting for more complex anion/cation compositions) and smectite/bentonite compositions (including presence of various types of accessory minerals)
3. The scaling effects of the process should be better understood when moving from laboratory scale to in-situ conditions. The lack of data at larger scale from underground research laboratories is an obvious challenge.
4. Natural montmorillonites should be further studied to understand their mode of occurrence as stable phases in repository-relevant environments.

Components for holistic analysis – what to do next:

From system understanding to PA

Holistic system understanding

Conceptual model(s) for erosion and other relevant processes

Modelling – less conservative assumptions

Performance assessment

Acknowledgements:

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

IRREVERSIBILITY OF BENTONITE COLLOID AGGREGATION UNDER DIFFERENT ENVIRONMENTS

Natalia Mayordomo, Ursula Alonso and Tiziana Missana

Motivation

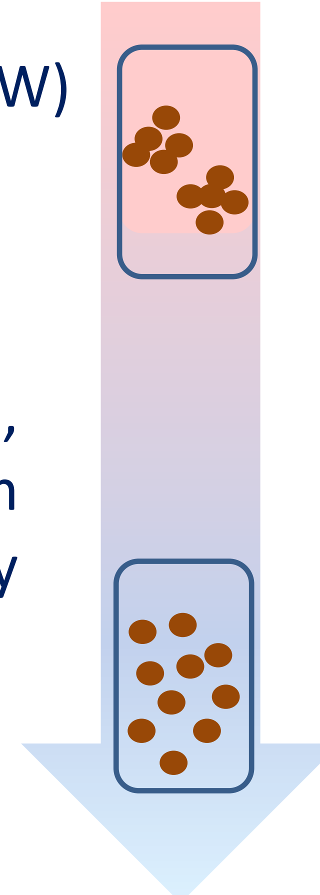
Bentonite colloid STABILITY is a necessary condition for bentonite erodibility and for colloid mobility.

- Stability studies analyse whether colloids aggregate as function of several chemical and physical parameters:

  **pH, ionic strength, temperature and presence of multivalent ions, or organic ligands, have been widely analysed.*

Motivation

- Repository scenarios with high saline groundwater (GW) expect negligible colloid concentration.



- In the time frame of repositories, GW conditions may evolve.

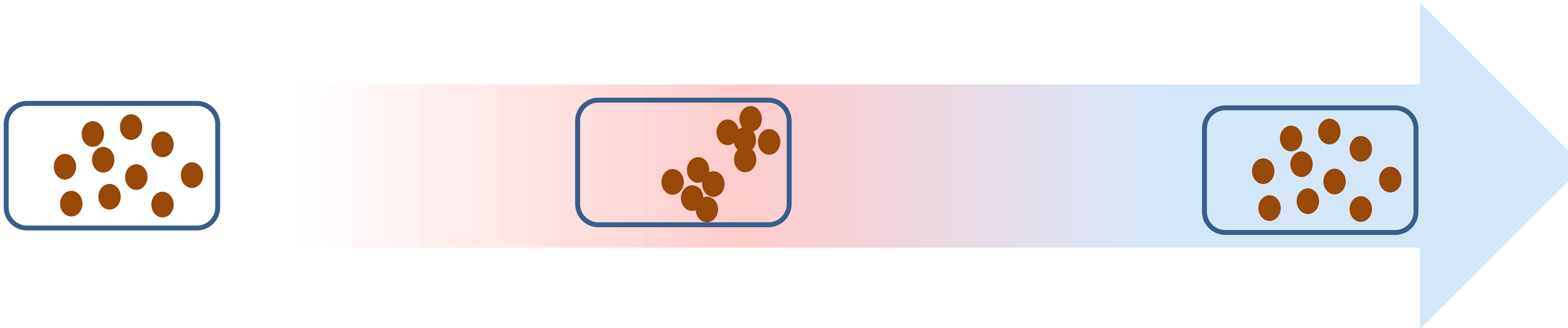
Recharge water (i.e. rivers, lakes, rain or water from melting ice sheet) may **reduce groundwater salinity.**

- Disaggregation processes have been scarcely investigated.

Bentonite colloid DISAGGREGATION?

Aim

To study the (ir)reversibility of clay colloid aggregation



STABLE BC | **AGGREGATION** | **DISAGGREGATION**

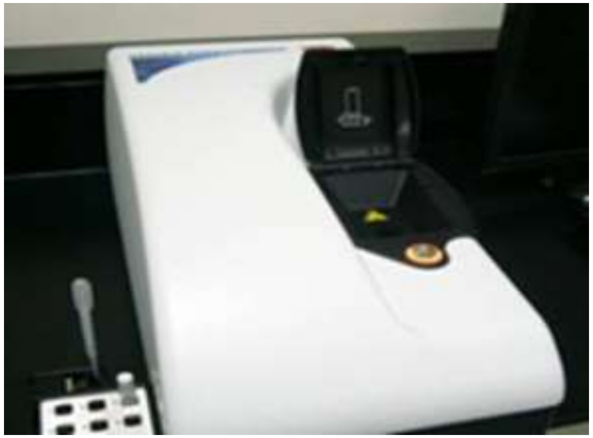
Ionic strength increase / decrease

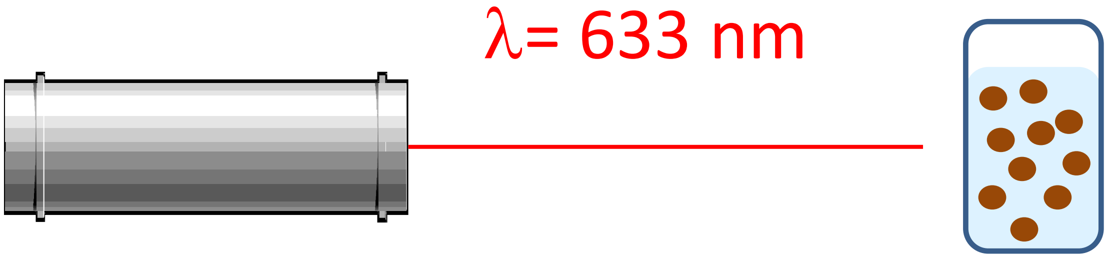
Different methods & experimental times

Summary of experiments

	Experiment	Output	Method
(I)	Aggregation kinetics (Na, Ca)	Diameter evolution (60 min)	TR-PCS
	Ionic strength (I) increase	***Attachment coefficients*	
(II)	Progressive disaggregation	Diameter progressive decrease	PCS
	I decrease- Dialysis	Diameter evolution (60 days)	
(III)	Disaggregation kinetics	Diameter evolution (60 min)	TR-PCS
	I decrease- dilution	***Detachment coefficients*	
		Size distribution - *stable fraction*	SPC
(IV)	<u>Aggregation history</u> ($NaClO_4$, Na-Ca, $CaCl_2$)	Diameter increase	PCS
	Disaggregation in different GW	Diameter decrease	

Photon Correlation Spectrometry (PCS) technique





- Time dependent fluctuations of scattering light intensity

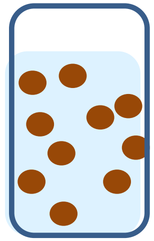
- Time-resolved dynamic light experiments:
- Kinetics of colloid (dis)aggregation (1 hour)

Average hydrodynamic diameter
Evolution

(I) Aggregation experiments: Experimental

INITIAL –Bentonite Colloids

- **Na-FEBEX** bentonite colloids.
- $NaClO_4$ 0.5 mM.

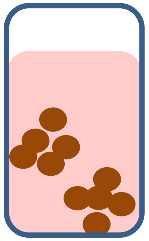


pH 6.5 ± 0.5.

Average diameter (PCS): 300 nm

Stable - REFERENCE

AGGREGATION

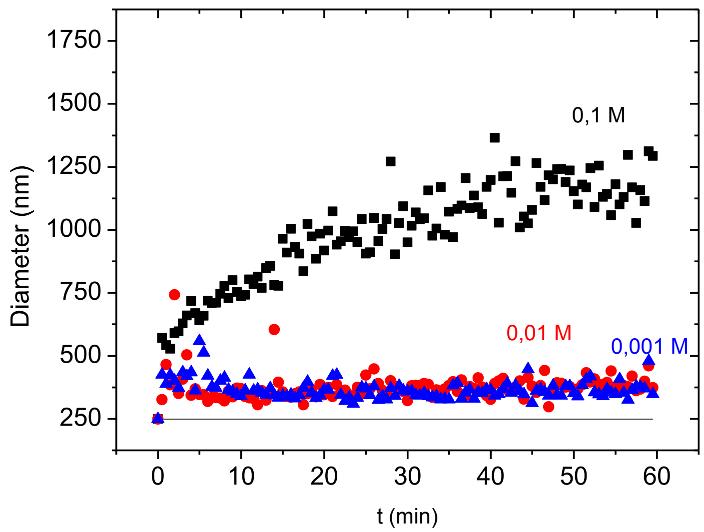


- Induced by ionic strength increase:
- Different electrolytes

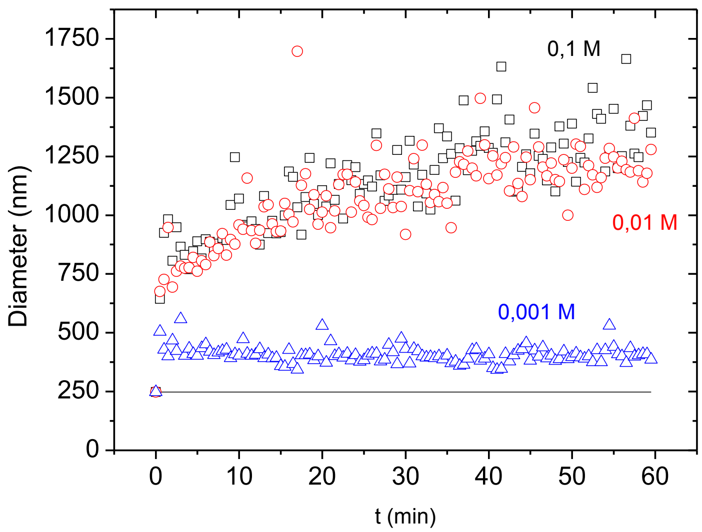
$NaClO_4$ **Na - Ca mixed** **$CaCl_2$**

(I) Aggregation experiments: Results

$NaClO_4$



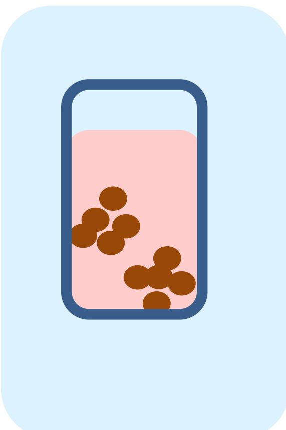
Na - Ca mixed



- ✓ Increasing ionic strength, bentonite colloid aggregation is fast.
- ✓ Bivalent ions favour aggregation (lower CCC), as Schulze-Hardly rule predicts.

(II) Disaggregation experiments: Dialysis

Aggregation in 0.1 M $NaClO_4$



(A) Progressive ionic strength decrease (no dilution)

--$1 \cdot 10^{-2}$ M
--$1 \cdot 10^{-3}$ M
--$5 \cdot 10^{-4}$ M

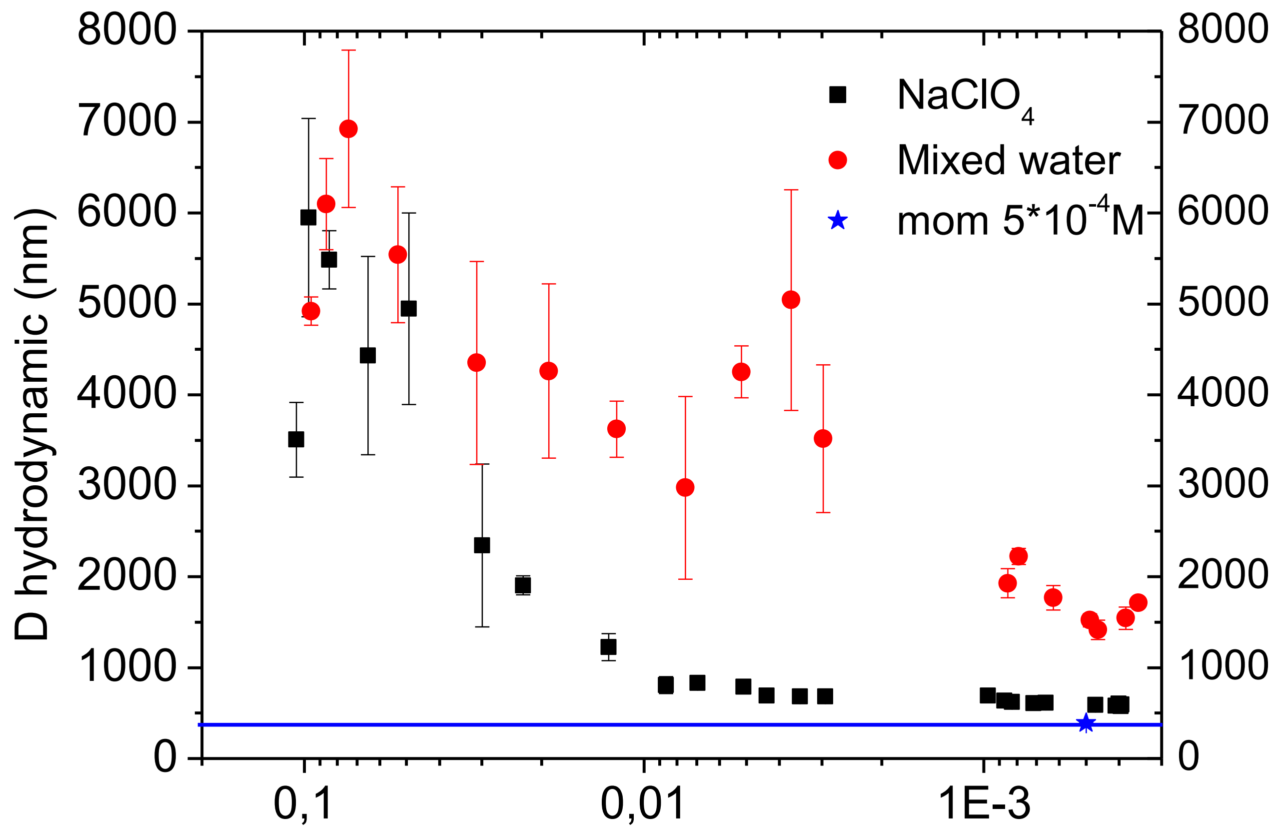
$CaCl_2$

Na - Ca mixed electrolyte

$NaClO_4$

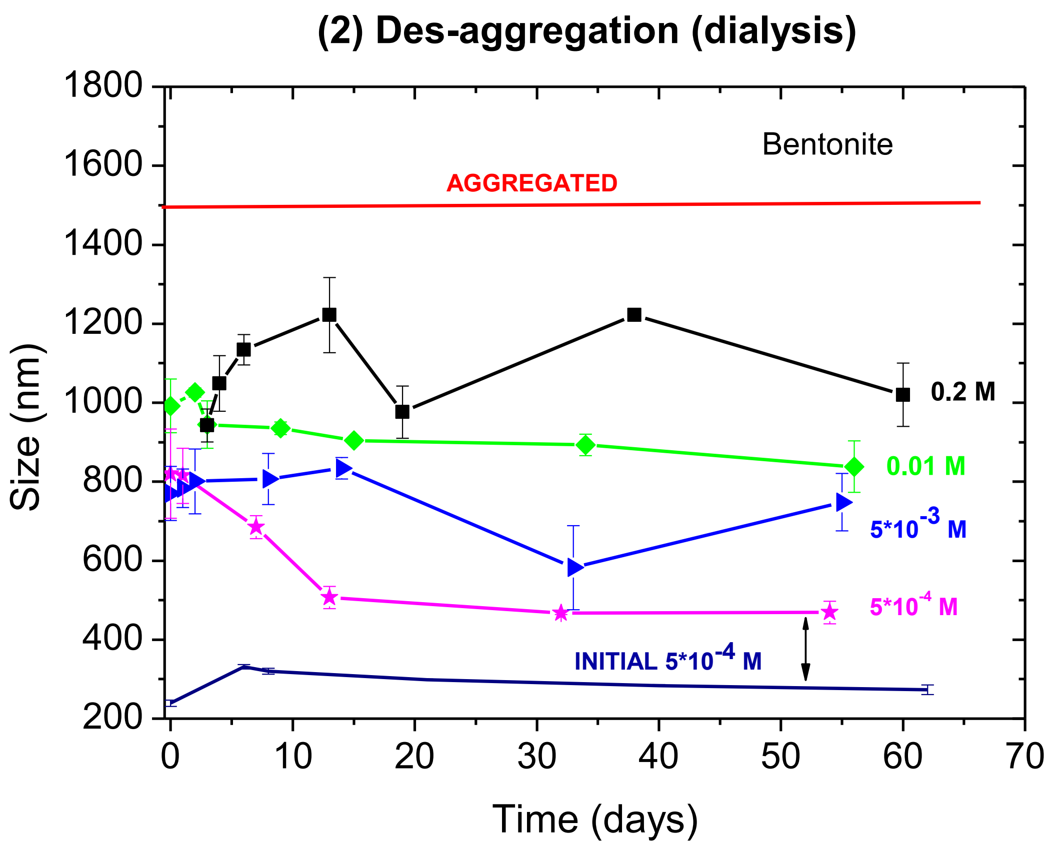
(B) Temporal evolution (60 days)

(II) Disaggregation experiments: Dialysis



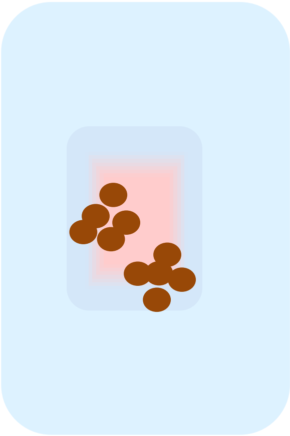
- ✓ By decreasing ionic strength bentonite particles are disaggregated, but not completely.
- ✓ Disaggregation is less effective in presence of Ca.

(II) Disaggregation experiments: Temporal evolution



- ✓ Average particle diameter in disaggregated decreases at lower ionic strength .
- ✓ Initial stable size (300 nm) is not recovered.

(III) Disaggregation kinetics by dilution



Aggregation 0.1 M 500 ppm

IONIC STRENGHT DECREASE + DILUTION
in the same electrolyte

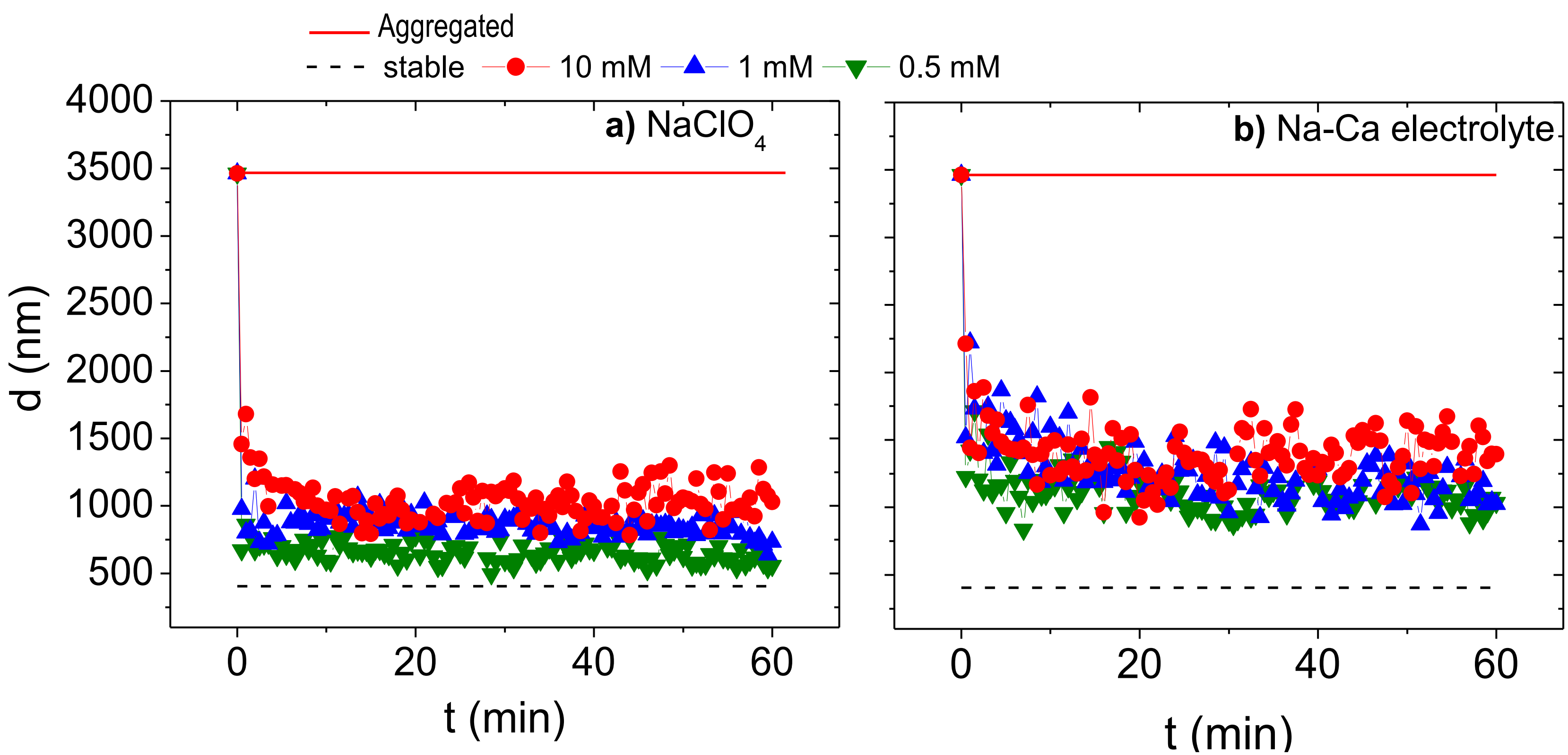
--$1\cdot10^{-2}$ M; --$1\cdot10^{-3}$ M; --$5\cdot10^{-4}$ M

CaCl2

Na - Ca mixed

$NaClO_4$

(III) Disaggregation kinetics by dilution



- ✓ By decreasing ionic strength, bentonite colloid disaggregation is promoted, more efficiently in absence of Ca.
- ✓ <u>Initial size (300 nm) is not recovered.</u>

(III) Fast disaggregation experiments by dilution

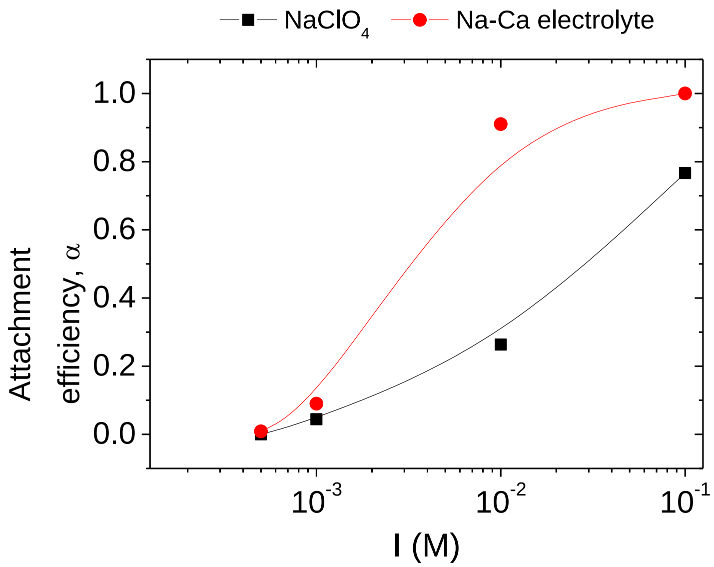
Attachment

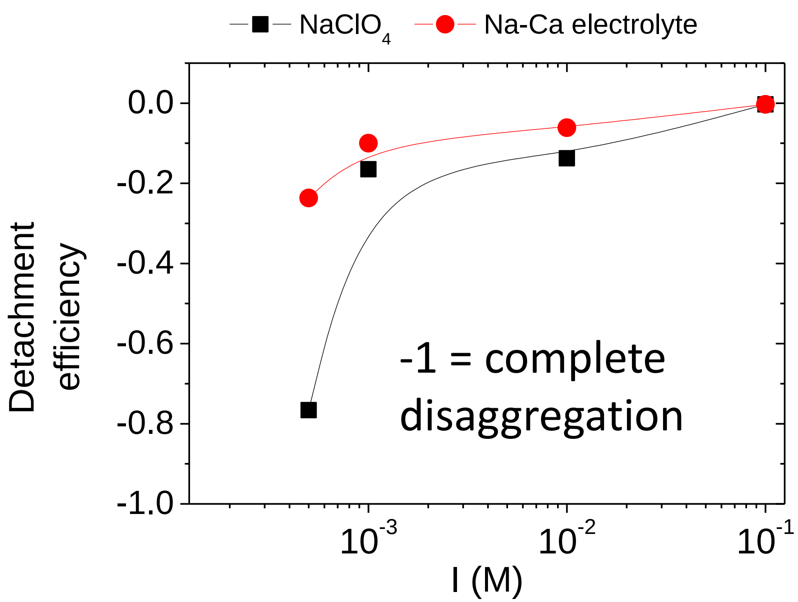
$$\alpha = \frac{1}{W} = \frac{\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}}{\left(\frac{\delta d_h}{\delta t}\right)_{fast}}$$

0 = stable
1 = fast regime
DL suppressed

Detachment

$$Det. = -\frac{\left(\frac{\delta d_h}{\delta t}\right)_{t\to 0}}{\left(\frac{\delta d_h}{\delta t}\right)_{fast}}$$





✓ Hysteresis, different kinetics: Irreversible process

(III) Fast disaggregation experiments by dilution: SPC

Single Particle Counter (SPC)

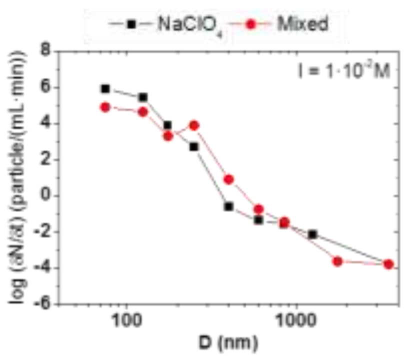
- Particle population within different size channels.

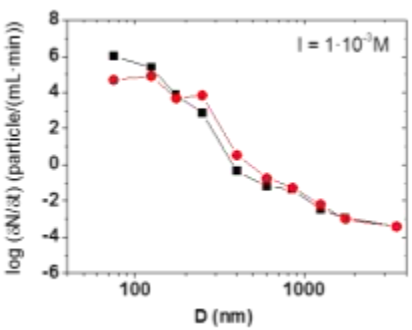
- Particle concentration normalized to size interval.

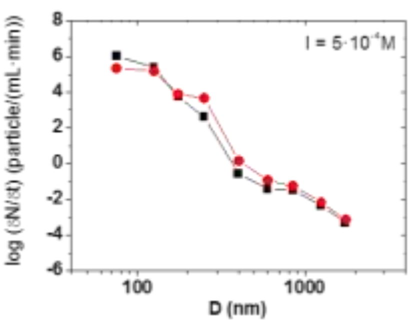
$$\frac{\delta N}{\delta d} = \frac{[particle\ concentration]}{(d_{upper} - d_{lower})_{channel\ i}}$$

- Disaggregated samples where not shaken to determine the size distribution of -only- **stable fraction of colloids.**

(III) Fast disaggregation experiments by dilution: SPC







- NaClO4: >99% BC in channels (50-150) nm
- Na-Ca: >99% BC in channels (50-300) nm

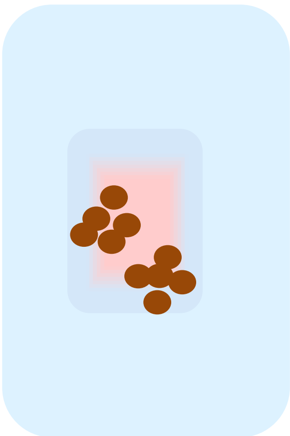
Particle % corresponding to each size channel

Channel (nm)	*Cl $1\cdot10^{-2}$M*	*Cl $1\cdot10^{-3}$M*	*Cl $5\cdot10^{-4}$M*	*M $1\cdot10^{-2}$M*	*M $1\cdot10^{-3}$M*	*M $5\cdot10^{-4}$M*
50-100	76.27	79.96	80.82	56.03	33.65	56.08
100-150	22.97	19.35	18.65	31.69	53.79	39.54
150-200	0.67	0.58	0.46	1.41	3.29	2.01
200-300	0.09	0.11	0.07	10.85	9.27	2.37
300-500	9.00 E-05	1.30 E-04	8.00 E-04	0.024	0.0098	0.0015
500-700	1.52 E-05	2.00 E-05	1.16E-05	5.03 E-04	4.90 E-04	1.19 E-04
700-1000	1.50 E-05	2.01 E-05	1.58E-05	1.47 E-04	2.19 E-04	8.47 E-05
1000-1500	6.61 E-06	2.48 E-06	3.36 E-06	0.00 E+00	4.12 E-05	1.73 E-05
1500-2000	0.00 E+00	9.06 E-07	3.73 E-07	1.73 E-06	6.60 E-06	1.79 E-06
2000-5000	8.82 E-07	1.76 E-06	0.00 E+00	6.92 E-06	1.48 E-05	0.00 E+00

Ratio of concentration	
$NaClO_4$ $1\cdot10^{-2}$M	0.82
$NaClO_4$ $1\cdot10^{-3}$M	0.95
$NaClO_4$ $5\cdot10^{-4}$M	0.97
Na-Ca water $1\cdot10^{-2}$M	0.10
Na-Ca water $1\cdot10^{-3}$M	0.11
Na-Ca water $5\cdot10^{-4}$M	0.30

✓ Concentration of stable BC in disaggregated samples is lower than in the initial suspension.

(IV) Aggregation history



Aggregation 0.1 M 500 ppm

$CaCl_2$ **Na - Ca mixed** **$NaClO_4$**

--$1\cdot10^{-2}$ M; --$1\cdot10^{-3}$ M; --$5\cdot10^{-4}$ M

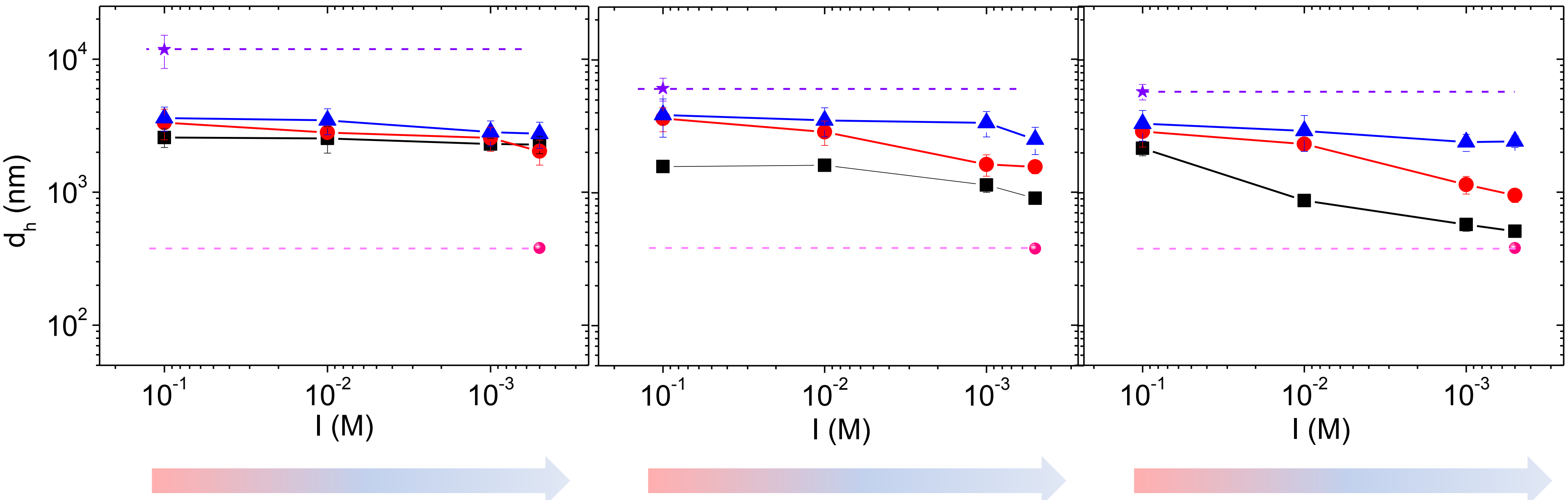
$CaCl_2$ **Na - Ca mixed** **$NaClO_4$**

Hydrodynamic diameter evolution

- Photon Correlation Spectrometry (PCS) measurements

(IV) Aggregation history

Aggregated in $CaCl_2$ | **Aggregated in Na - Ca** | **Aggregated in Na**



- ▲ Disaggregation in Ca^{2+}
- ● Disaggregation in Na^{+}-Ca^{2+}
- ■ Disaggregation in Na^{+}

✓ Particles aggregated in Ca waters are less effectively disaggregated.

Conclusions

- **Disaggregation of FEBEX bentonite colloids promoted by dilution to lower ionic strength was studied.**
- **Disaggregation was initially fast but, complete disaggregated state was not achieved, even at low ionic strength and in absence of divalent cations.**
- **In presence of Ca, the stable fraction of disaggregated colloids was low compared to the primary sample (< 10 %).**
- **The history of aggregation plays a role on further disaggregation.**
- **Overall results showed that the aggregation is not completely reversible, but disaggregation at longer times is not discarded.**

N. Mayordomo, C. Degueldre, U. Alonso, T. Missana. ***Size distribution of FEBEX bentonite colloids upon fast disaggregation in low ionic strength water (Clay Minerals, In press).***

Acknowledgments

Thank you for your attention!

- This work was supported by the EU FP7/2007-2011 program, under the EC-BELBAR project (Nº 295487).
- PSI & Prof. Claude Degueldre
- N. Mayordomo acknowledges the FPI BES-2012-056603 grant from MINECO (Spain).

INFLUENCE OF TEMERATURE ON SMECTITE CLAY GELS

Emelie Ekvy Hansen

Magnus Hedström

Clay Technology AB

Clay Colloids in Aqueous Systems, Berlin 3-4 Feb. 2016

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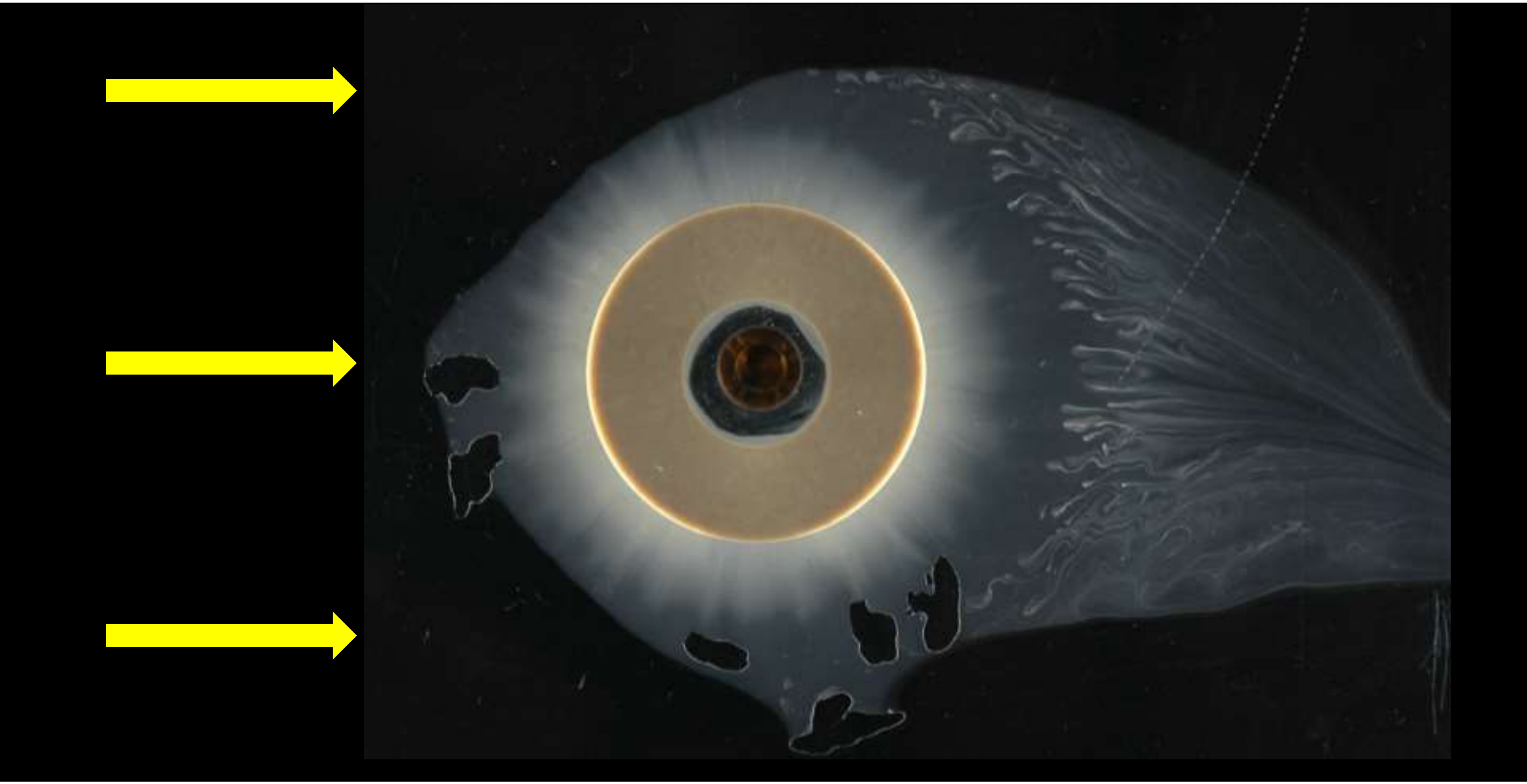
Erosion at low salinity



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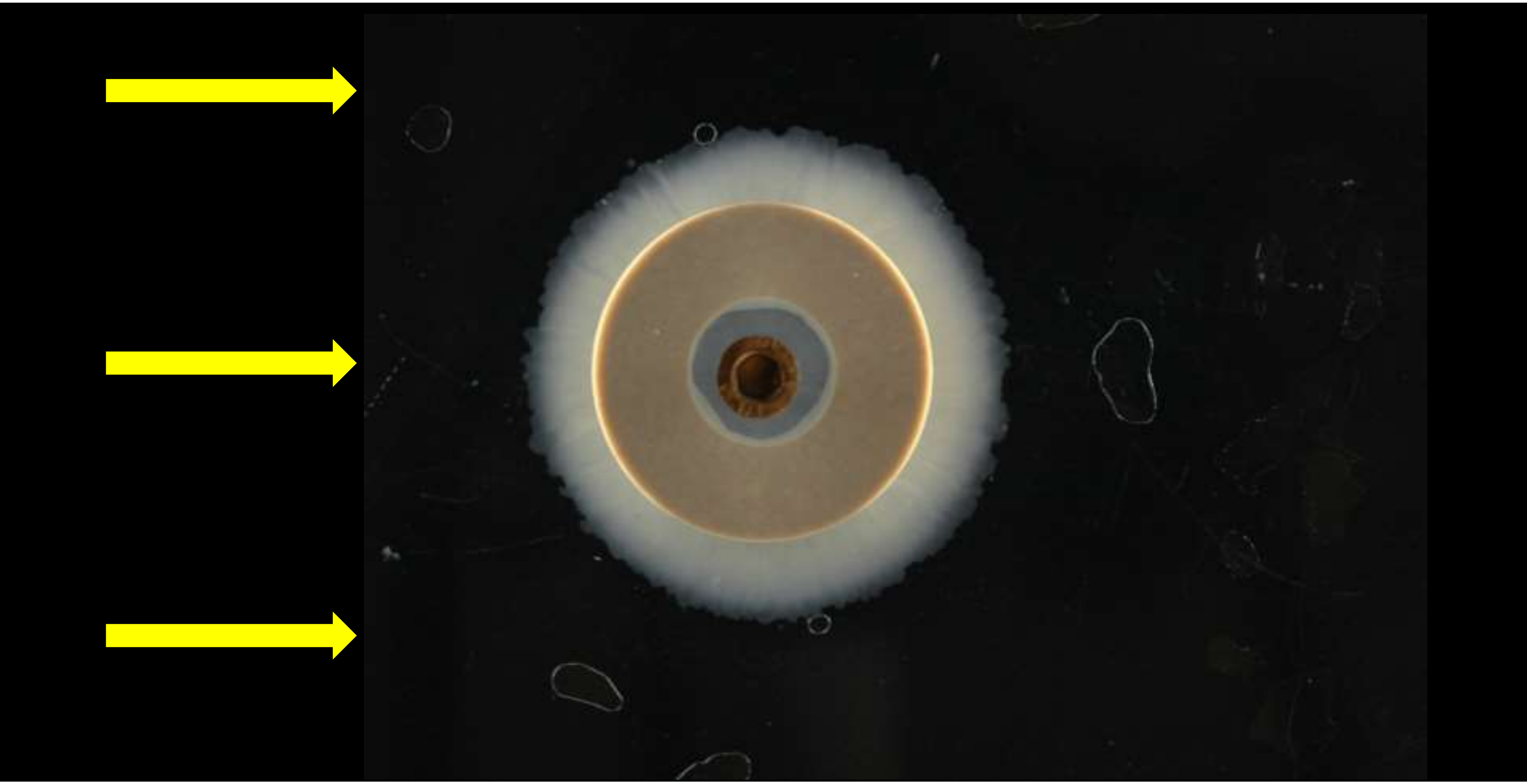
Formation of gel prevents erosion



Clay phases – from sol to gel

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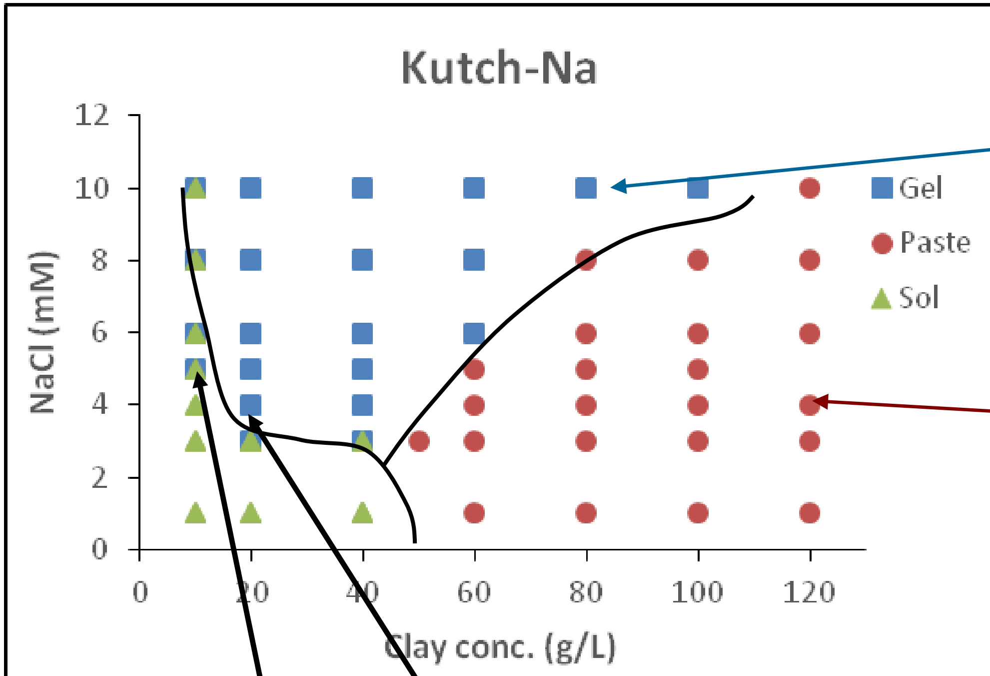
Phase diagram
ionic strength, clay concentration



Immediate gelation

What forces cause gelation?

Gel formed within 18 h

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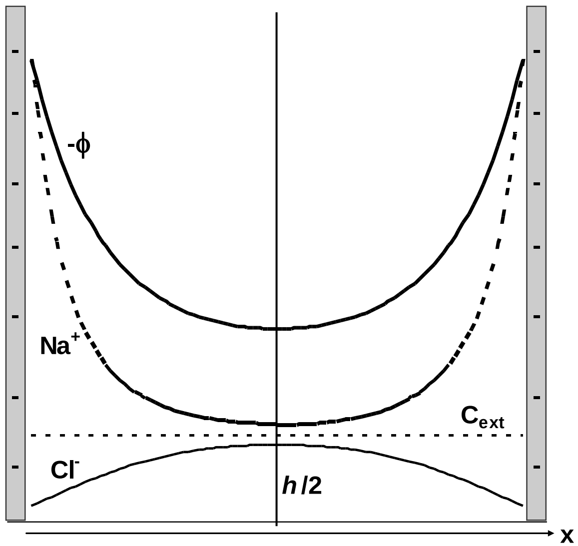
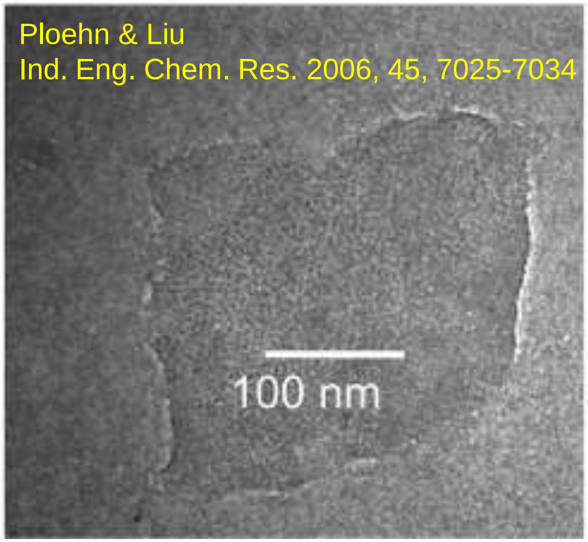
Colloid stability

- Conditions for sol to be stable
- Range of repulsion extend beyond distance where attraction is $\sim kT$ or less



DLVO theory
Parallel clay layers
Poisson-Boltzmann: osmotic repulsion
van der Waals attraction: Hamaker

van der Waals ~kT



$$\frac{F_{\mathrm{vdW}}}{\mathrm{area}} = -\frac{A_H}{6\pi}\left(\frac{1}{h^3} + \frac{1}{(h+2\delta)^3} - \frac{2}{(h+\delta)^3}\right)$$

$$\frac{U_{\mathrm{vdW}}}{\mathrm{area}} = -\frac{A_H}{12\pi}\left(\frac{1}{h^2} + \frac{1}{(h+2\delta)^2} - \frac{2}{(h+\delta)^2}\right)$$

$A_H = 5kT$ ~$2\cdot 10^{-20}$ J
area = 10^5 nm^2
δ =1 nm
h =16 nm → U_{vdW}=-1kT

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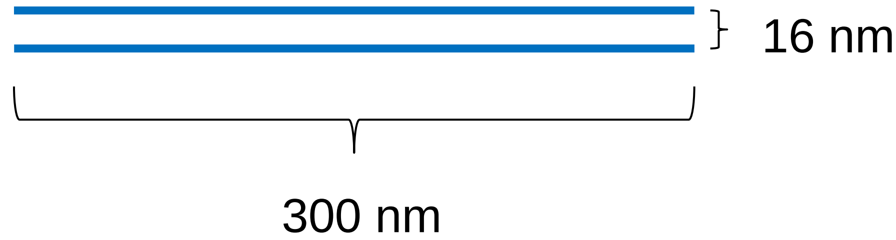
van der Waals ~kT

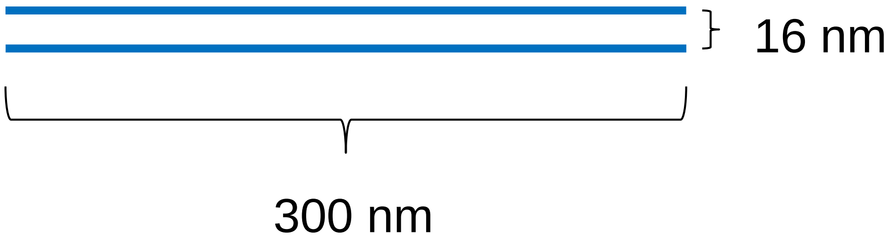
$A_H = 5kT$
area= 10^5 nm^2
h=16 nm → U_{vdW}=-1kT



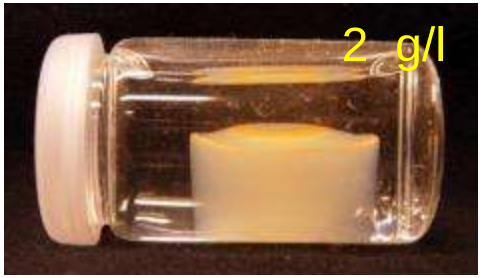
Volume fraction ϕ_c = 1/17
160 g clay/l

van der Waals insignificant for gelation

$A_H = 5kT$
area= 10^5 nm^2
h=16 nm $\rightarrow U_{\mathrm{vdW}}$=-1$kT$



Volume fraction $\phi_c = 1/17$
160 g clay/l



Conclusion: Gelation is not caused by van der Waals interaction

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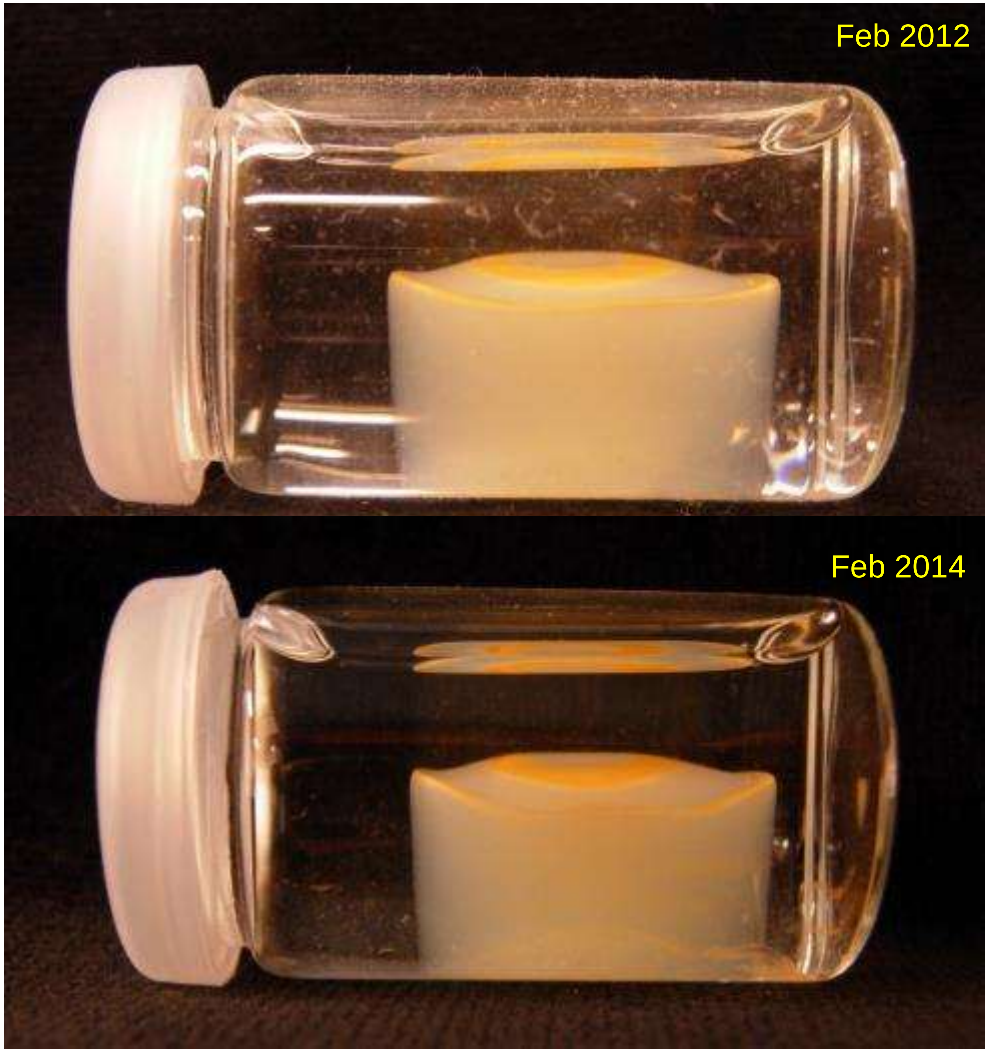
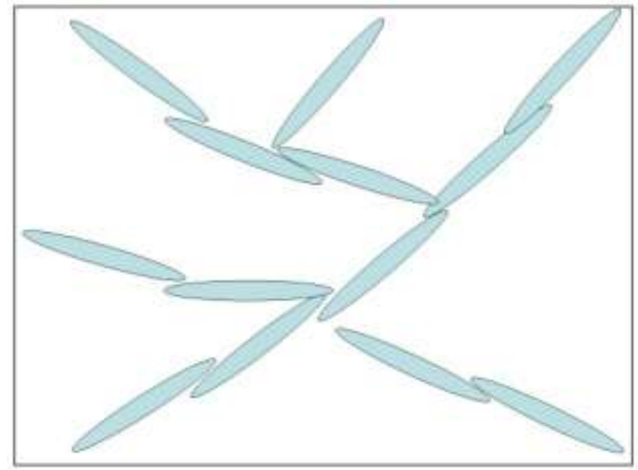
Structure of smectite gels



Proposal



~1400 nm of water between clay layers
Diameter of typical clay platelet 100-500 nm

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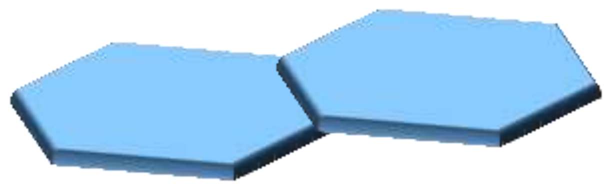
Hypothetical binding modes in gels

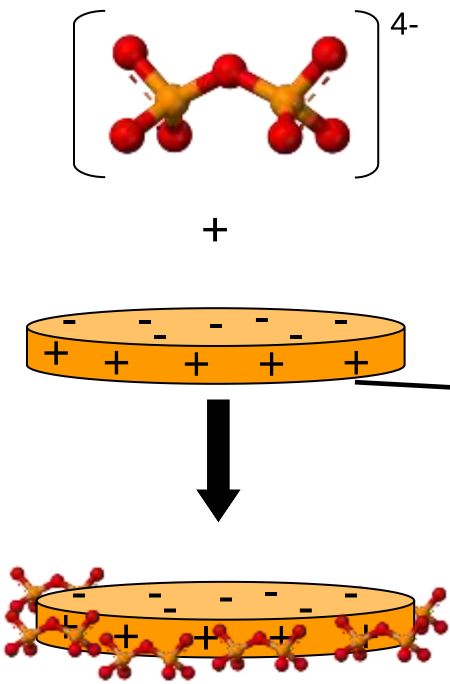
Face (-) – edge(+) attraction

T-shape

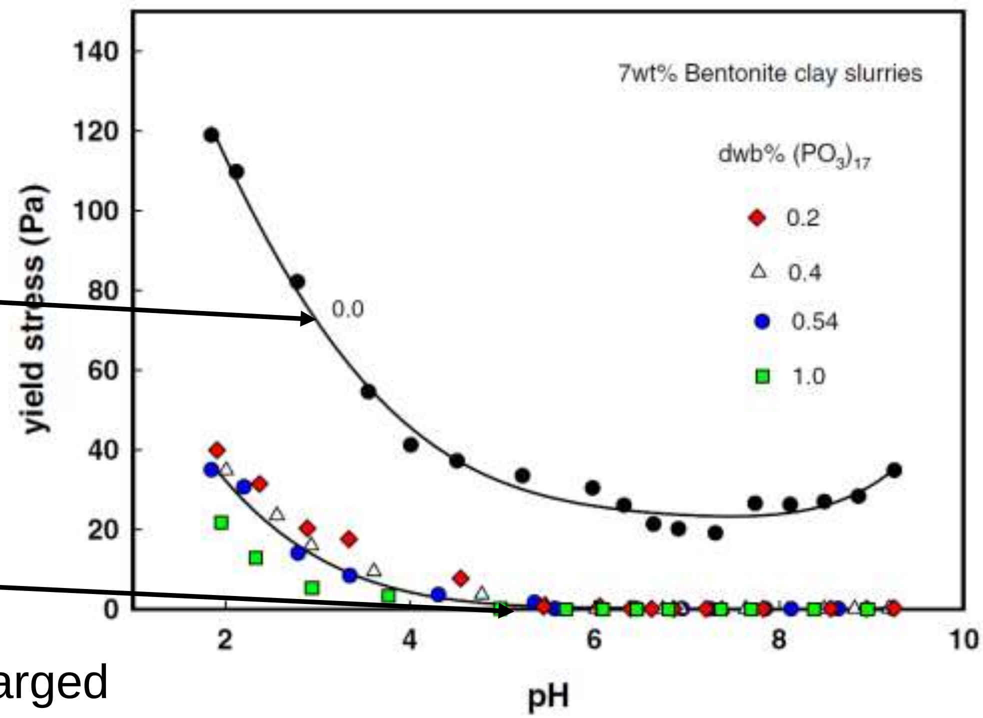
Overlapping coin



Edge(+) – face (-) interaction
Effect of polyphosphates



Yield stress in 7 wt% bentonite slurry



Both edge and face negatively charged
gel → sol

Goh., Leong ,Lehane *Rheol. Acta.* **50**, 29-38 (2011).

Indirect "proof" of positive edge charge

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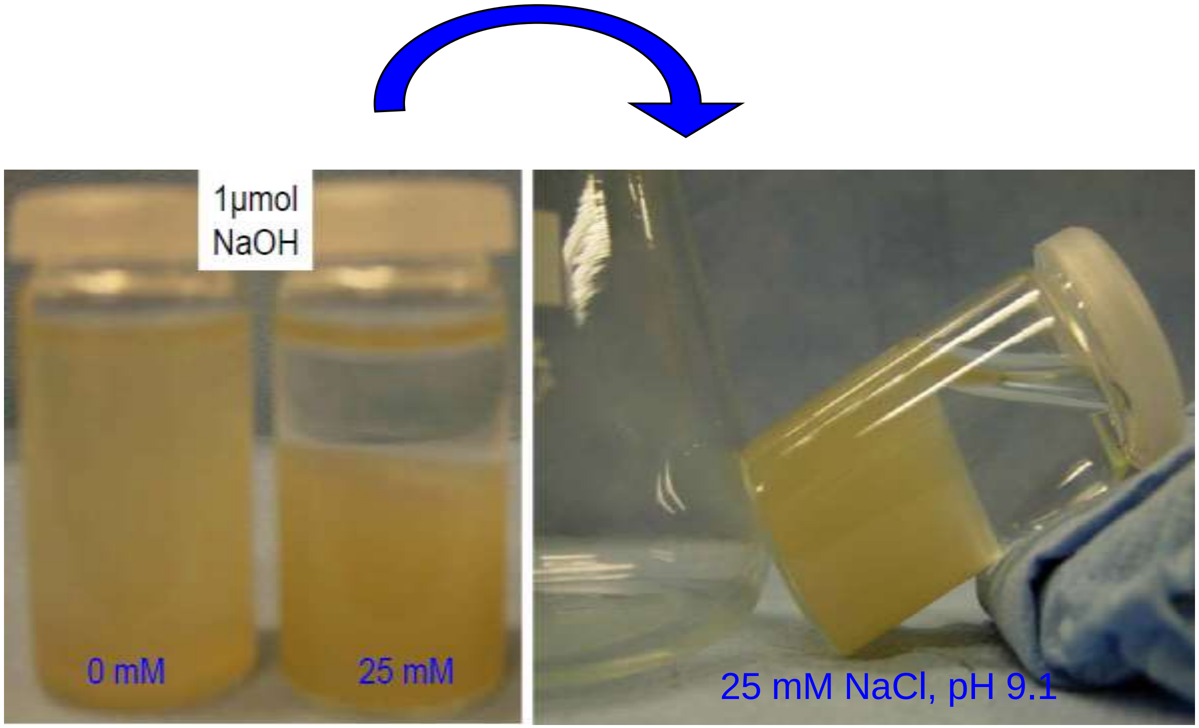
Ionic strength determines gel formation



Birgersson et al. SKB-TR 09-34 (2009).

The nature of the clay edge charge must still be positive at high pH

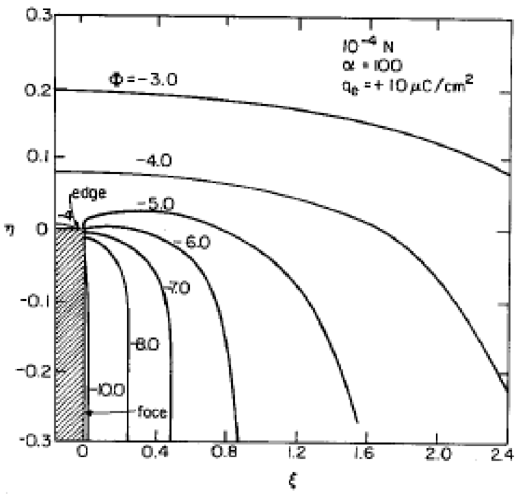
Edge(+) – face(-) attraction

- Is it possible to demonstrate this hypothesis without modify the clay i.e. without pyrophosphate?

- Is there a way to test the concept of spillover of negative potential from faces to edge-region?

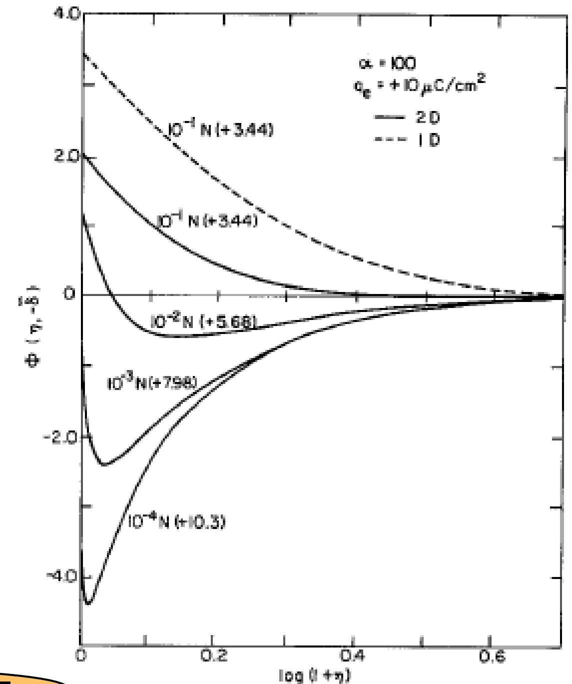
Spillover of diffuse double layers

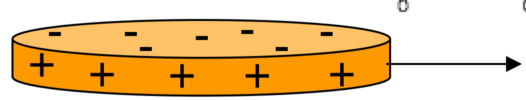
Equipotentials around a montmorillonite particle



The positive potential near the positive edge is hidden due to spillover of negative potential from the face

Electrostatic potential along the montmorillonite particle's midplane





Poisson-Bolzmann calculation by
Secor & Radke, *J. Colloid Interf. Sci.* **1985**, *103*, 237.

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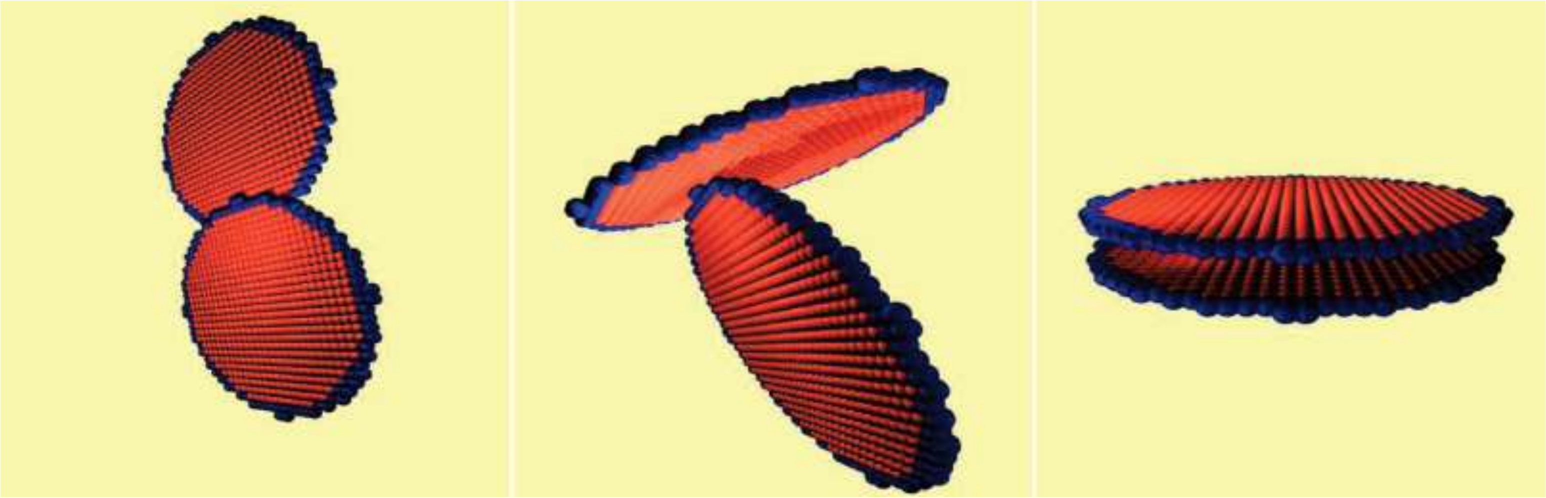
Monte Carlo: Screened Coulomb interactions + vdW

Laponite-like w.r.t. size and layer charge



Jönsson, Labbez, Cabane Langmuir 24, 11406 2008.

Above ~200 mM most electrostatic interactions are screened and van der Waals dominates

Effect of screening due to excess NaCl

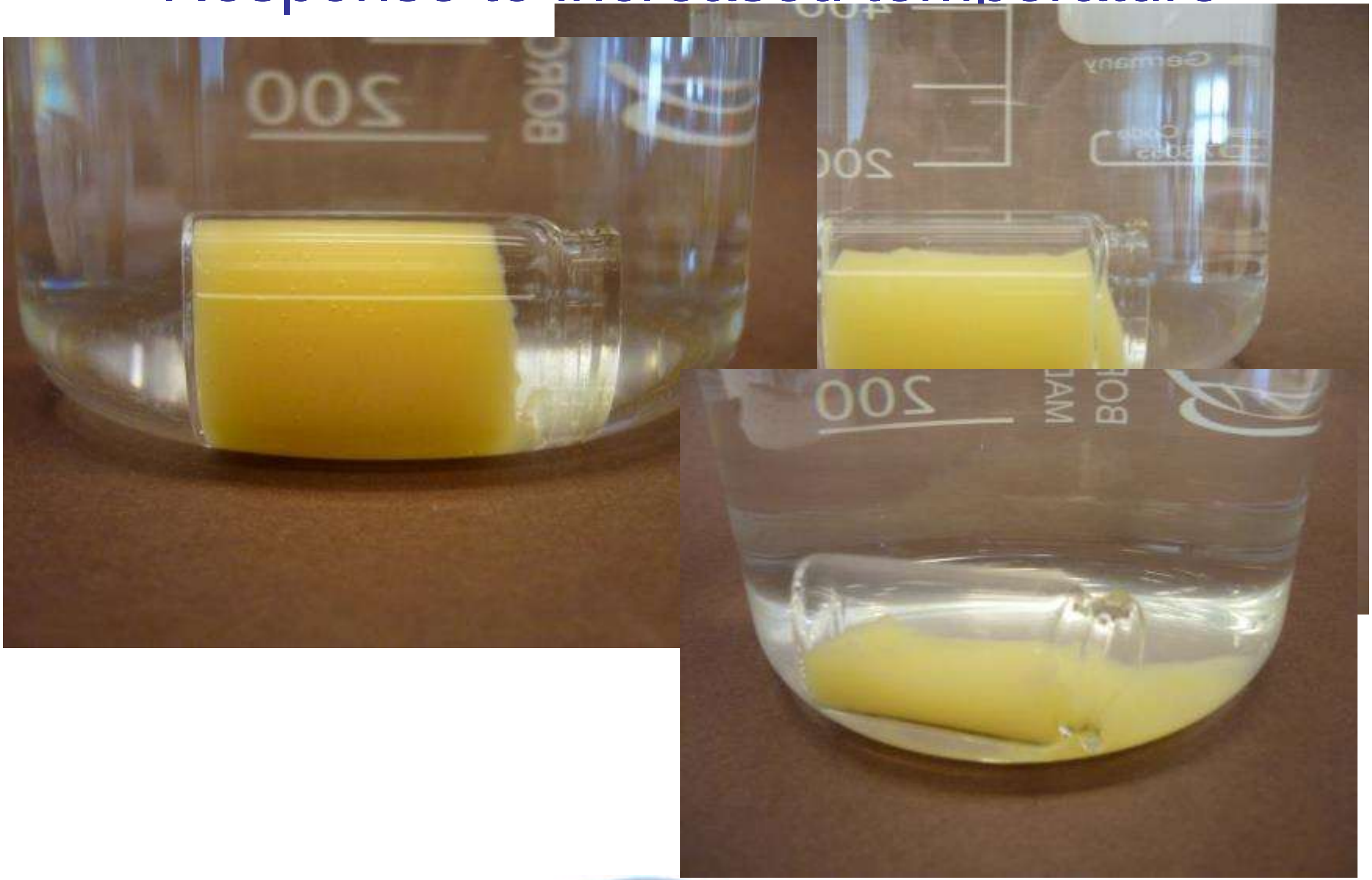
- Screening make the spillover smaller

- Screening applies both to positive and negative charge
  - Thus electrostatic attraction will also be weakened
  - Competition between spillover and weakened electrostatic attraction

- There might be a maximum strength of the gel at an intermediate NaCl conc.
  - at *sufficiently* high concentration van der Waals will be the important attraction

- Test this prediction/hypothesis by heating clay gels

Response to increased temperature



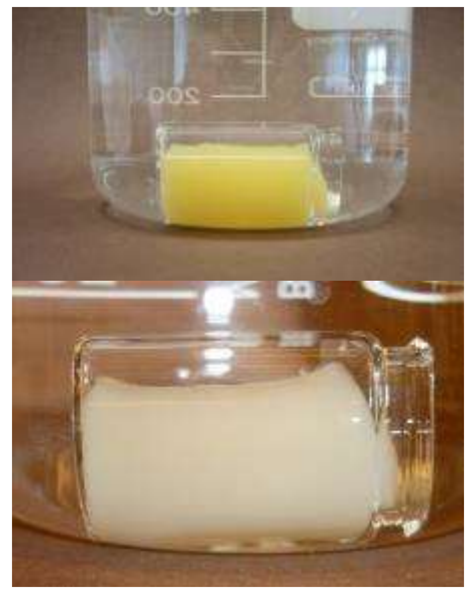
At the “transition” temperature

Melting

- Transfer from a gel to a liquid
- Loss of solid-like structure
- Exhibits a flow
- Return to gel on cooling

Deformation

- Retention of some solid-like structure
- Behaves partly as a liquid



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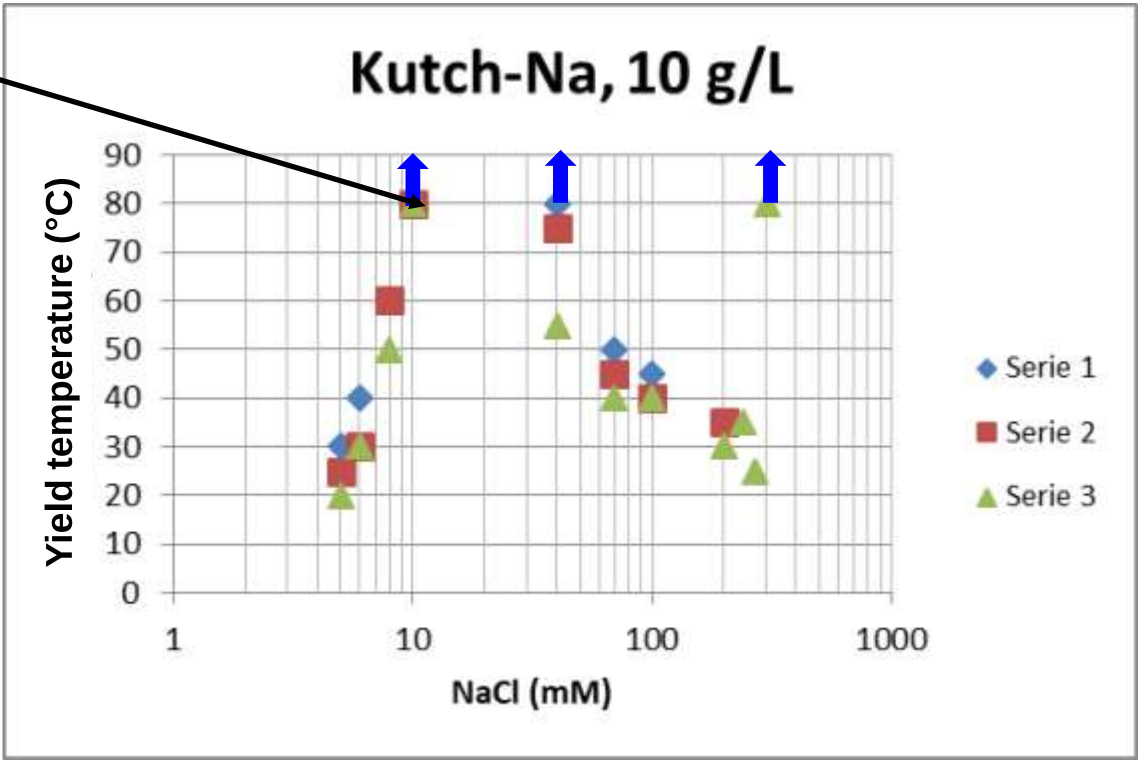
Yield temperatures of attractive gel
Ionic strength influence

First sign of deformation upon heating → transition temperature

Transition not observed



The ionic strength have a direct impact on the strength of the inter-particle bonds, in accordance with the spillover effect.

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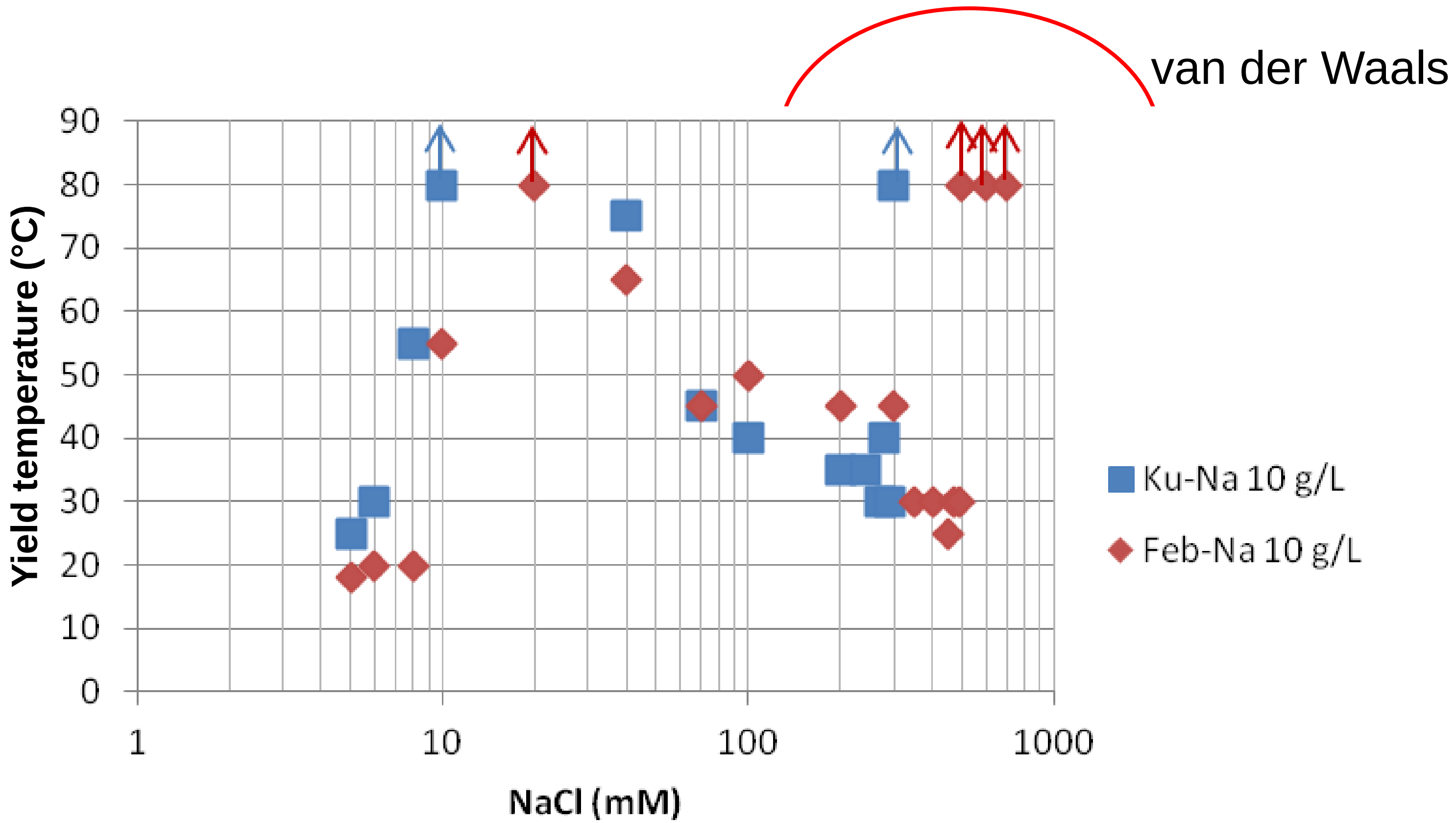
Ku-Na and FEBEX-Na



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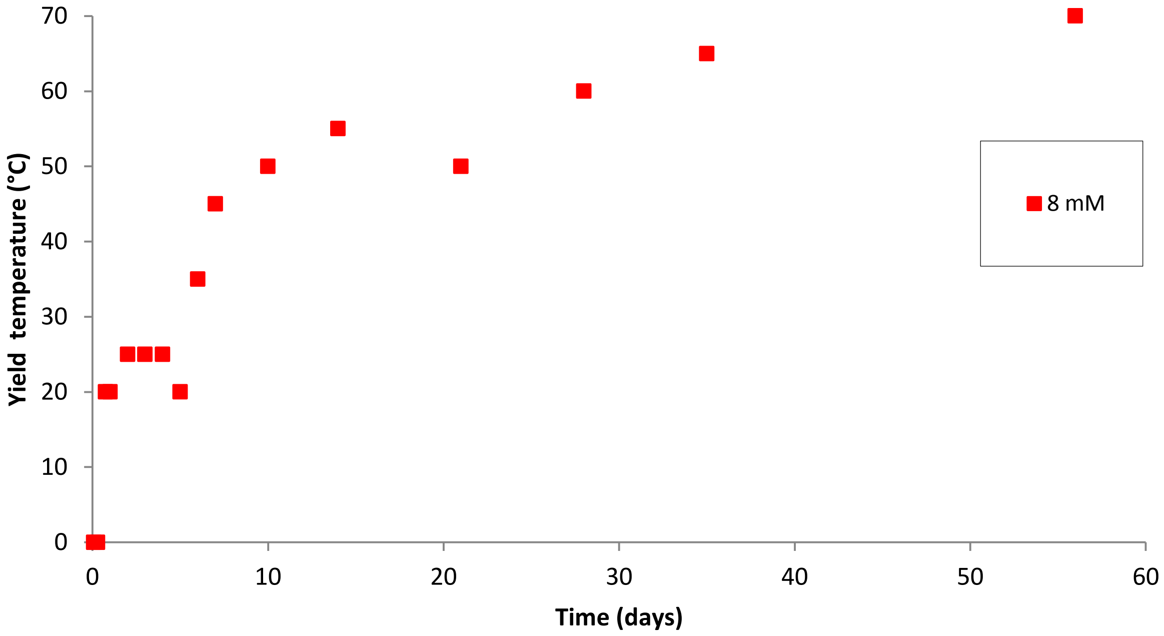
Effect of ageing

FEBEX-Na, 10g/l



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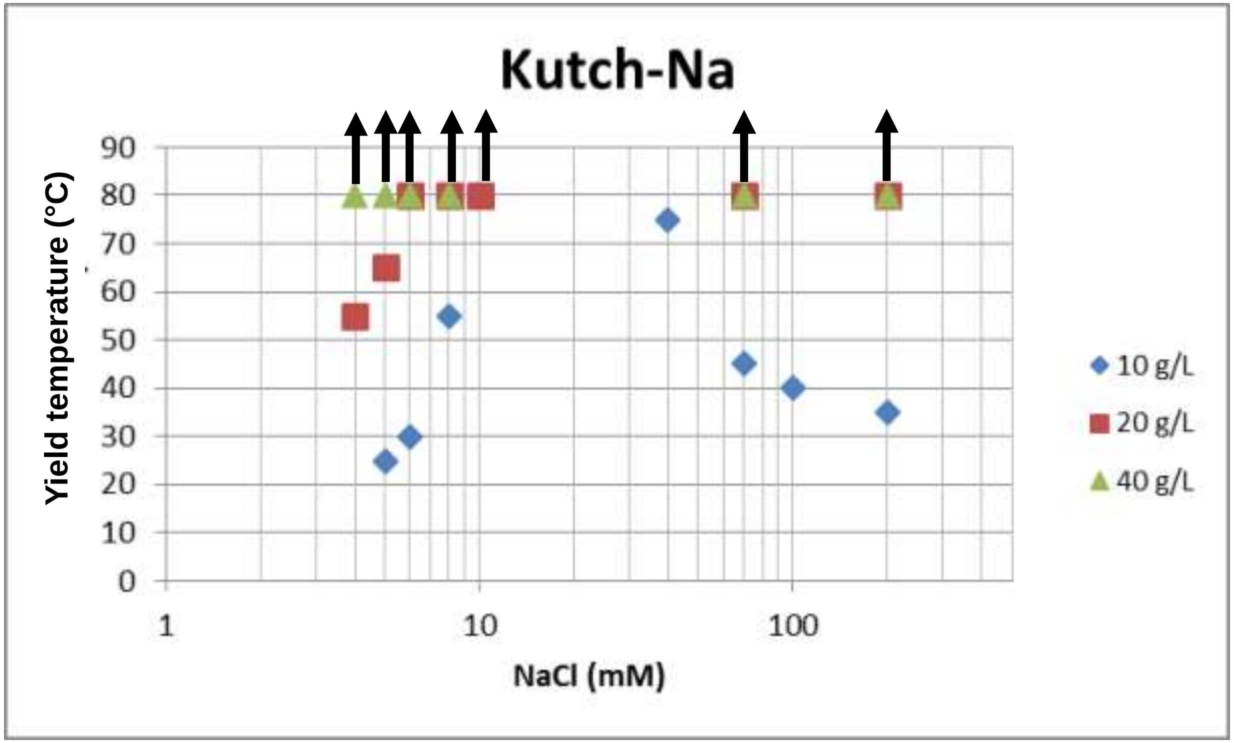
Influence of clay concentration



Higher clay concentration gives stronger structure
Gelatine gels show similar behaviour Eldridge & Ferry (1954)
Typical for **percolation gels**

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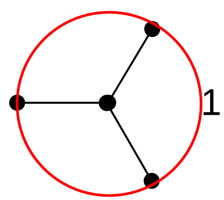
Bond percolation: Bethe lattice

Each “particle” can connect to z other particles, probability g. In this case z=3. Number of particles in generation n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

Bethe lattice 1st generation



Each “particle” can connect to z other particles, probability g.
In this case z=3.
Number of particles in generation n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$N_1 = 3$$

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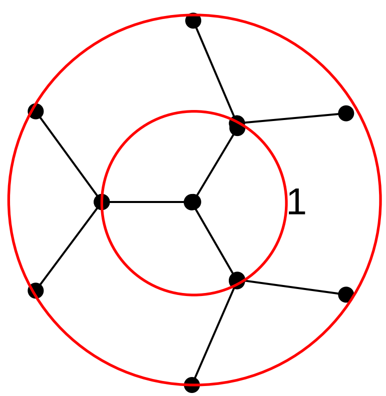
Bethe lattice 2nd generation

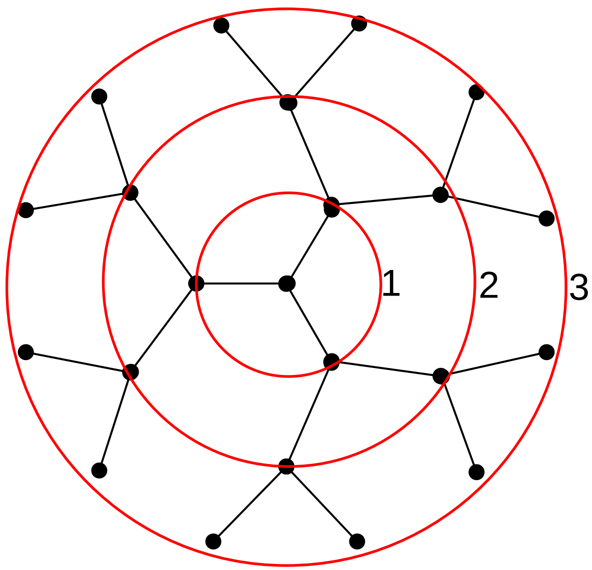


Each "particle" can connect to
z other particles, probability g.
In this case z=3.
Number of particles in generation
n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$N_2 = 6$$

Bethe lattice 3rd generation



Each "particle" can connect to z other particles, probability g.
In this case z=3.
Number of particles in generation n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$N_3 = 12$$

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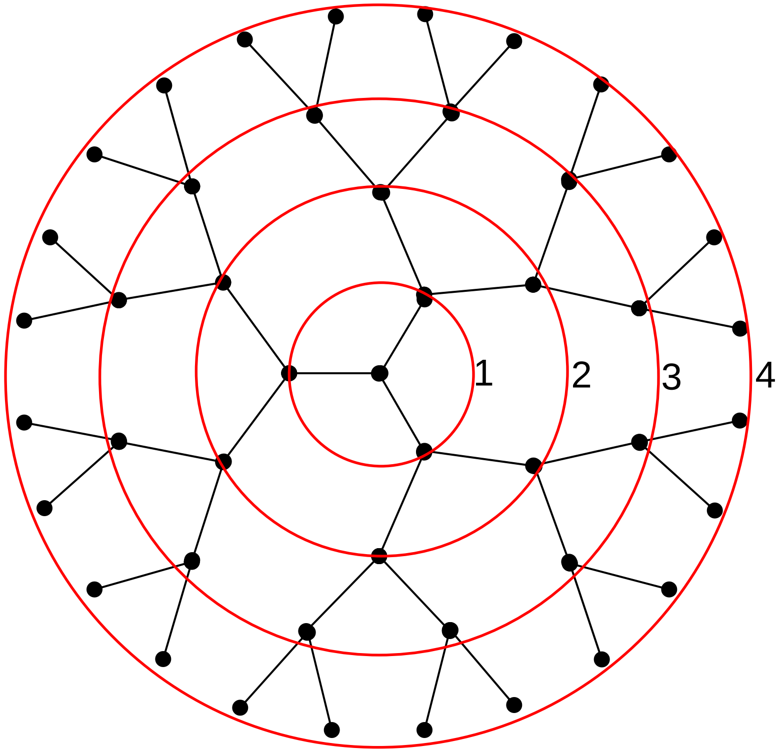
Bethe lattice 4th generation

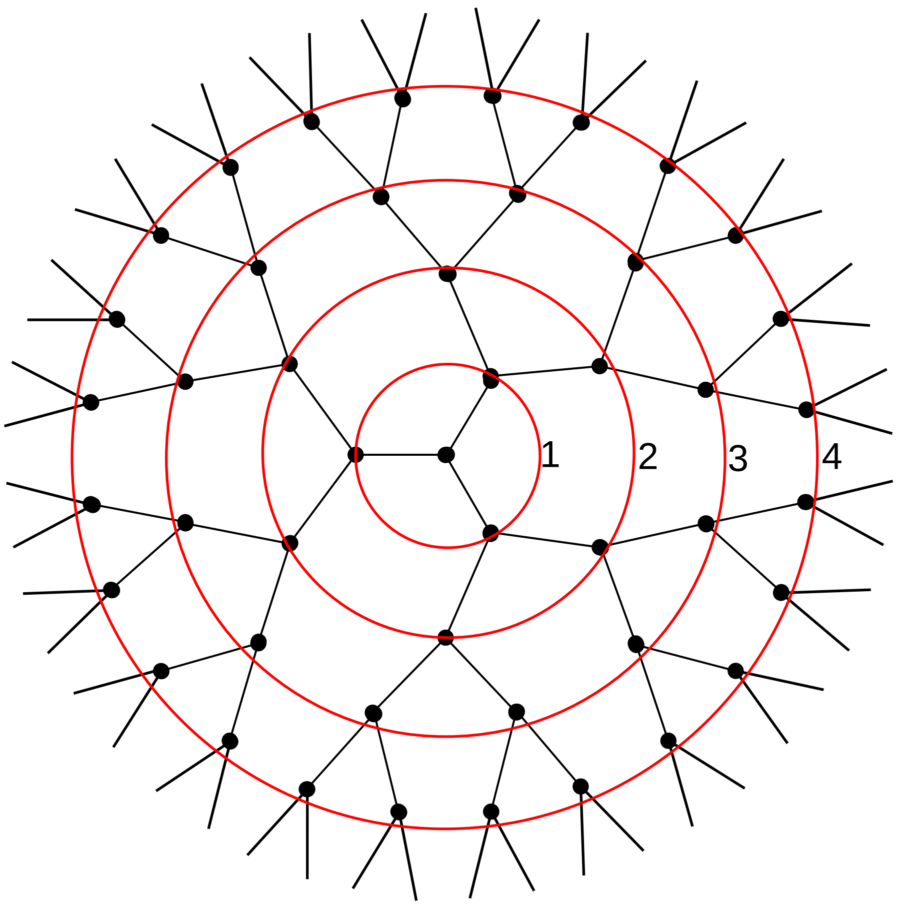


Each "particle" can connect to z other particles, probability g.
In this case z=3.
Number of particles in generation n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$N_4 = 24$$

Bethe lattice 5th generation

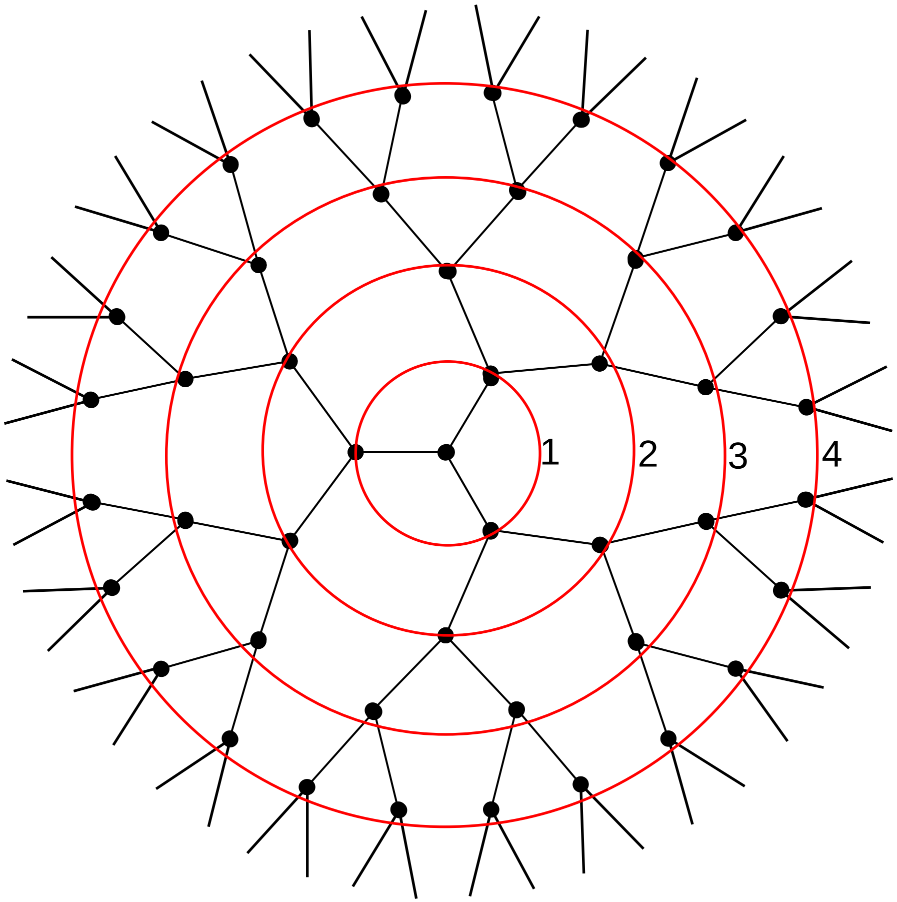


Each “particle” can connect to z other particles, probability g.
In this case z=3.
Number of particles in generation n is a quantity of interest

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$N_5 = 48$$

Percolation limit – infinite cluster



Existence of a critical bond probability g_c

$$N_n \sim \left[g \times (z-1)\right]^n$$

$$\text{if } g < g_c = \frac{1}{z-1} \text{ then}$$

$$N_n \to 0 \text{ as } n \to \infty$$

$$\text{if } g > g_c = \frac{1}{z-1} \text{ then}$$

$$N_n \to \infty \text{ as } n \to \infty$$

Infinite cluster is equivalent to a space-filling connected structure, i.e. a gel

edge+face → edge-face

Equilibrium e + f ↔ e-f

$$K = \frac{[\mathrm{e-f}]}{[\mathrm{e}][\mathrm{f}]} = \exp\left(-(\Delta H - T\Delta S)/RT\right)$$

assume

$$[\mathrm{e}] \propto [\mathrm{f}] \propto c \times (1-g)$$

$$[\mathrm{e-f}] \propto c \times g$$

c= clay concentration

(1-g)=fraction non-reacted bonds

At transition temperature T^*, $g =$ the critical value g_c

$$\frac{[\mathrm{e-f}]}{[\mathrm{e}][\mathrm{f}]} \propto \frac{c \times g_c}{c^2(1-g_c)^2} \propto \exp\left(-(\Delta H - T^*\Delta S)/RT^*\right)$$

$$\boxed{\ln c = \frac{\Delta H}{RT^*} + const.}$$

plot $\ln c$ vs. 1000/RT^* and the slope should give ΔH in kJ/mol

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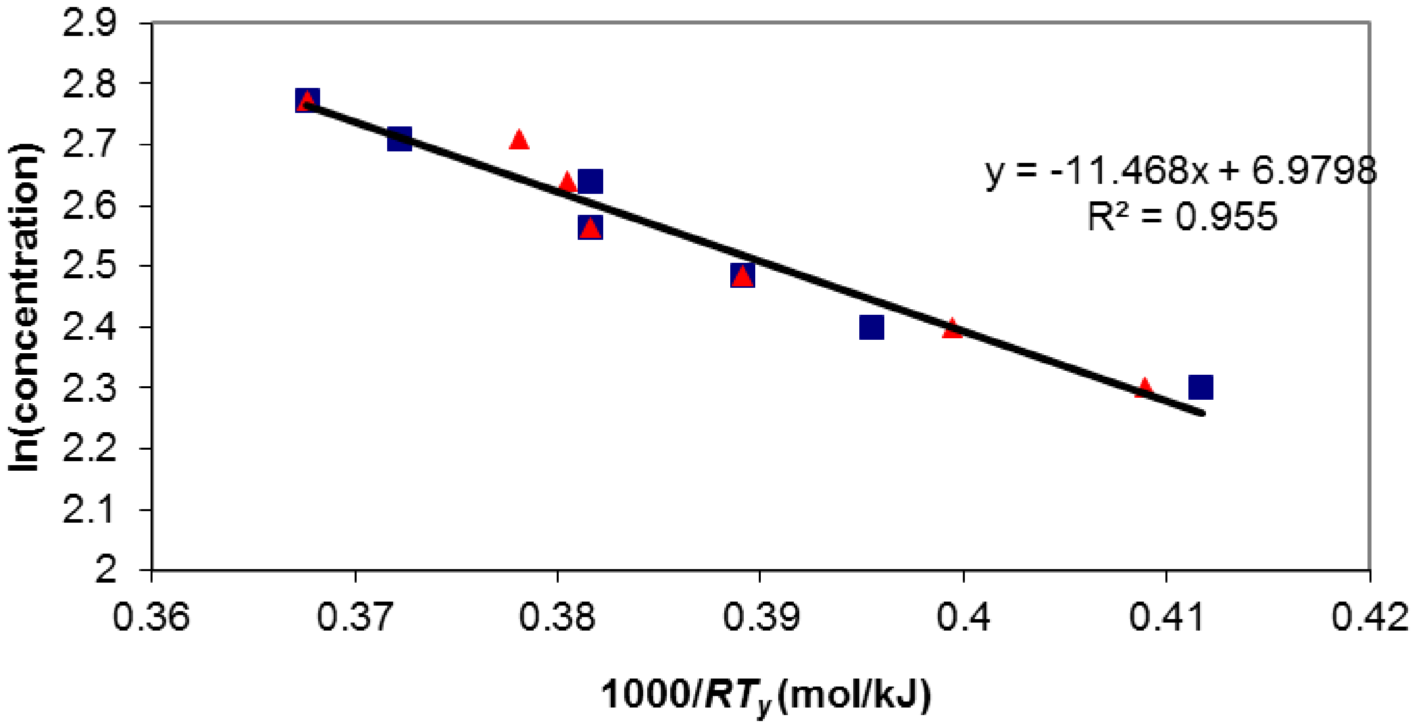
Results for binding enthalpy Ku-Na at 5 mM



ΔH=11.5 ± 0.7 kJ/mol or 4.6 ± 0.3 kT

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Conclusions & Outlook

- Gel formation is determined by ionic strength, with only minor pH dependence (pH<10) (see, e.g., Goh et al. 2015)

- Edge – face electrostatic attraction cause gel formation
  - Primitive model or DLVO, for parallel layers is not relevant
  - Simulations with clay platelets carrying positive rim charge possible way forward

- Spillover effect corroborated from gel yield temperatures

Conclusions & Outlook

- Strength of attractive gel increases with clay content
  - Yield temperature increases
  - Yield stress increases

- Clay gels seem to behave in agreement with percolation theory

- Possible to estimate binding enthalpy for edge – face binding
  - Important input for realistic theory and modelling
  - Monte Carlo results for laponite similar order of magnitude

- Edge-face binding for non gelled structures (Angelini et al Nature Comm. 2014, Birgersson et al. TR-09-34 2009)
  - Sloped fractures

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Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no295487, the BELBaR project, and from the Swedish Nuclear Fuel and Waste Management Company (SKB).

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Interaction Pressure between Charged Plate-like Particles in Electrolyte Solutions

An Application of Density Functional Theory with the Solvent Primitive Model

Longcheng Liu and Ivars Neretnieks

Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement n° 295487

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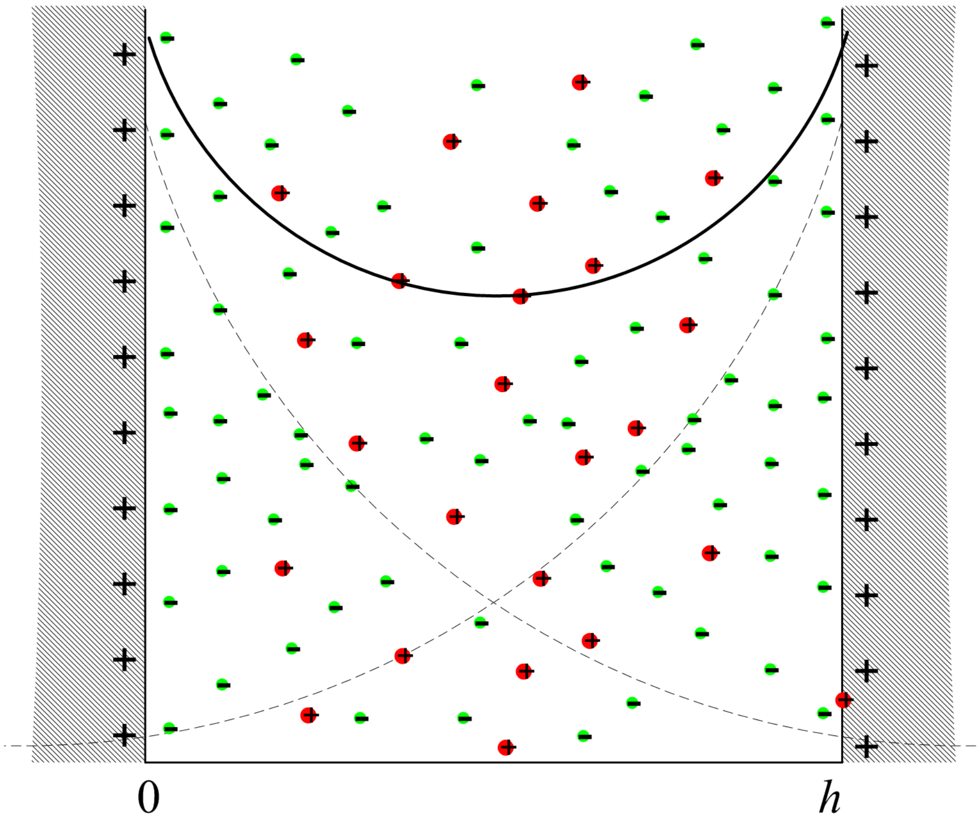
Question-Are our models realistic?



Ion-ion correlation and steric effect of ions and solvent?

Modelling useful to

Give an insight into

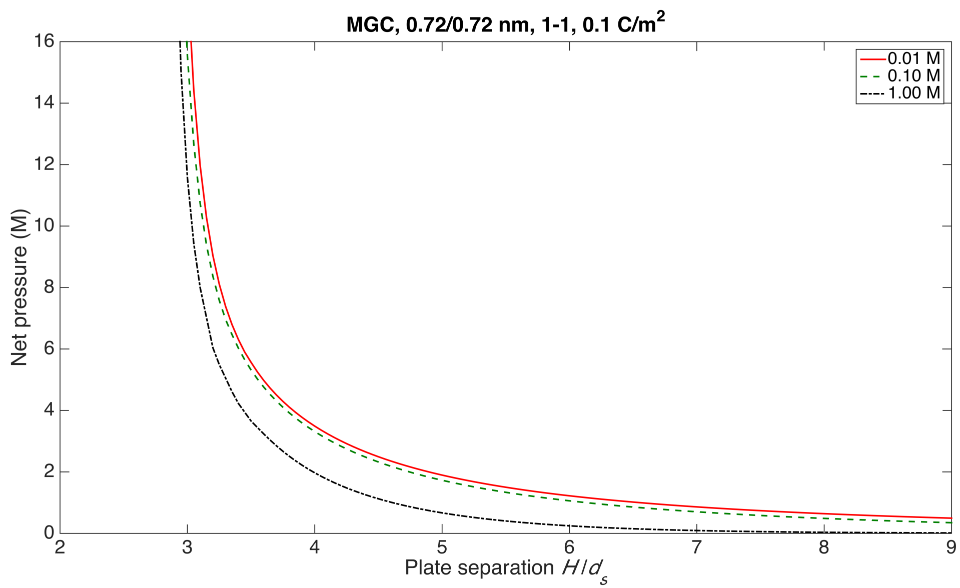
- **Swelling behavior of bentonite**
- **Formation of montmorillonite stacks**
- **Formation of flocs and band-type agglormates**
- **Stability of colloidal dispersions**
- **Hysteretic effect of wetting/drying processes**
- **Ion exchange equilibria and selectivity coefficients**

Simplifying approches in modelling

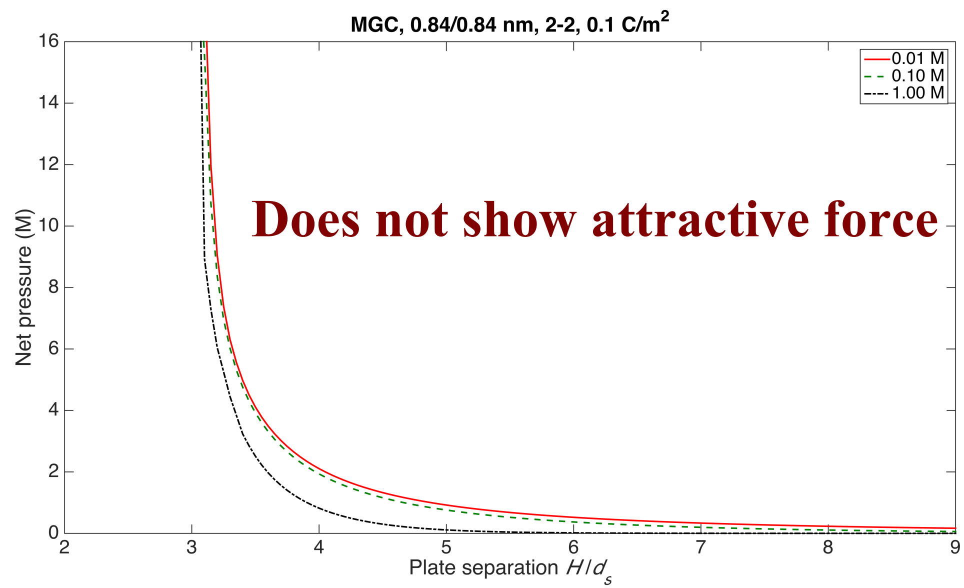
- Gouy-Chapman theory
- Modified Gouy-Chapman theory
- Modified Poisson-Boltzmann theory
- Integral equation theory (HNC…)
- Density functional theory (WDA…)

Interaction pressure MGC

0.72/0.72/- nm, 1-1, x M, 0.1 C/m^2



0.84/0.84/- nm, 2-2, x M, 0.1 C/m^2



Simulation methods- Atom by atom

- **Monte-Carlo**

  based on Metropolis algorithm for configuration

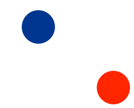
- **Molecular dynamics**

  Based on Newton's law of motion till equilibrium

Models and concepts

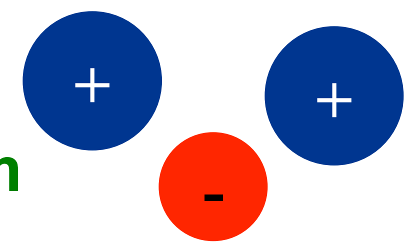
- **Gouy-Chapman model**

  point-charge; dielectric continuum

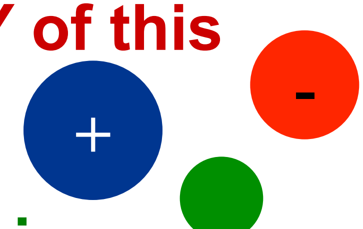


- **Primitive model**

  ionic hard spheres; dielectric continuum



- **Solvent Primitive model- MAIN NOVELTY of this presentation**

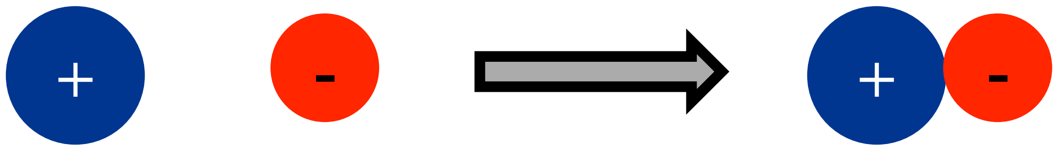


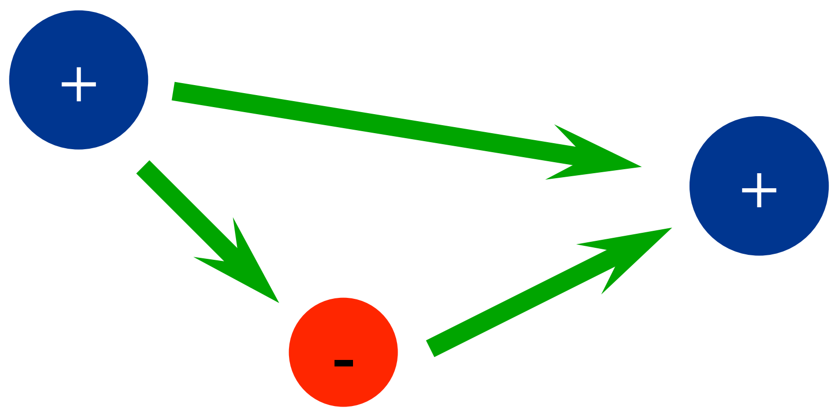
  ionic hard spheres; hard sphere+dielectric continuum

- **……**

DFT and Weighted correlation approach

Trying to describe the steric effect and the correlation effects accurately





DFT-Weighted correlation approach

- **Density distribution at equilibrium**

$$\frac{\rho^{(1)}(\mathbf{r})}{\rho^{(1)}(\mathbf{r};0)} = \exp\left[-\beta\Delta u(\mathbf{r}) + \Delta c^{(1)}(\mathbf{r})\right]$$

- **Change of singlet correlation function**

$$\Delta c^{(1)}(\mathbf{r}) = \int \mathrm{d}\mathbf{s}\,\overline{c}^{(2)}(\mathbf{r},\mathbf{s})\Delta\rho(\mathbf{s})$$

$$\overline{c}^{(2)}(\mathbf{r},\mathbf{s}) = \frac{\int c^{(2)}(\mathbf{r},\mathbf{s};f)\,f(\mathbf{r}')\,\mathrm{d}\mathbf{r}'}{\int f(\mathbf{r}')\,\mathrm{d}\mathbf{r}'}$$

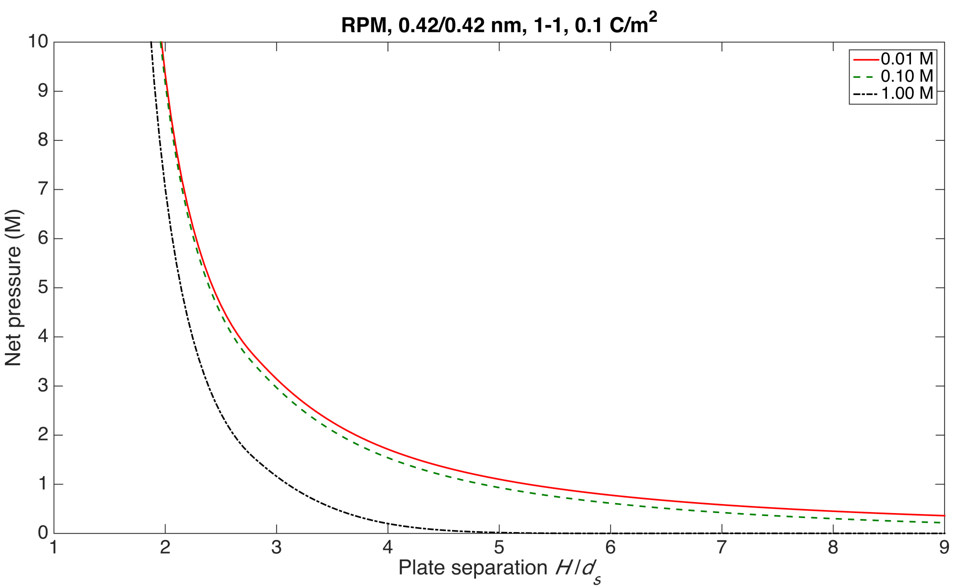
Key data needed for MC and DFT models

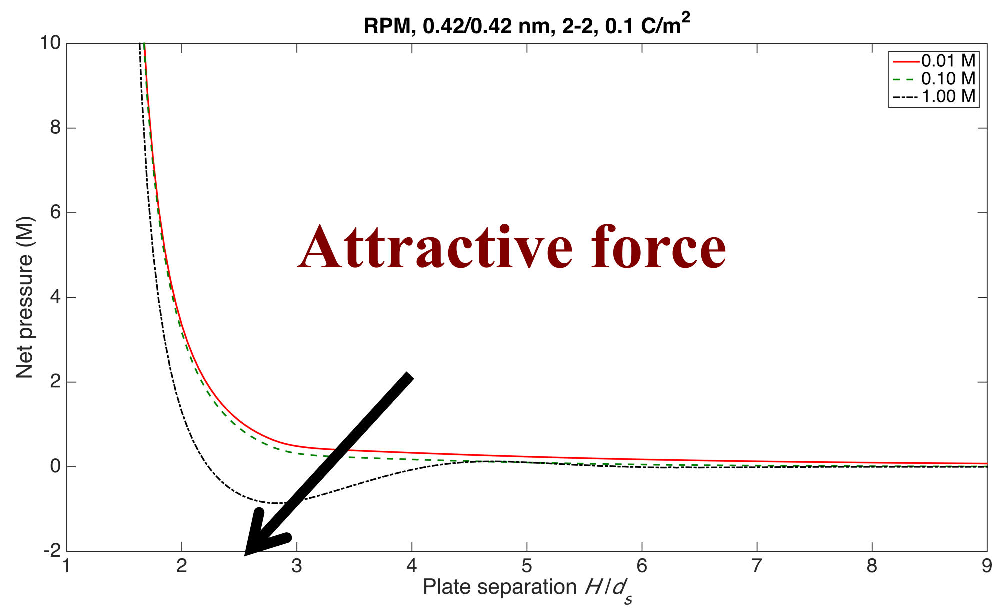
- Surface charge density
- Ionic strength
- **Ion and molecule sizes**
  - Cation anion, water molecule
  - Hydration shell
- **Ion charges**
  - Cations, anions

Interaction pressure RPM-Equal ion size, water molecule size not accounted for

0.42/0.42/- nm, 1-1, x M, 0.1 C/m² **0.42/0.42/- nm, 2-2, x M, 0.1 C/m²**

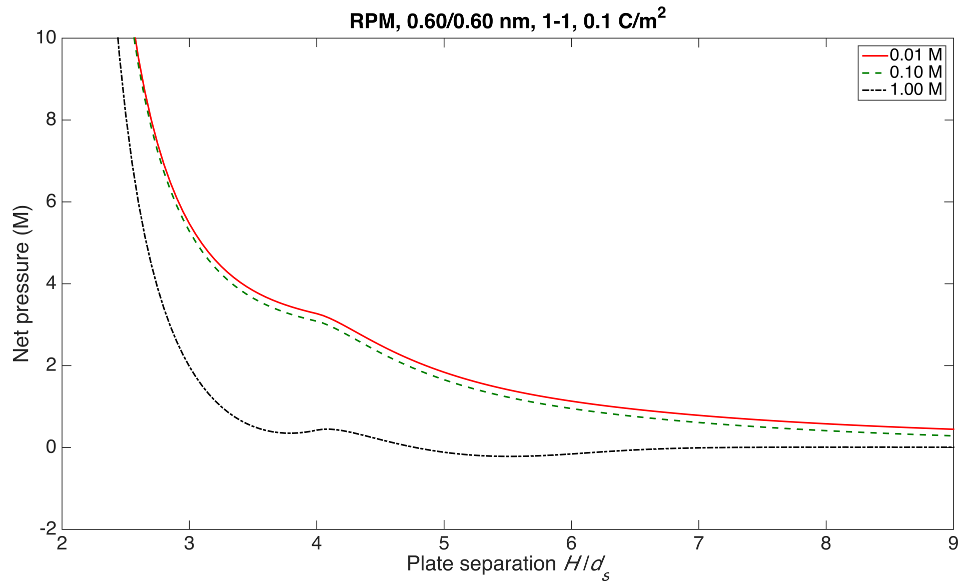
cat/an/water size nm, charge cat-an, charge density C/m²



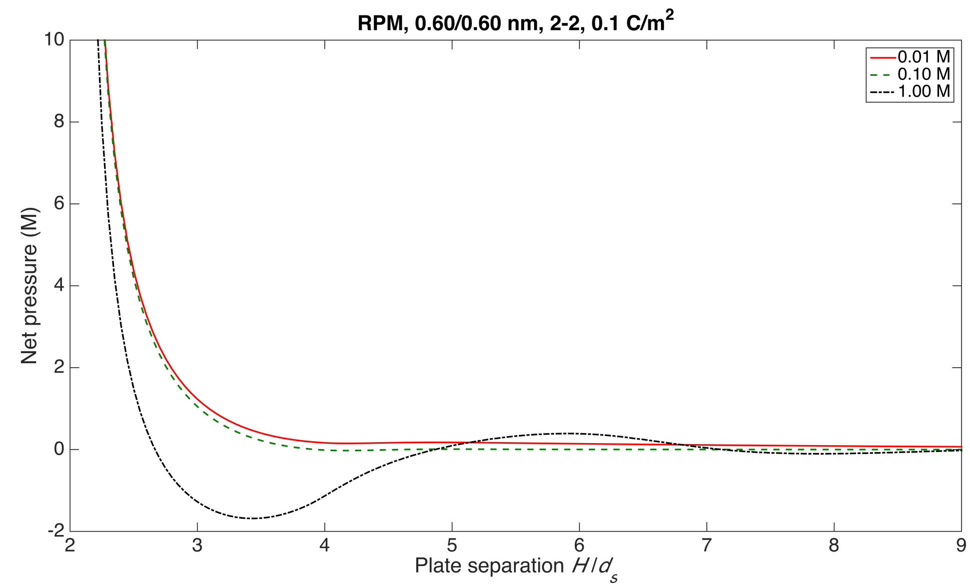


Interaction pressure RPM

0.6/0.6/- nm, 1-1, x M, 0.1 C/m²



0.6/0.6/- nm, 2-2, x M, 0.1 C/m²



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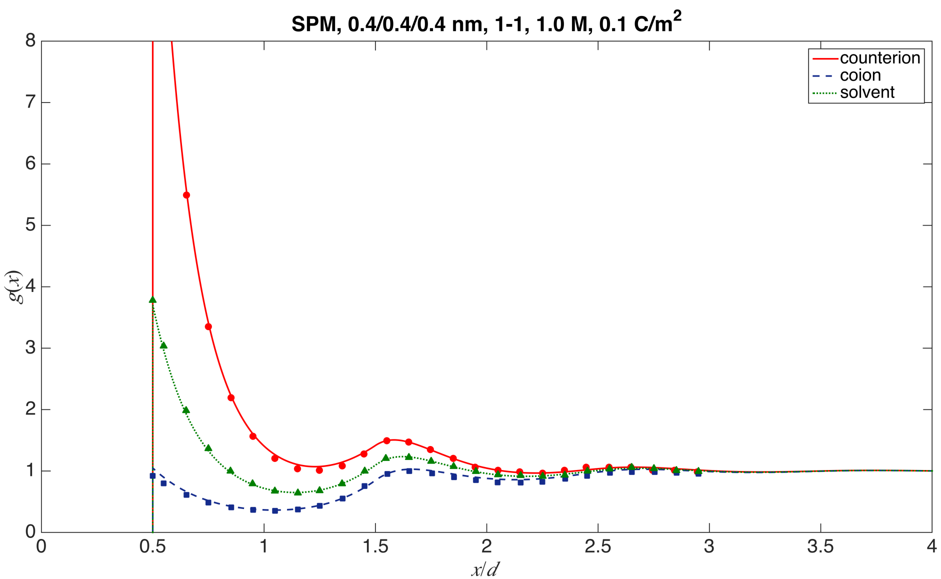
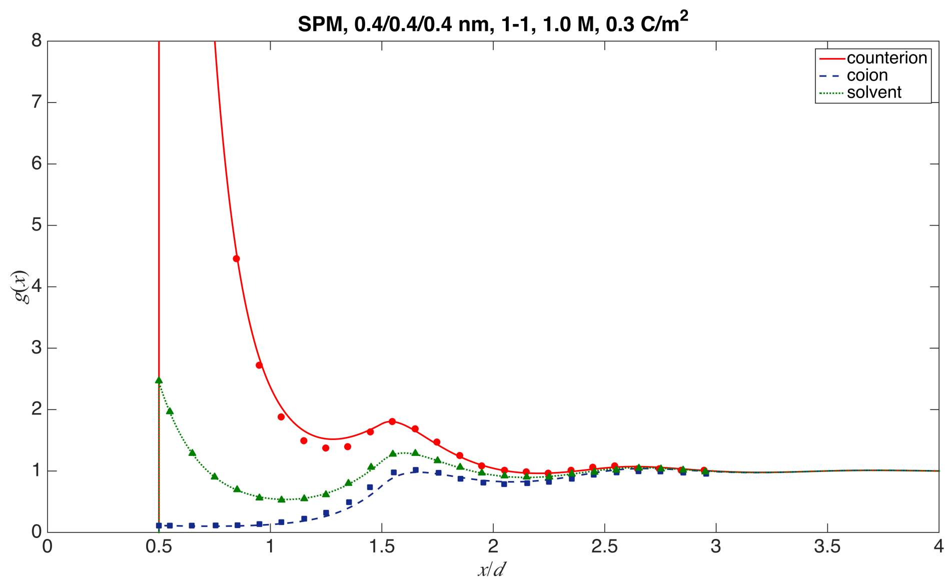
Density structures. Solvent primitive model- SPM

0.4/0.4/0.4 nm, 1-1, 1M, 0.1C/m²

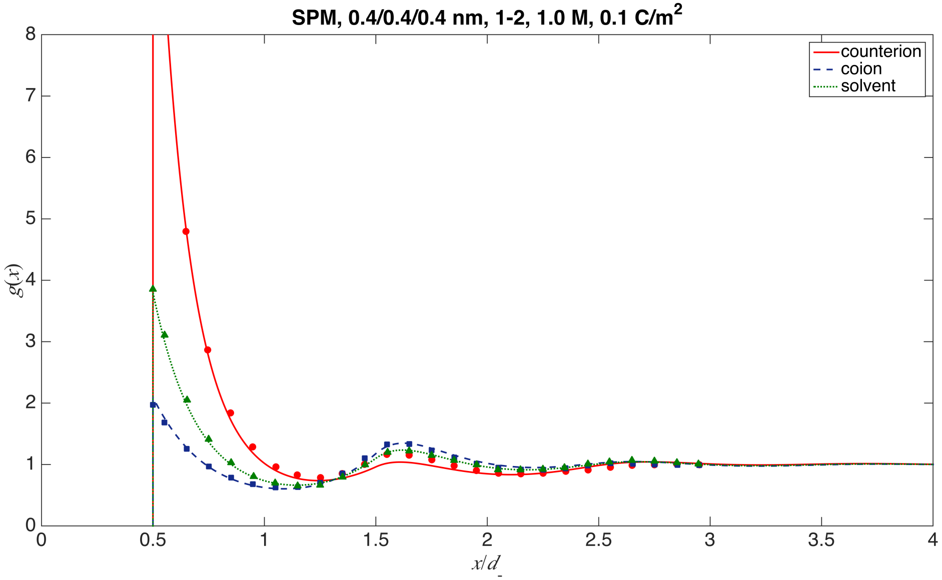


0.4/0.4/0.4 nm, 1-1, 1M, 0.3 C/m²

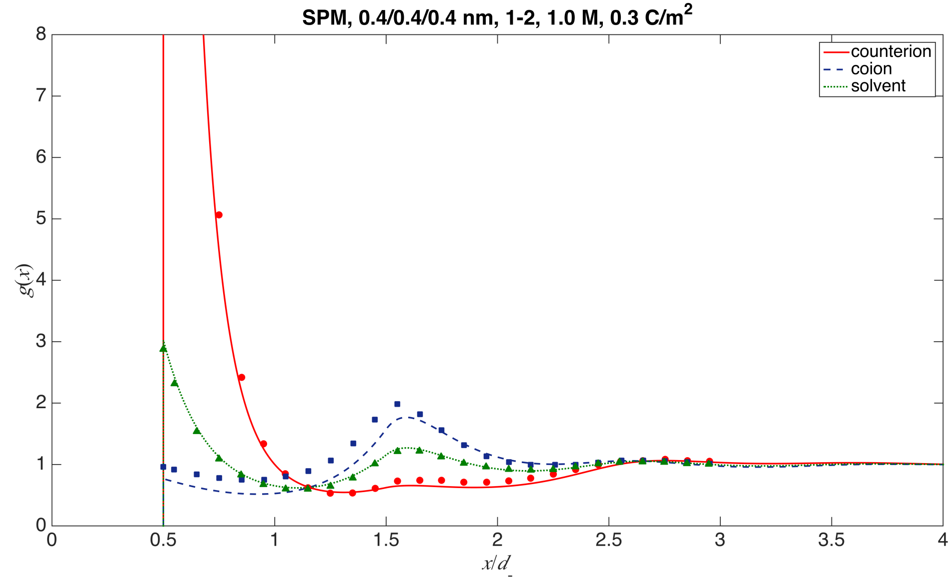


Structures SPM

0.4/0.4/0.4 nm, 1-2, 1M, 0.1C/m^2

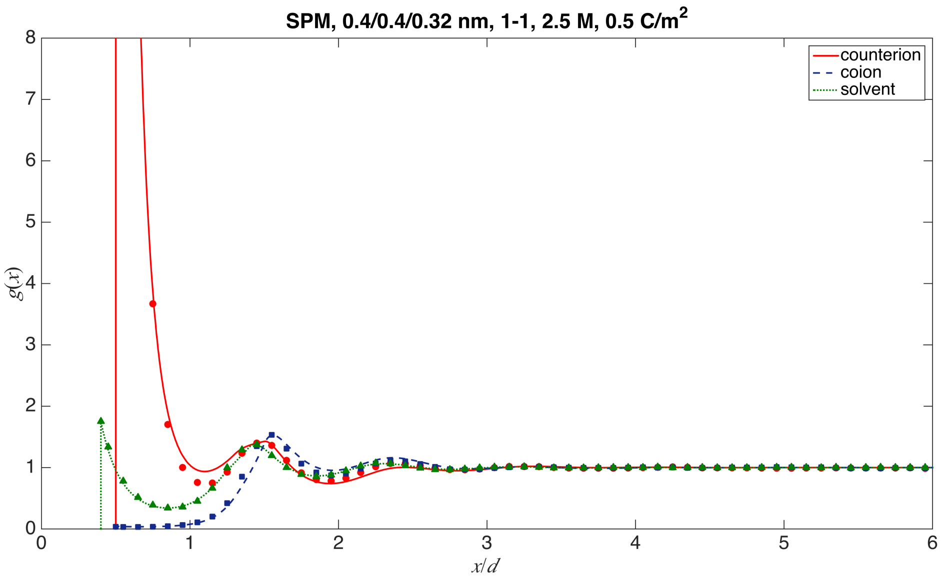


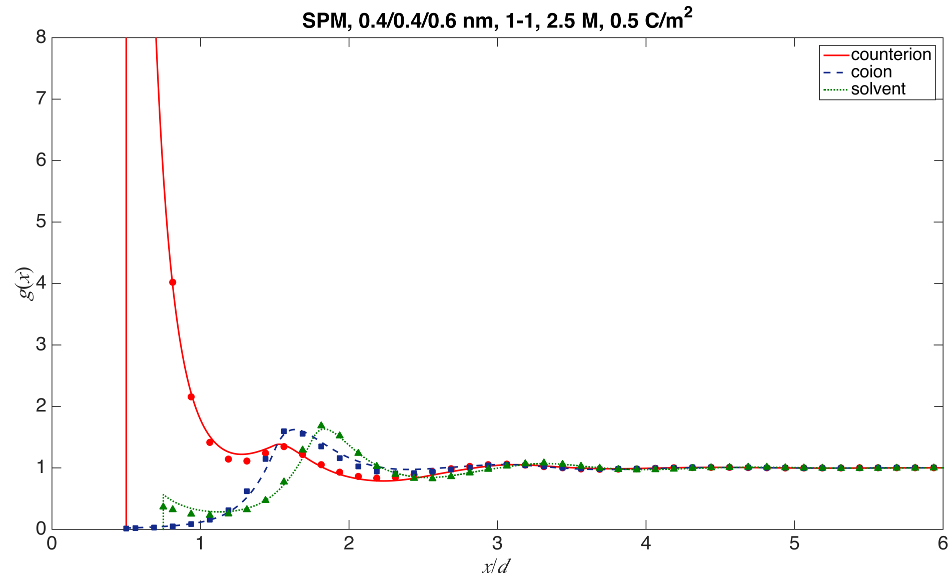
0.4/0.4/0.4 nm, 1-2, 1M, 0.3C/m^2



Structures SPM

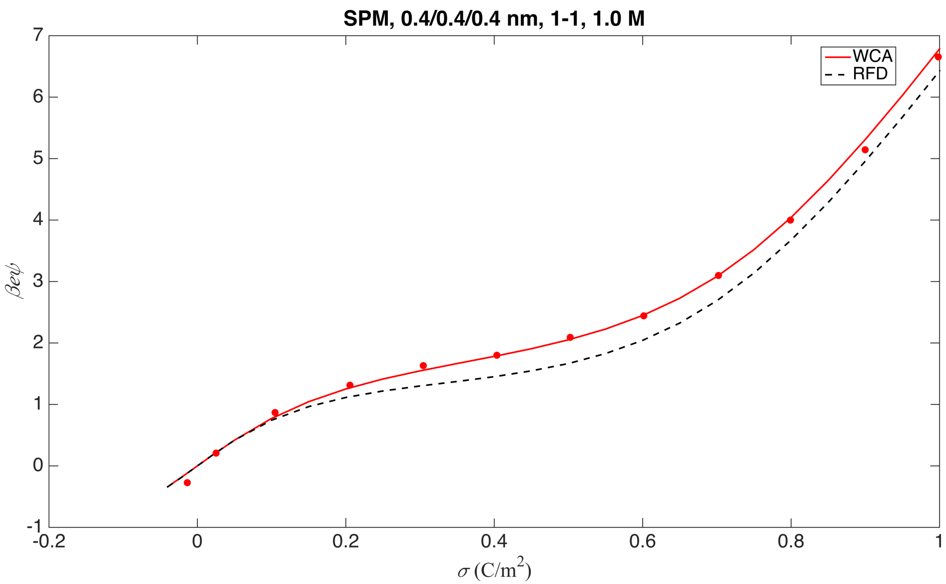
0.4/0.4/0.32 nm, 1-1, 2.5M, 0.5 C/m^2 0.4/0.4/0.6 nm, 1-1, 2.5M, 0.5 C/m^2

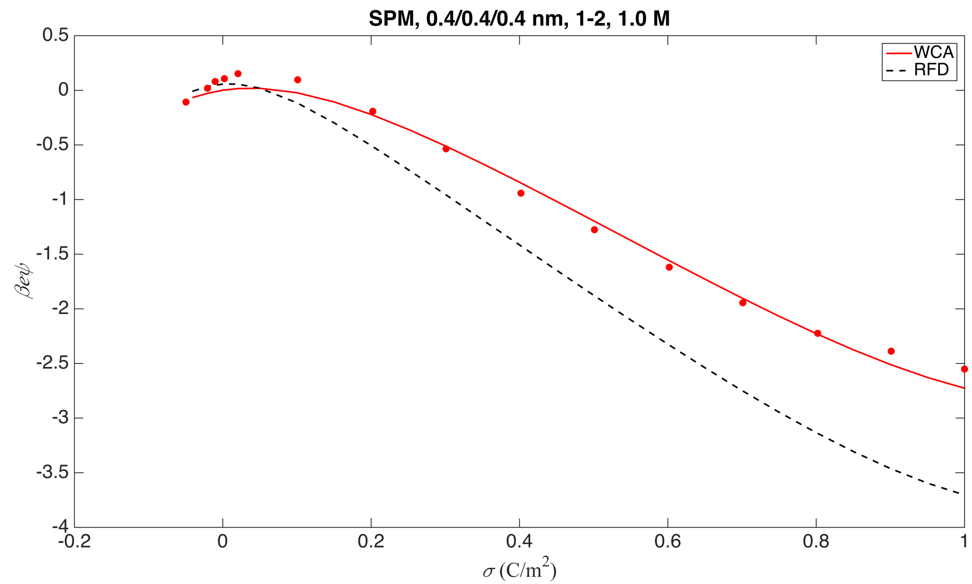




Diffuse potential SPM

0.4/0.4/0.4 nm, 1-1, 1M, 0.5C/m² **0.4/0.4/0.4 nm, 1-2, 1M, 0.5C/m²**





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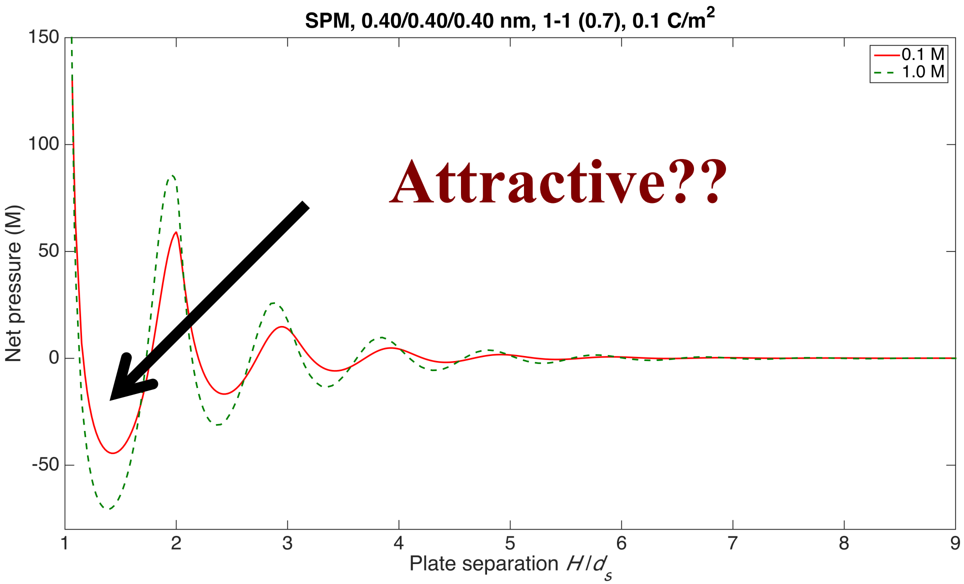
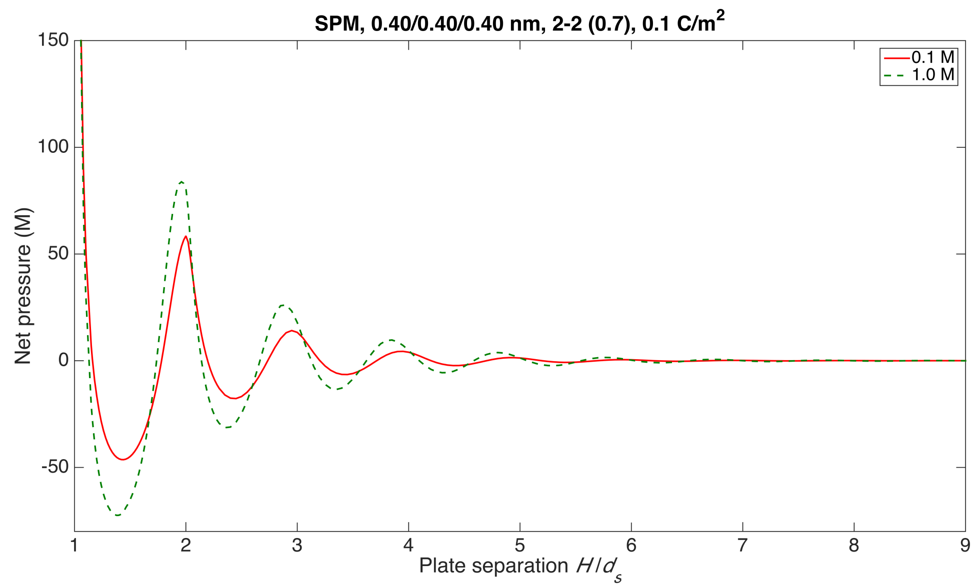
Interaction pressure SPM

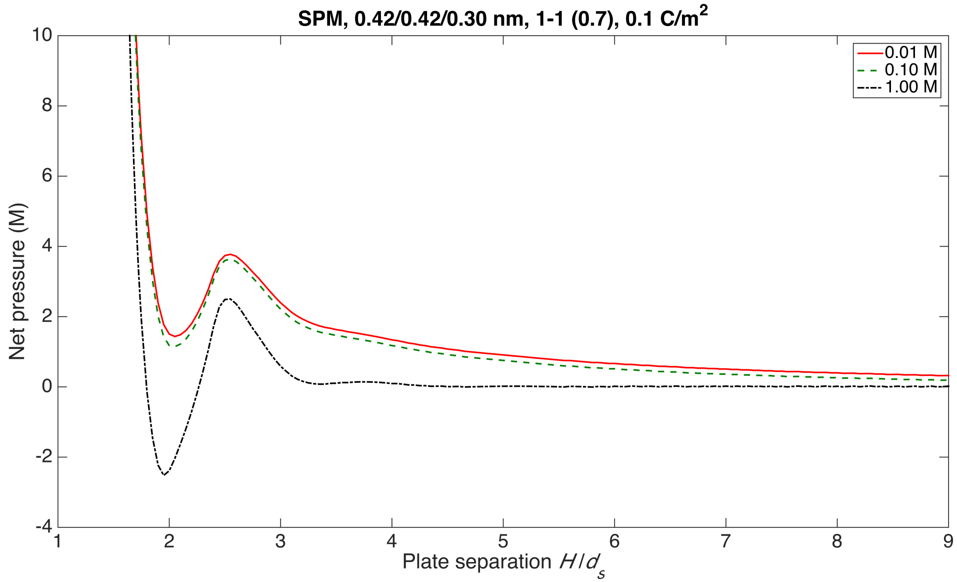
0.4/0.4/0.4 nm, 1-1, x M, 0.1 C/m^2 　 **0.4/0.4/0.4 nm, 2-2, x M, 0.1 C/m^2**



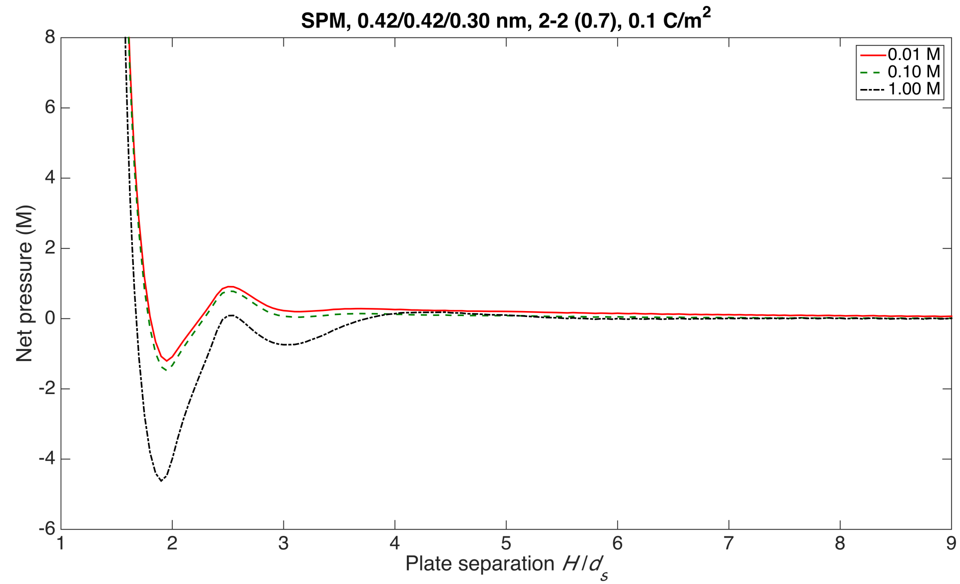


Interaction pressure SPM, small water

0.42/0.42/0.3 nm, 1-1, x M, 0.1 C/m^2

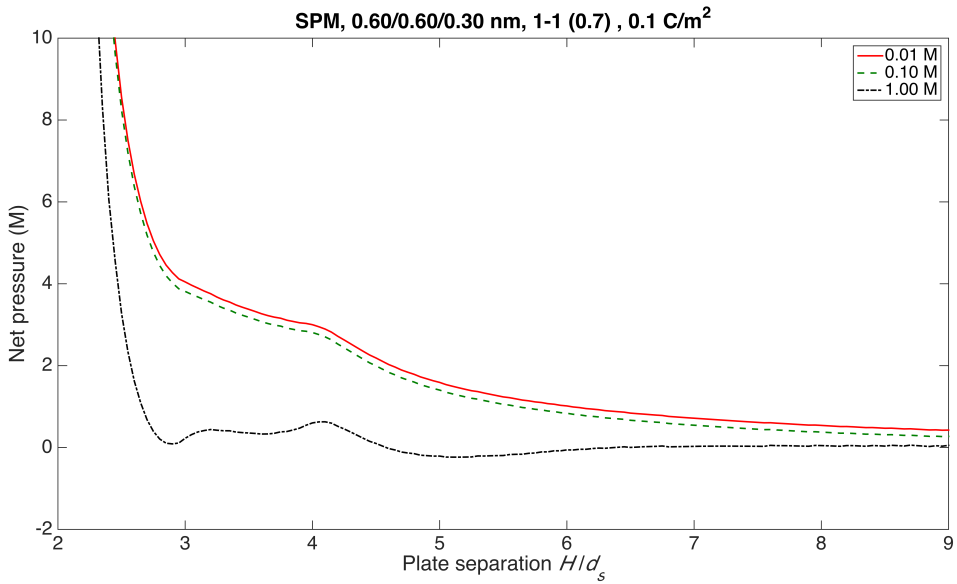


0.42/0.42/0.3 nm, 2-2, x M, 0.1 C/m^2

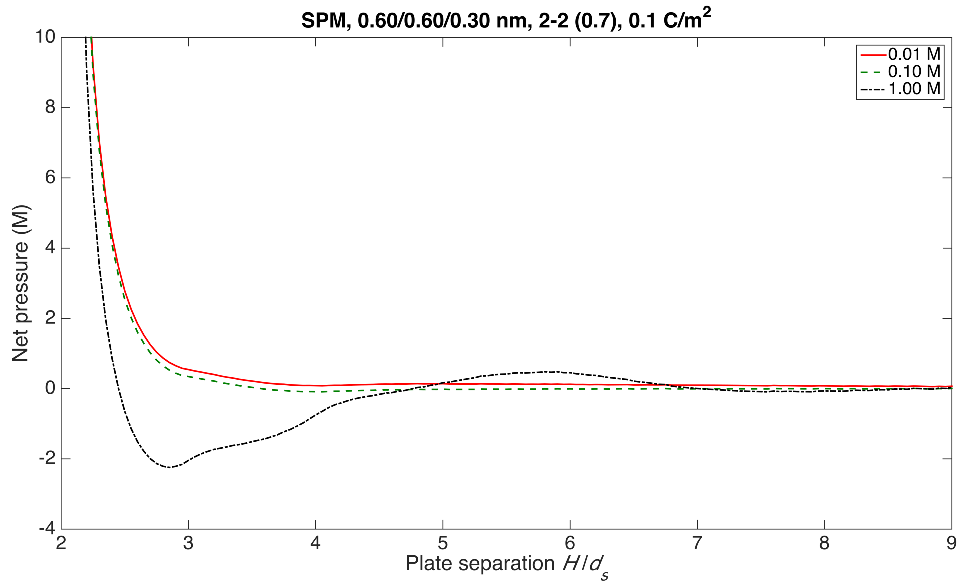


Interaction pressure SPM

0.6/0.6/0.3 nm, 1-1, x M, 0.1 C/m^2

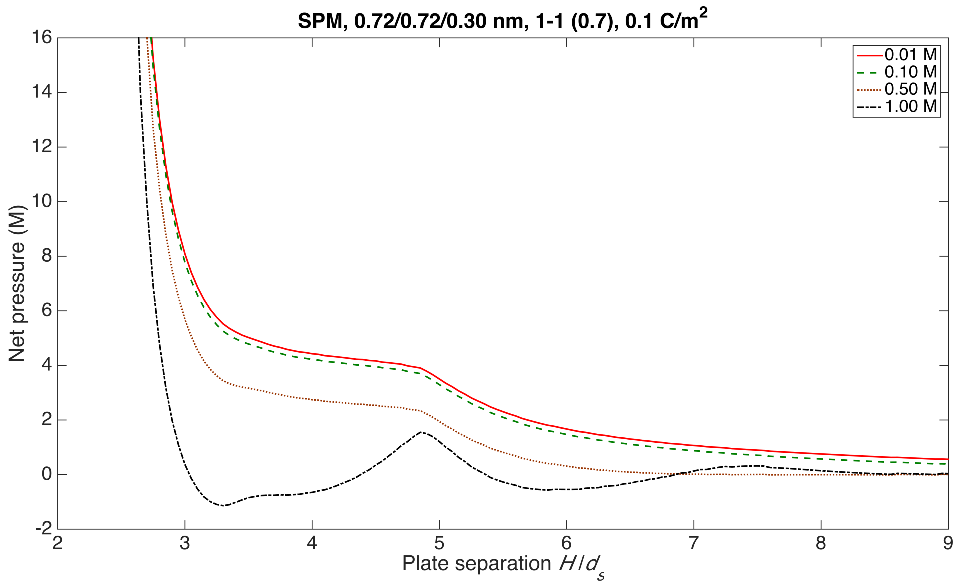


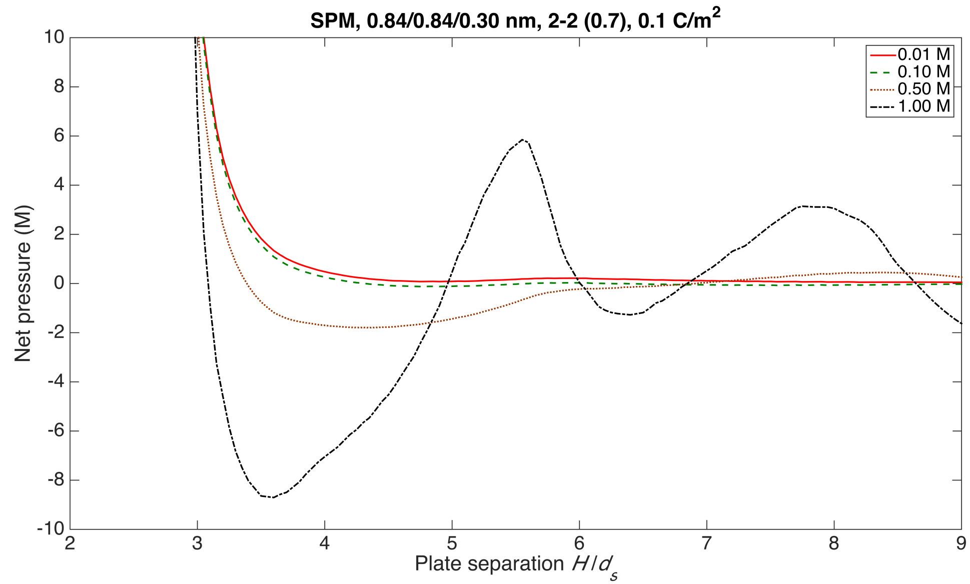
0.6/0.6/0.3 nm, 2-2, x M, 0.1 C/m^2



Interaction pressure SPM

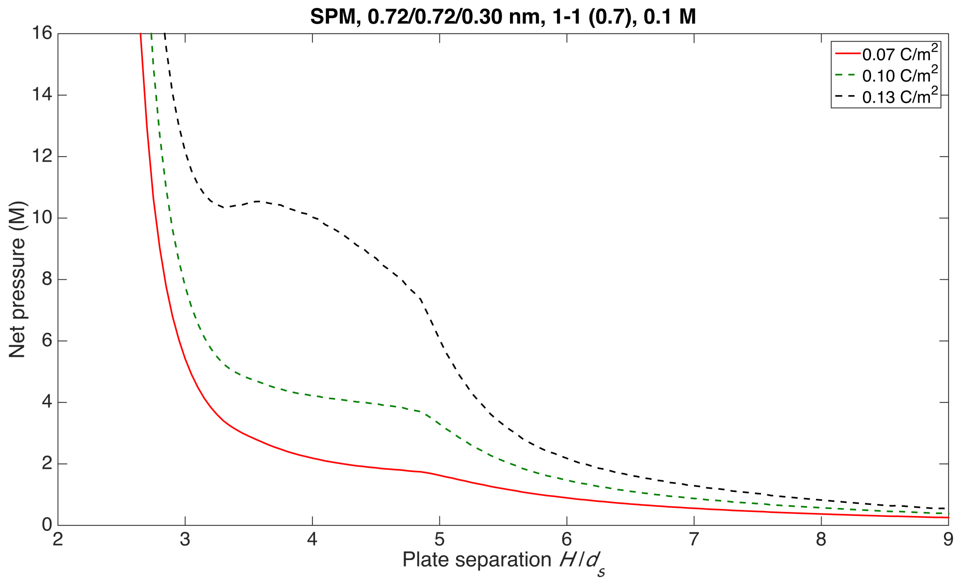
0.72/0.72/0.3 nm, 1-1, x M, 0.1 C/m^2 0.84/0.84/0.3 nm, 2-2, x M, 0.1 C/m^2

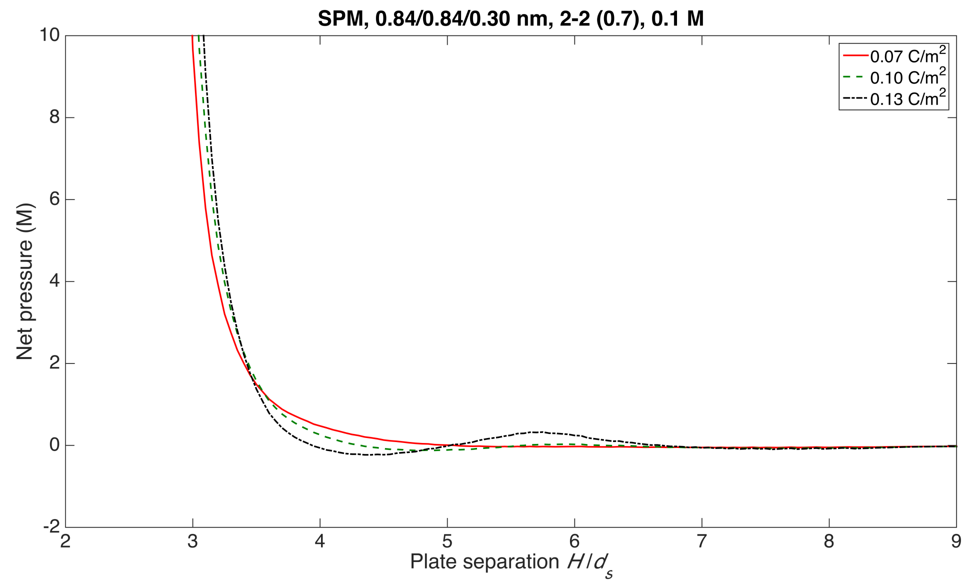




Interaction pressure SPM

0.72/0.72/0.3 nm, 1-1, x M, 0.1 C/m^2 0.84/0.84/0.3 nm, 2-2, x M, 0.1 C/m^2





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Limitations and outlook

- Size of hydrated ions
- Deformation of hydrated ions

- Water moleculeas as dipoles
- Heterogeneous surface charge density
- Floc formation
- Edge to face and overlap

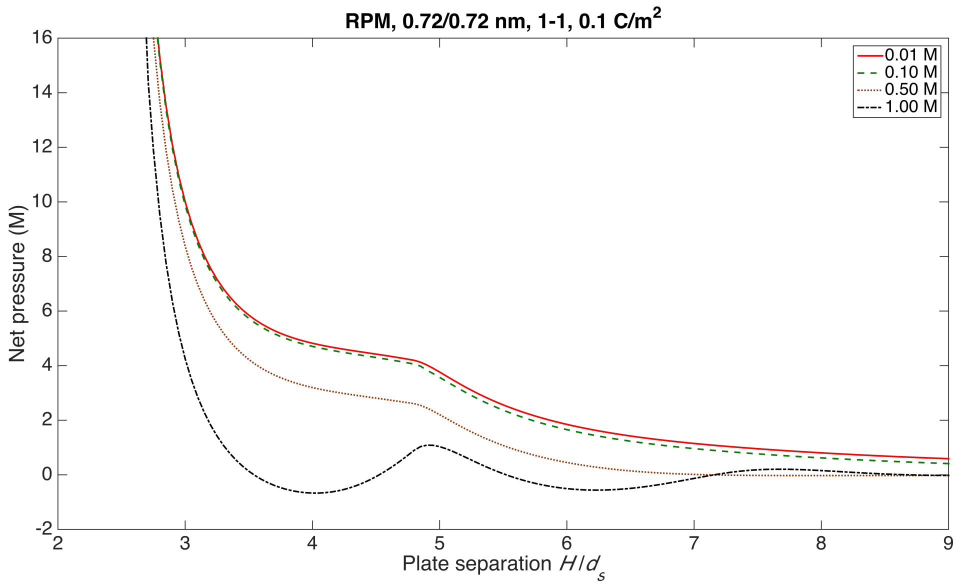
Conclusion

- The hard-core exclusions of water molecules are important in cases where the separations are less than the thickness of ~ 4 water layers
- Heterogenous charge distribution among clay particles are responsible for the limited swelling of Ca-bentonite and for the stack formation
- The oscillatory forces resulting from the presence of water molecules are responsible for hysteresis

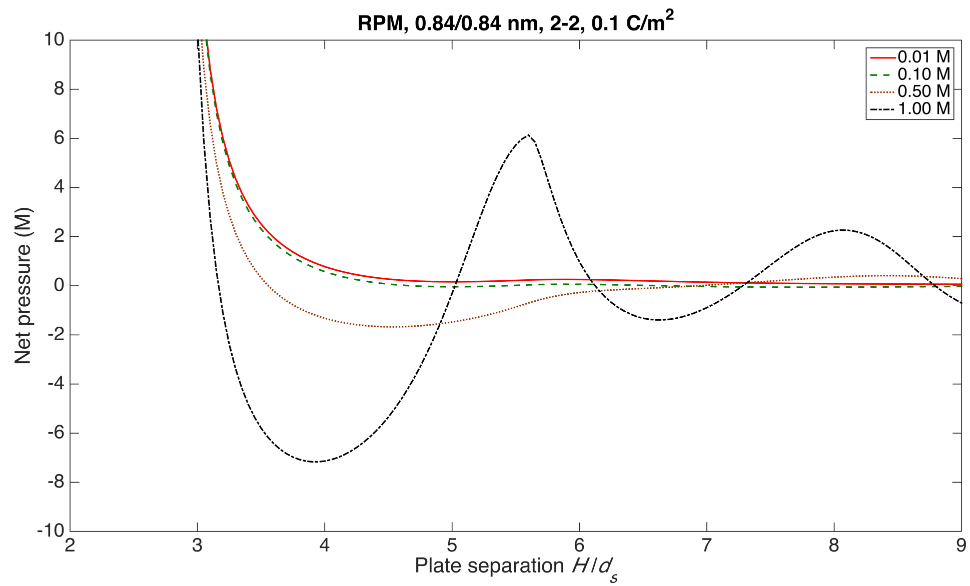
Thank you for your attention

Interaction pressure RPM

0.72/0.72/- nm, 1-1, x M, 0.1 C/m²

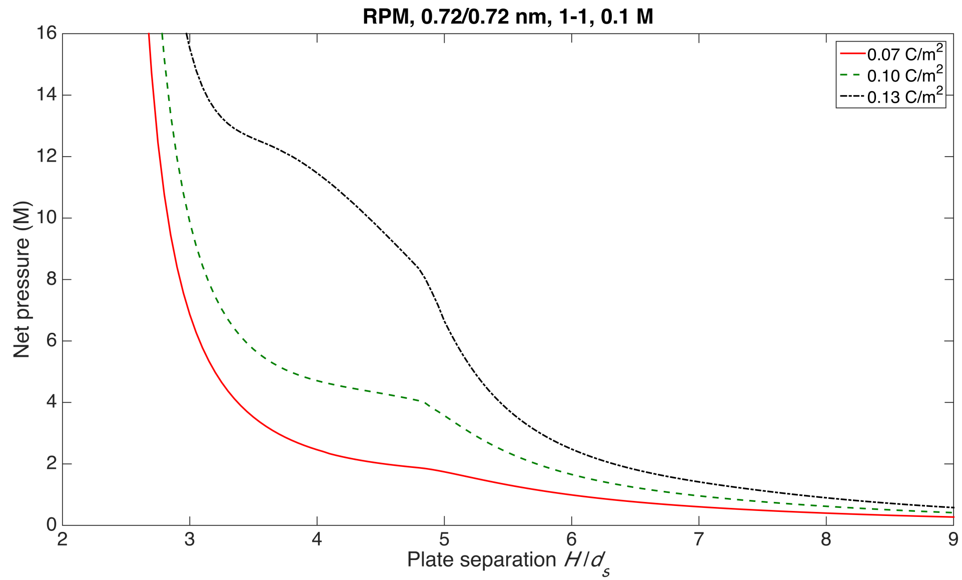


0.84/0.84/- nm, 2-2, x M, 0.1 C/m²

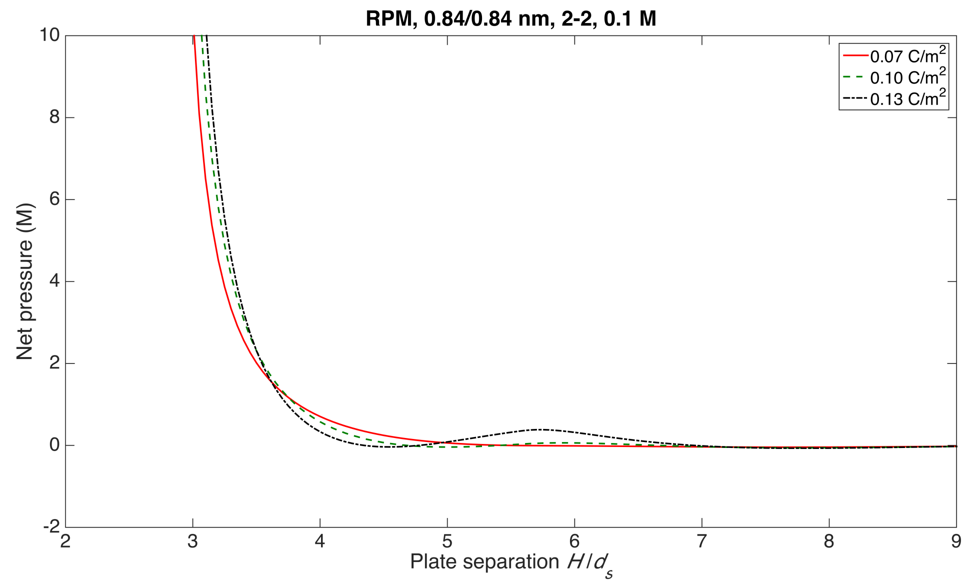


Interaction pressure RPM

0.72/0.72/- nm, 1-1, x M, 0.1 C/m²



0.84/0.84/- nm, 2-2, x M, 0.1 C/m²



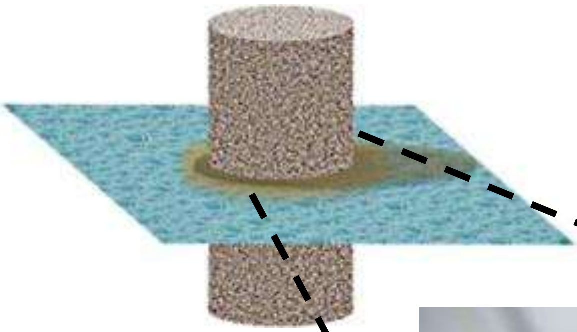
Detachment of colloids at a swelling clay-water interface: ***Conclusions based on rheological measurements***

Rasmus Eriksson

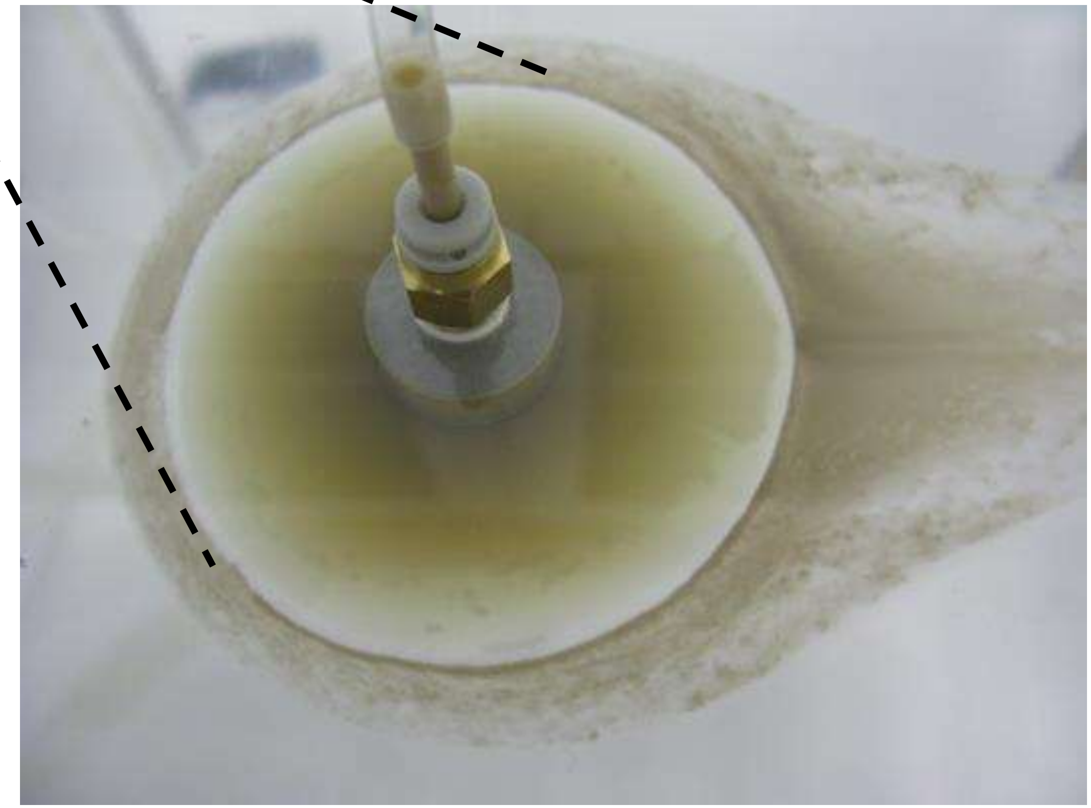
B+Tech Oy

Clay colloids in aqueous systems
3-4 Feb 2016, Berlin, Germany

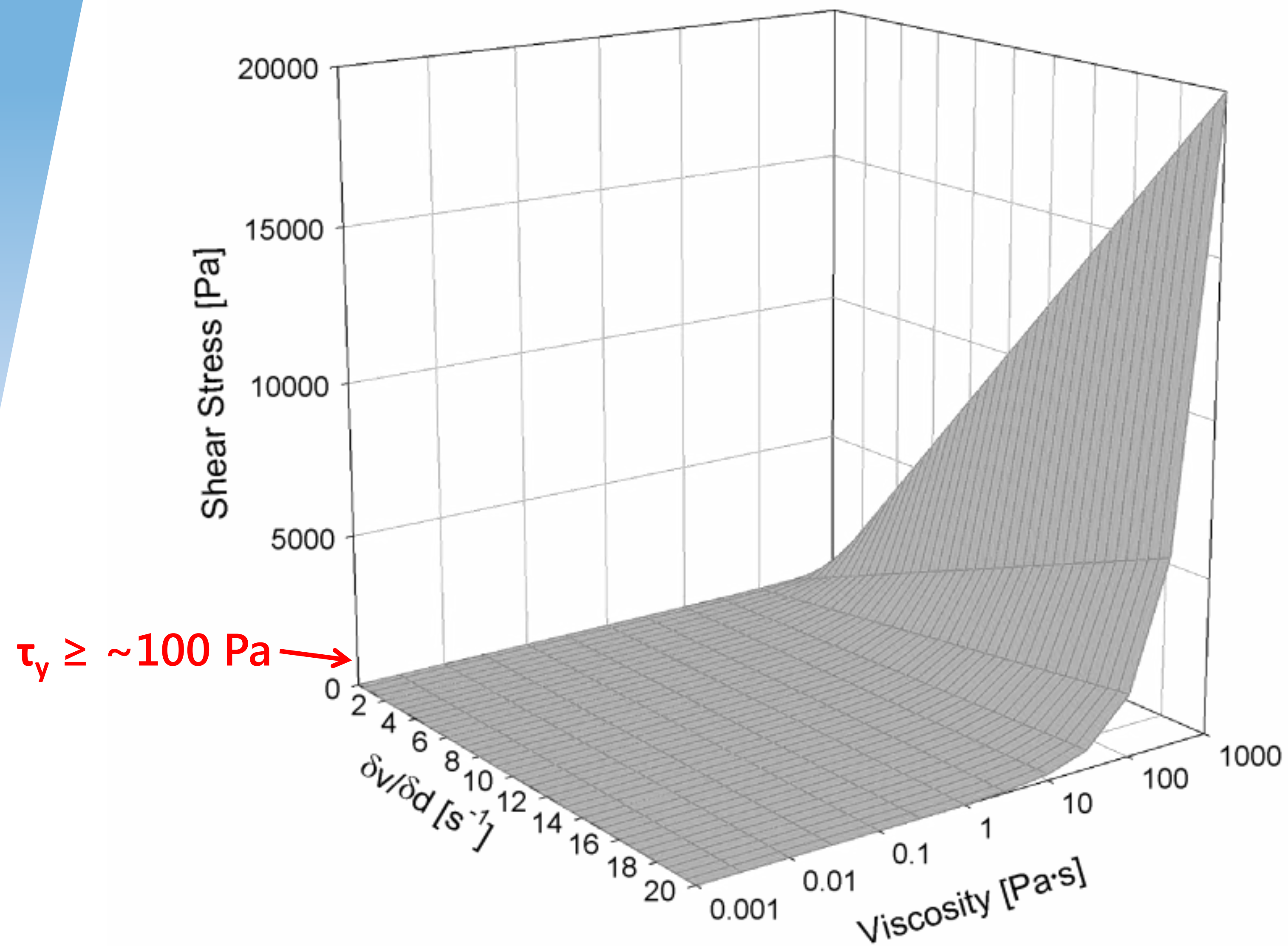
Background



Detachment mechanism?

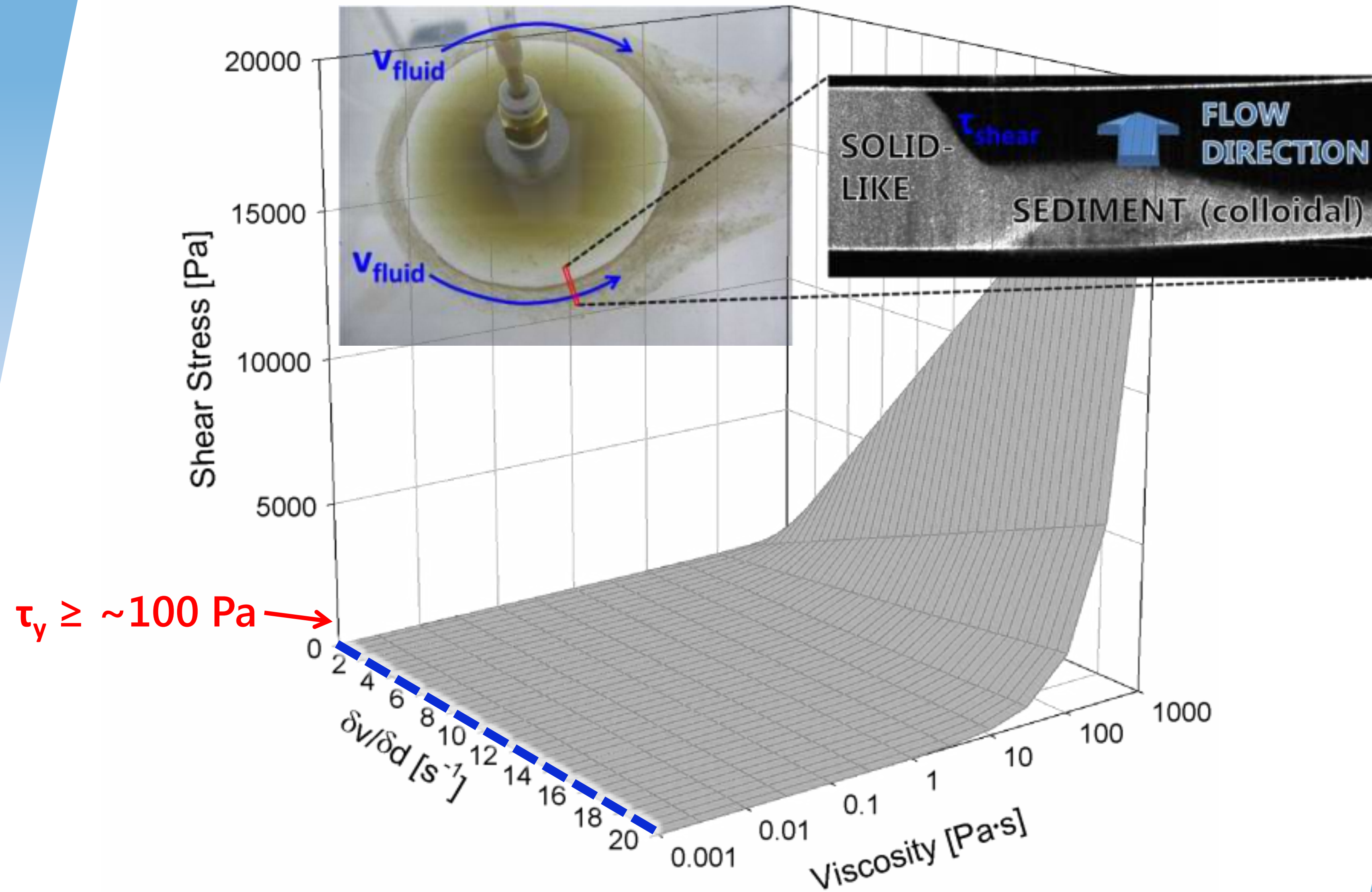


Shear stress



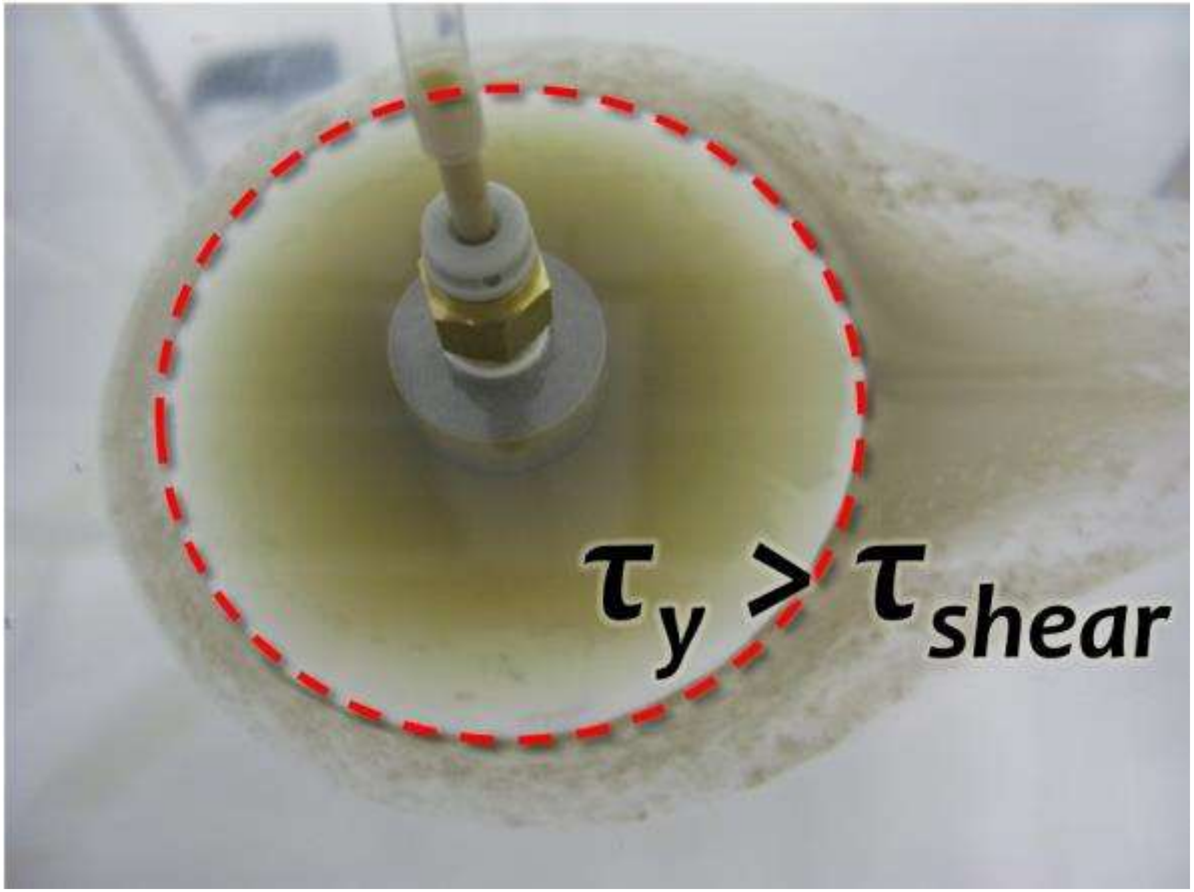
Eriksson & Schatz, Appl. Clay Sci. 108 (2015), 12.

Shear stress



Eriksson & Schatz, Appl. Clay Sci. 108 (2015), 12.

Shear stress



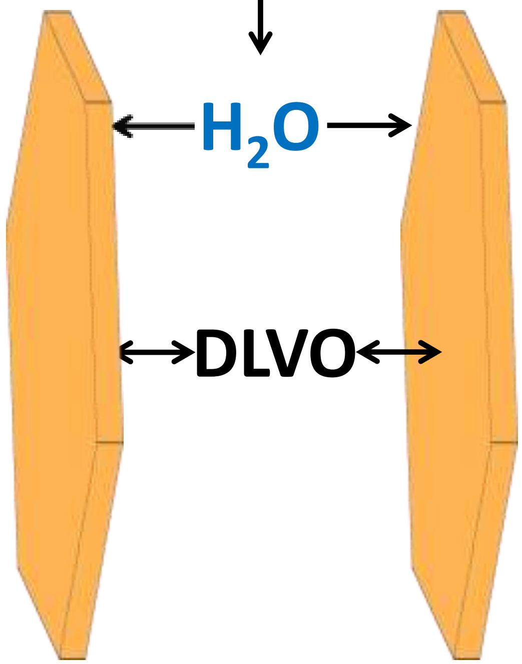
Effect of prolonged small shear stress?

Swelling mechanism

Assumption: ***chemical forces induce detachment***

~~Brownian motion~~ (too weak to overcome adhesion)

Osmosis

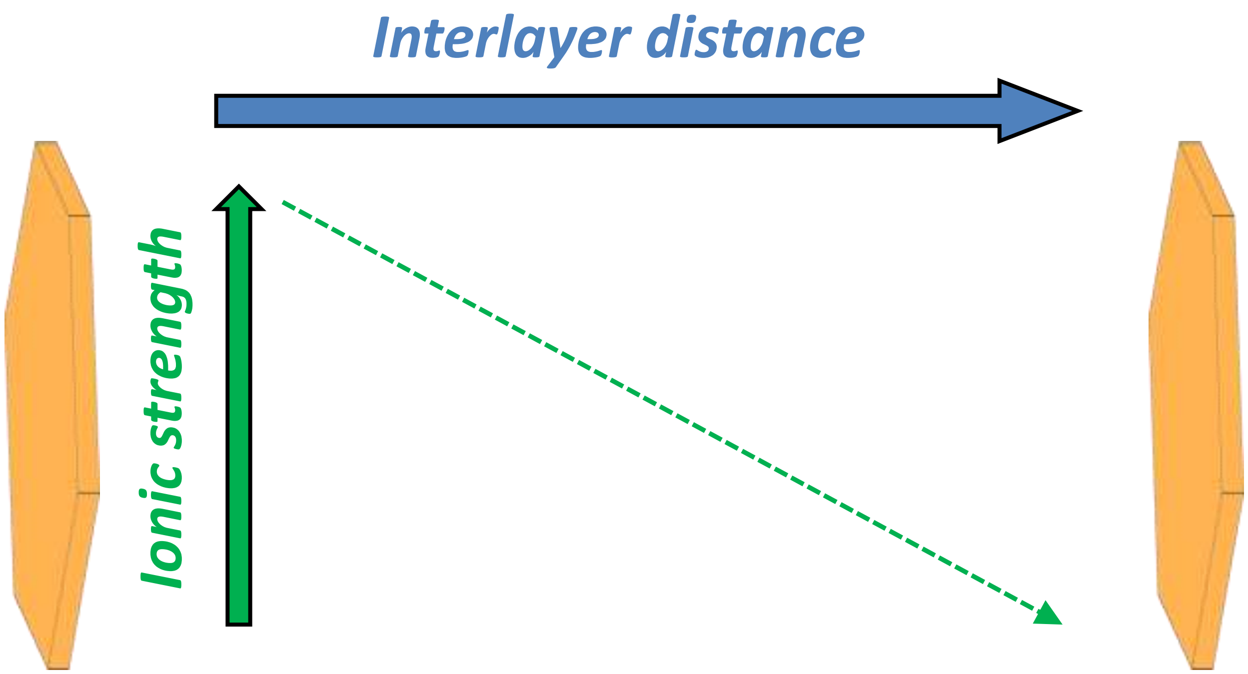


Swelling

Interaction energy as a function of interlayer distance:

- Assume constant number of (counter)-ions

- Ψ_0 = -100 mV, A_H = $2 \cdot 10^{-20}$ J



Results – particle interactions

1 nm (3 M) → **Φ:** *Negative (Attraction)*
Slope: *Negative (strong repulsion)*

2 nm (1.5 M) → **Φ:** *Negative (Attraction)*
Slope: *Positive (Attraction)*

5 nm (0.6 M) → **Φ:** *Negative (Attraction)*
Slope: *Positive (Attraction)*

Detachment

10 nm (0.3 M) → **Φ:** *Negative (Attraction)*
Slope: *Positive (Weak attraction)*

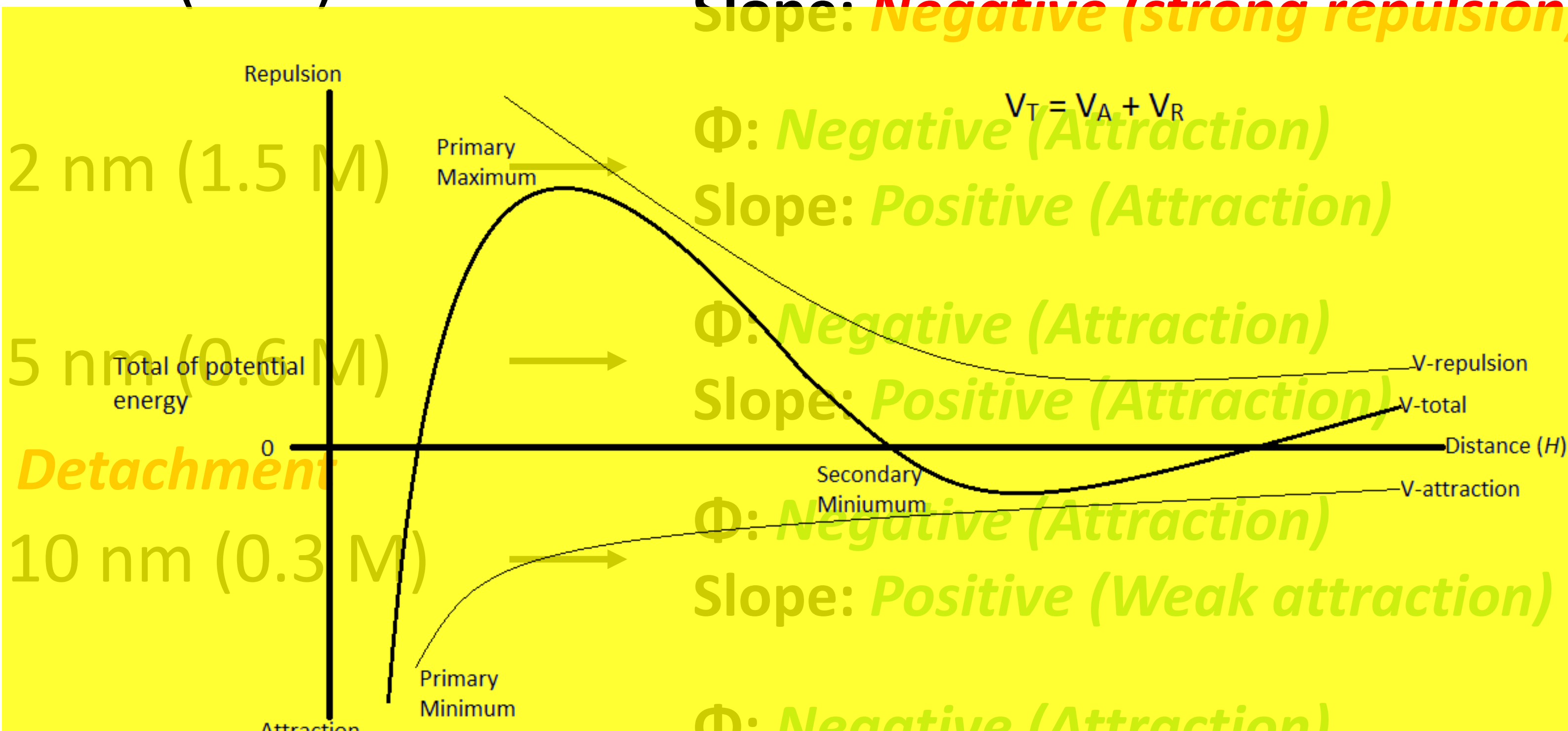
50 nm (0.06 M) → **Φ:** *Negative (Attraction)*
Slope: *Positive (Negligible attraction)*

Less than one kT

Results – particle interactions

B+TECH

1 nm (3 M) → **Φ:** ***Negative (Attraction)***
Slope: ***Negative (strong repulsion)***



2 nm (1.5 M) → **Φ:** ***Negative (Attraction)***
Slope: ***Positive (Attraction)***

5 nm (0.6 M) → **Φ:** ***Negative (Attraction)***
Slope: ***Positive (Attraction)***

Detachment

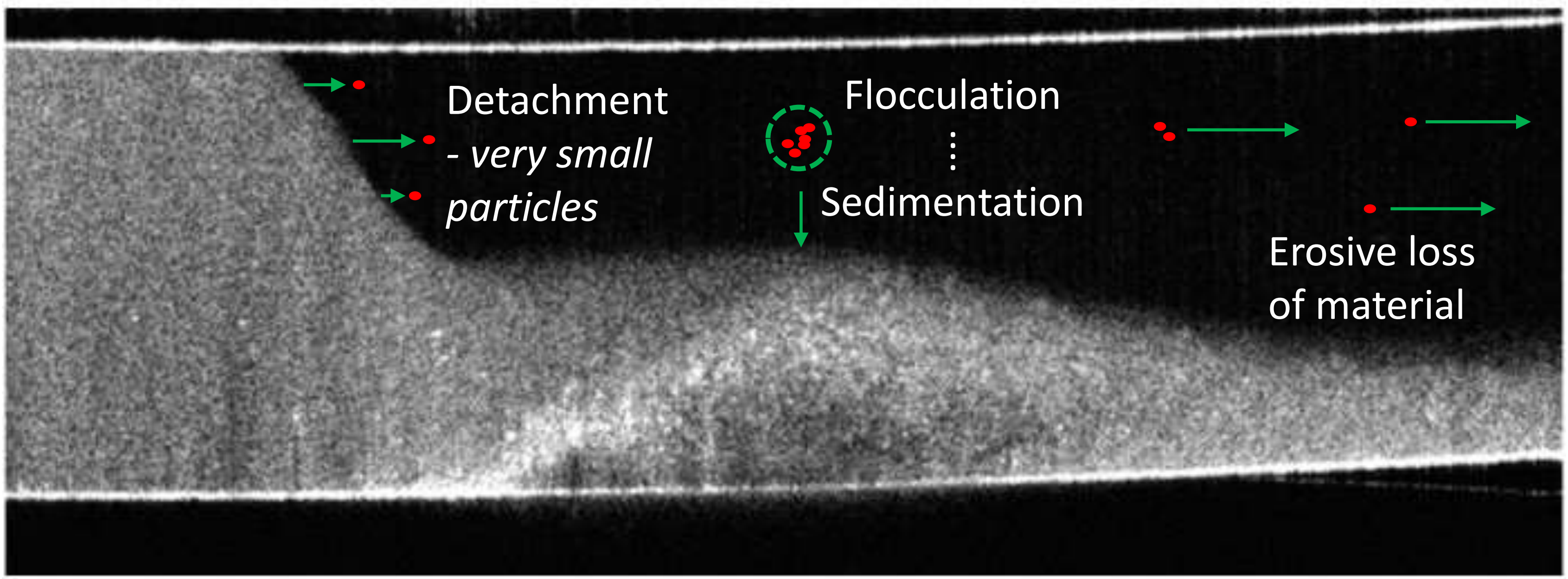
10 nm (0.3 M) → **Φ:** ***Negative (Attraction)***
Slope: ***Positive (Weak attraction)***

50 nm (0.06 M) → **Φ:** ***Negative (Attraction)***
Slope: ***Positive (Negligible attraction)***

Less than one kT

Results – particle interactions

Constant charge model: Non-vdW interaction energy much larger → vdW forces are overcome at shorter distances → detachment at smaller distance.



Conclusions

Particle detachment mechanism	Osmotic swelling (balance of forces: osmotic pressure / particle interactions / GW flow (velocity) / Brownian motion)
Groundwater chemistry / Clay – groundwater interactions	Increased ionic strength (of GW) → reduced osmotic driving force / flocculation due to compressed double layers Porewater composition largely depends on pore model (single vs. multi)
Groundwater velocity	Should have limited to no effect within expected range of velocities

Division of Radiochemistry

Lomonosov Moscow State University, Department of Chemistry

Sorption behavior of Np(V) onto clays from Russian and Indian deposits

Anna Romanchuk[1], I.E. Vlasova[1], P.K. Verma[2], V.V. Krupskaya[1,3], V.G. Petrov[1], P.K. Mohapatra[2], S.N. Kalmykov[1]

[1]*Lomonosov Moscow State University*

[2] *Bhabha Atomic Research Centre. Mumbai, India*

[3] *Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry Russian Academy of Science, Moscow, Russia*

romanchuk.anna@gmail.com

Clays samples

Khakassia Rajastan Kutch

Characterization of clays

Characterization of clays

XRF: Elemental composition

Sample	Composition. %										
	LOI	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5
Rajastan clay	20.06	1.15	4.64	16.28	35.12	0.30	6.67	3.09	0.16	12.27	0.11
Kutch clay	21.43	0.72	2.02	12.33	42.52	0.11	2.77	1.42	0.19	15.58	0.27
Khakassia clay	12.74	2.98	2.48	15.19	58.36	0.97	3.05	0.63	0.09	3.42	0.11

Characterization of clays

XRF: Elemental composition

Sample	Composition. %										
	LOI	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	P_2O_5
Rajastan clay	20.06	1.15	4.64	16.28	35.12	0.30	6.67	3.09	0.16	12.27	0.11
Kutch clay	21.43	0.72	2.02	12.33	42.52	0.11	2.77	1.42	0.19	15.58	0.27
Khakassia clay	12.74	2.98	2.48	15.19	58.36	0.97	3.05	0.63	0.09	3.42	0.11

Characterization of clays

XRD: Phase composition

Khakassia clay

Smectite	66.0
Kaolinite	1.3
Quartz	16.9
Albite	6.6
Microcline	3.7
Orthoclase	1.6
Calcite	2.6
Dolomite	0.5
Gypsum	0.8

Rajastan clay

Smectite	46.8
Illite-smectite MLM	8
Kaolinite	14
Quartz	1.4
Goethite	1.3
Hematite	0.5
Calcite	2.8
Dolomite	8.0
Brushite	2.8
Gypsum	0.7
Anatase	1.7
Amorphous	

Kutch clay

Smectite	76
Goethite	2.5
Calcite	2.9
Quartz	3.0
Anatase	0.5
Amorphous	

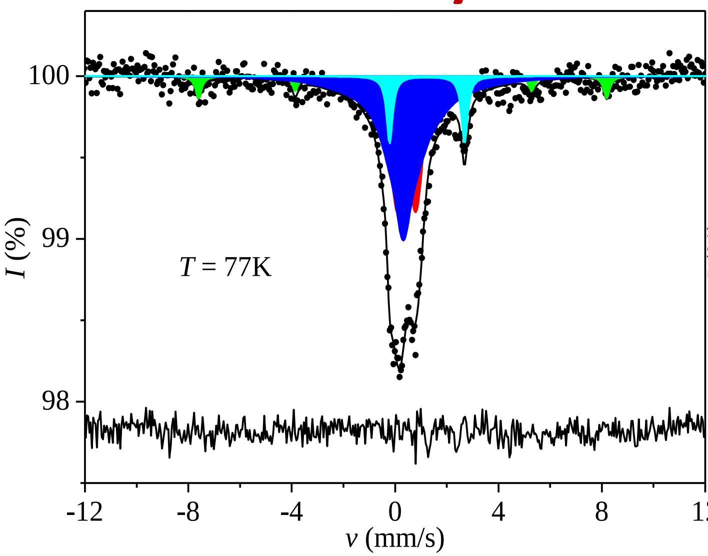
Clay minerals:

67 % 69% 76%

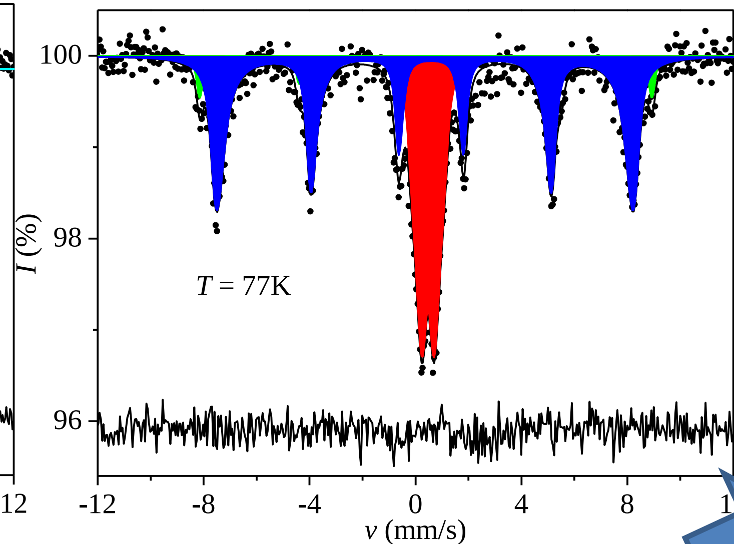
Characterization of clays

Mòssbauer spectroscopy: Iron speciation

Khakassia clay

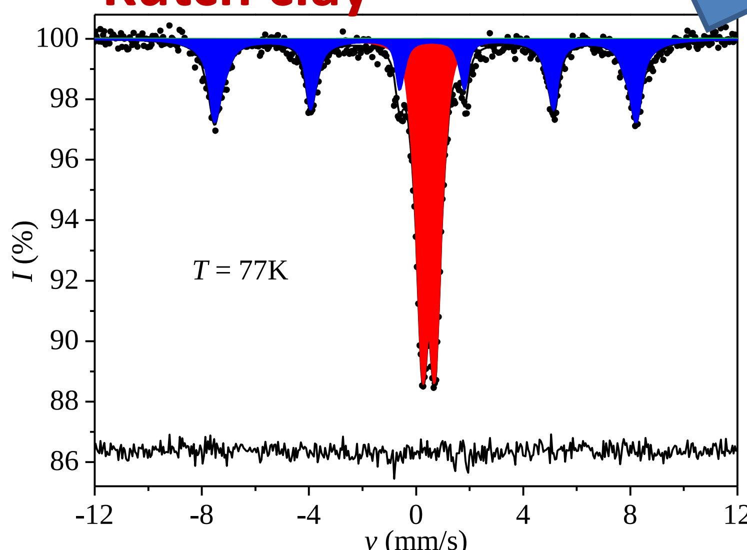


Rajastan clay



Fe(II): structural iron
Fe(III): structural iron and nanoparticles of goethite

Kutch clay



Only Fe(III):
- structural iron,
- hematite (around 5%)
- Nanoparticles of goethite

Summary of characterization

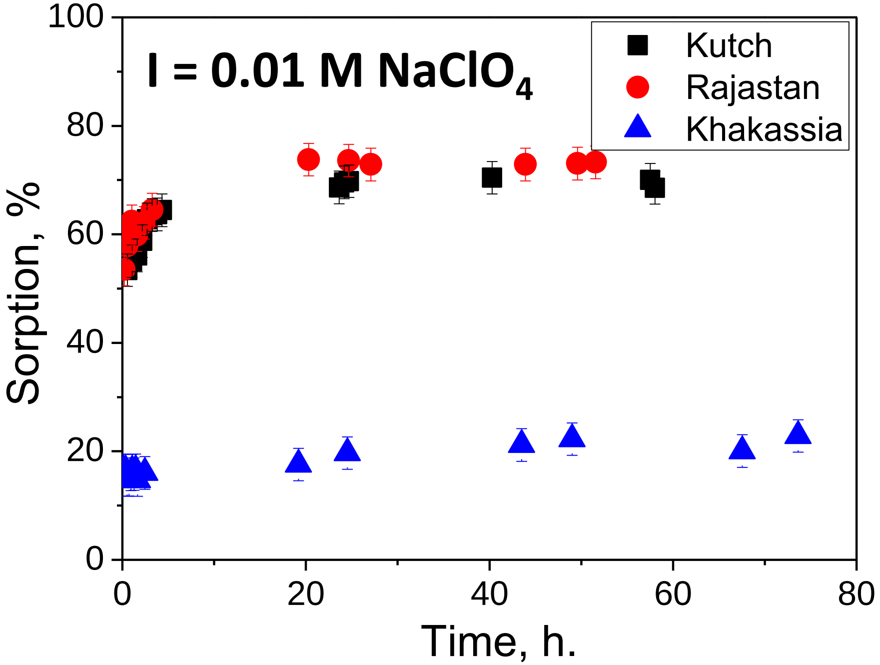
Na-Montmorillonite – 66%
Goethite – around 1.5%
No anatase
SA=15 m^2/g

Na-Montmorillonite – 47%
Illite-smectite MLM – 8%
Kaolinite – 14%
nanoparticles of Goethite – 12%
Hematite – 0.5%
Anatase – 1.7%
SA=50 m^2/g

Ca-Montmorillonite – 76%
nanoparticles of Goethite – 15%
Hematite – 0.5%
Anatase – 0.5%
SA=115 m^2/g

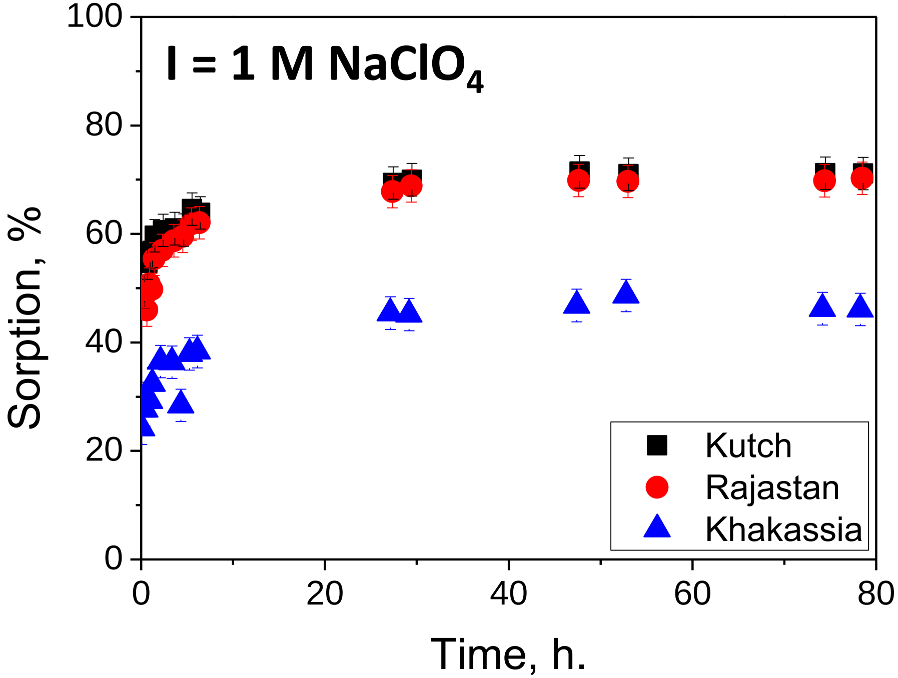
Sorption study

Kinetics of Np(V) sorption onto clay



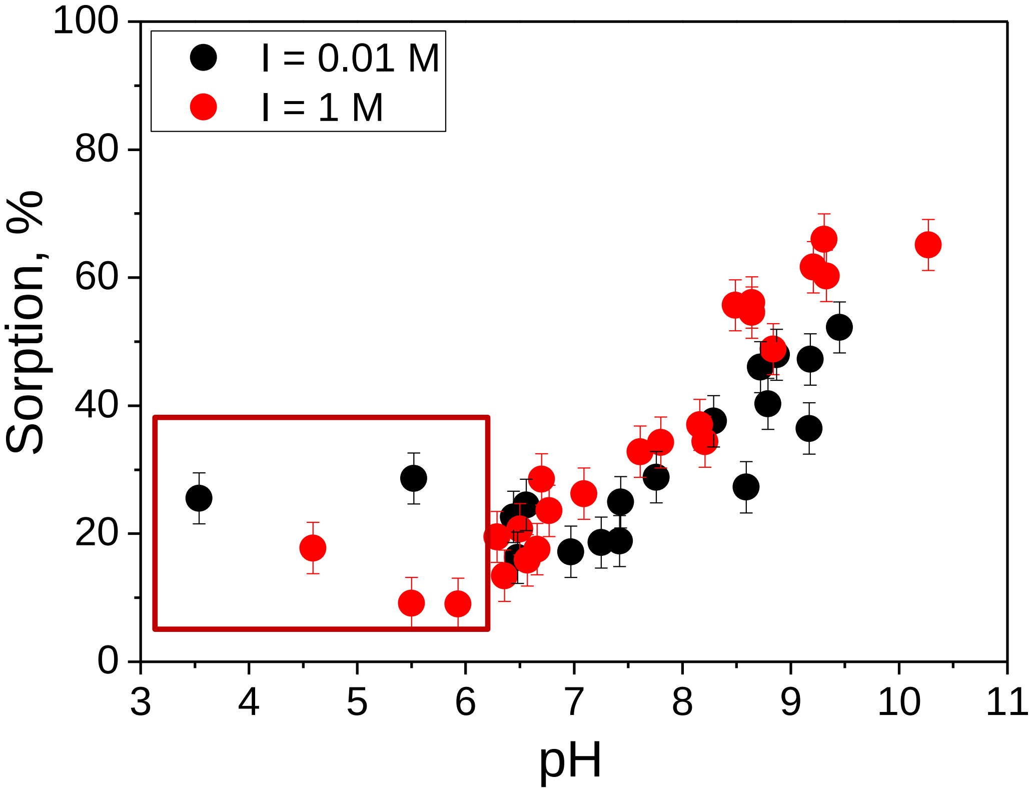
✓Steady state for Np(V) sorption onto clay in ~24 hours

✓Sorption of Np(V) onto Khakassia clay is lower but faster



Np(V) sorption pH-edge

Khakassia clay



✓ At pH > 6.5 sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption

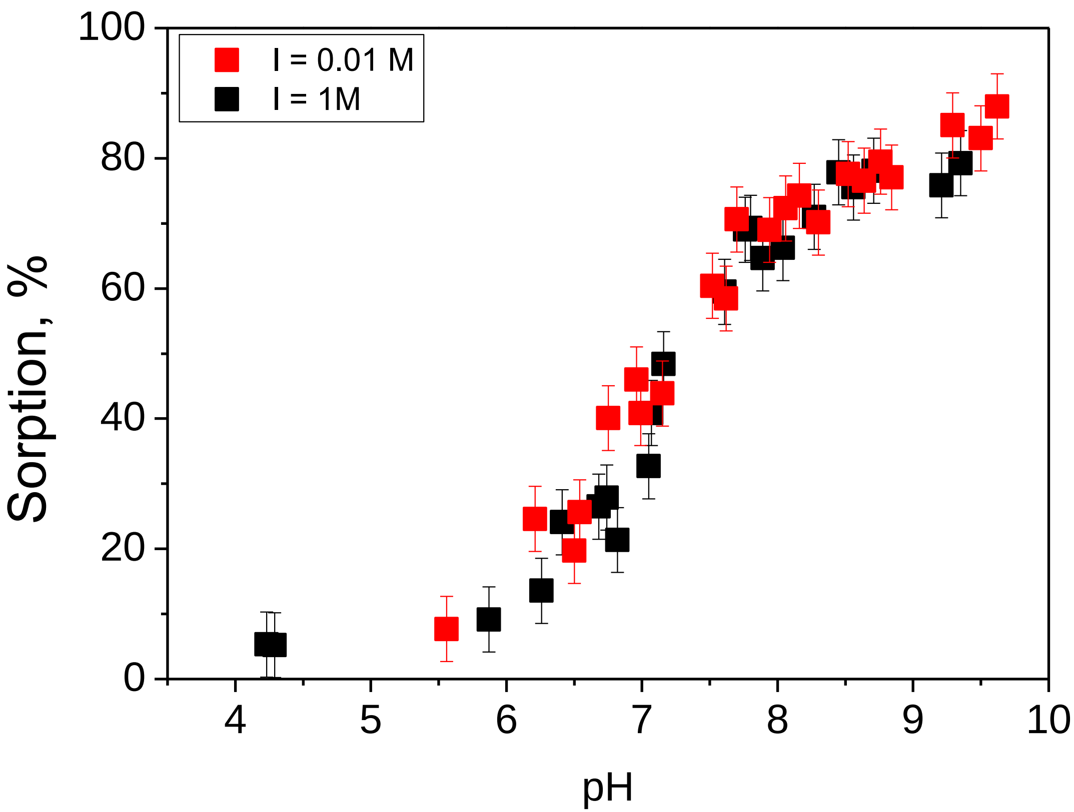
✓ At pH < 6.5 sorption increase with decreasing ionic strength – ion exchange is predominant mechanism

[solid phase] = 0.5 g/L

[Np] = $4 \cdot 10^{-14}$ M

Np(V) sorption pH-edge

Rajastan clay

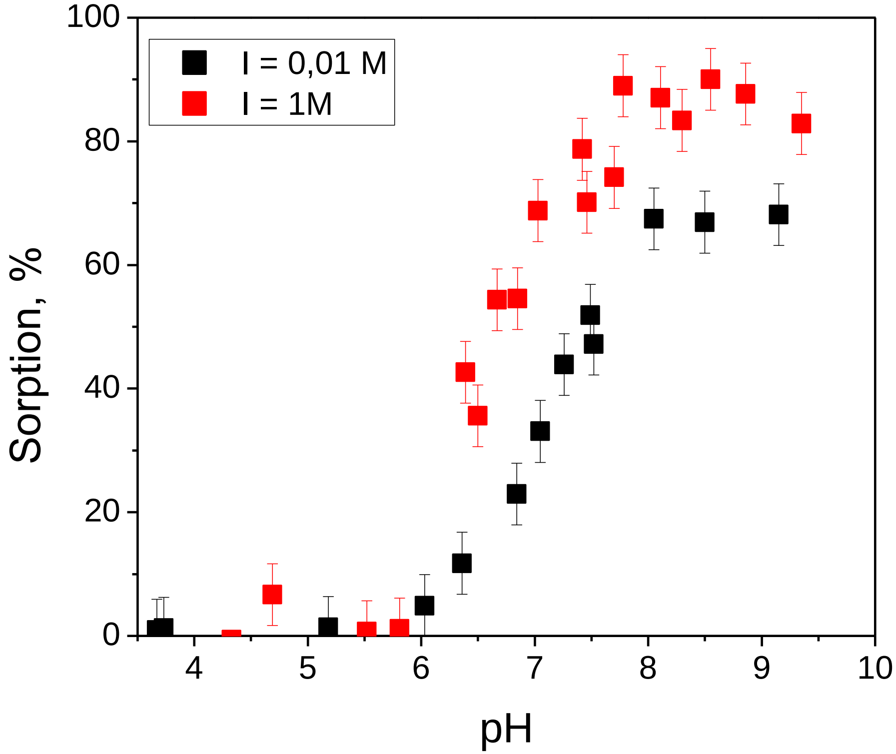


- ✓In all pH range sorption is not dependent on ionic strength – surface complexation is predominant mechanism of sorption
- ✓Sorption is higher than on Khakassia clay

[solid phase] = 0.5 g/L
[Np] = $4 \cdot 10^{-14}$ M

Np(V) sorption pH-edge

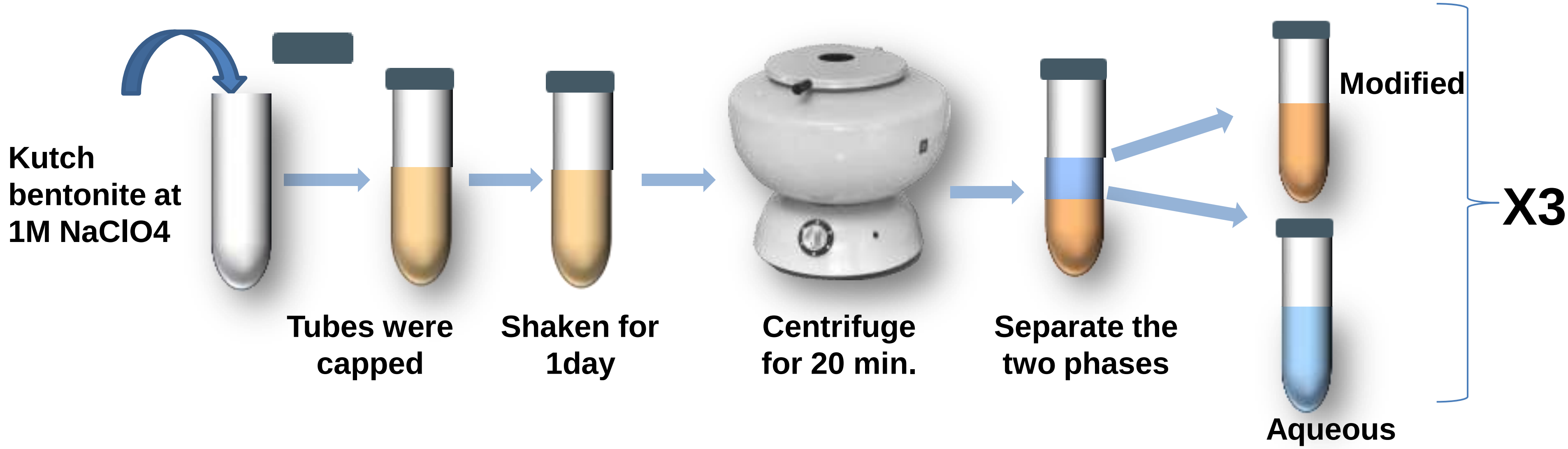
Kutch clay



✓Sorption is higher at I = 1MNaClO4

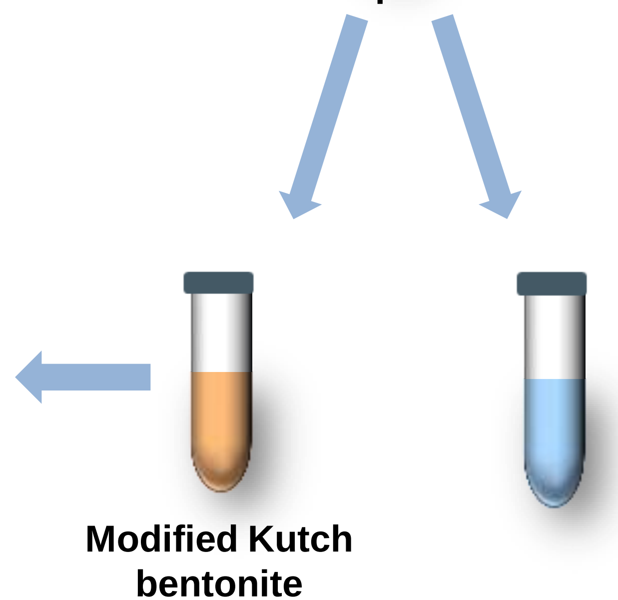
Ca-Montmorillonite influence???

[solid phase] = 0.5 g/L
[Np] = $4 \cdot 10^{-14}$ M

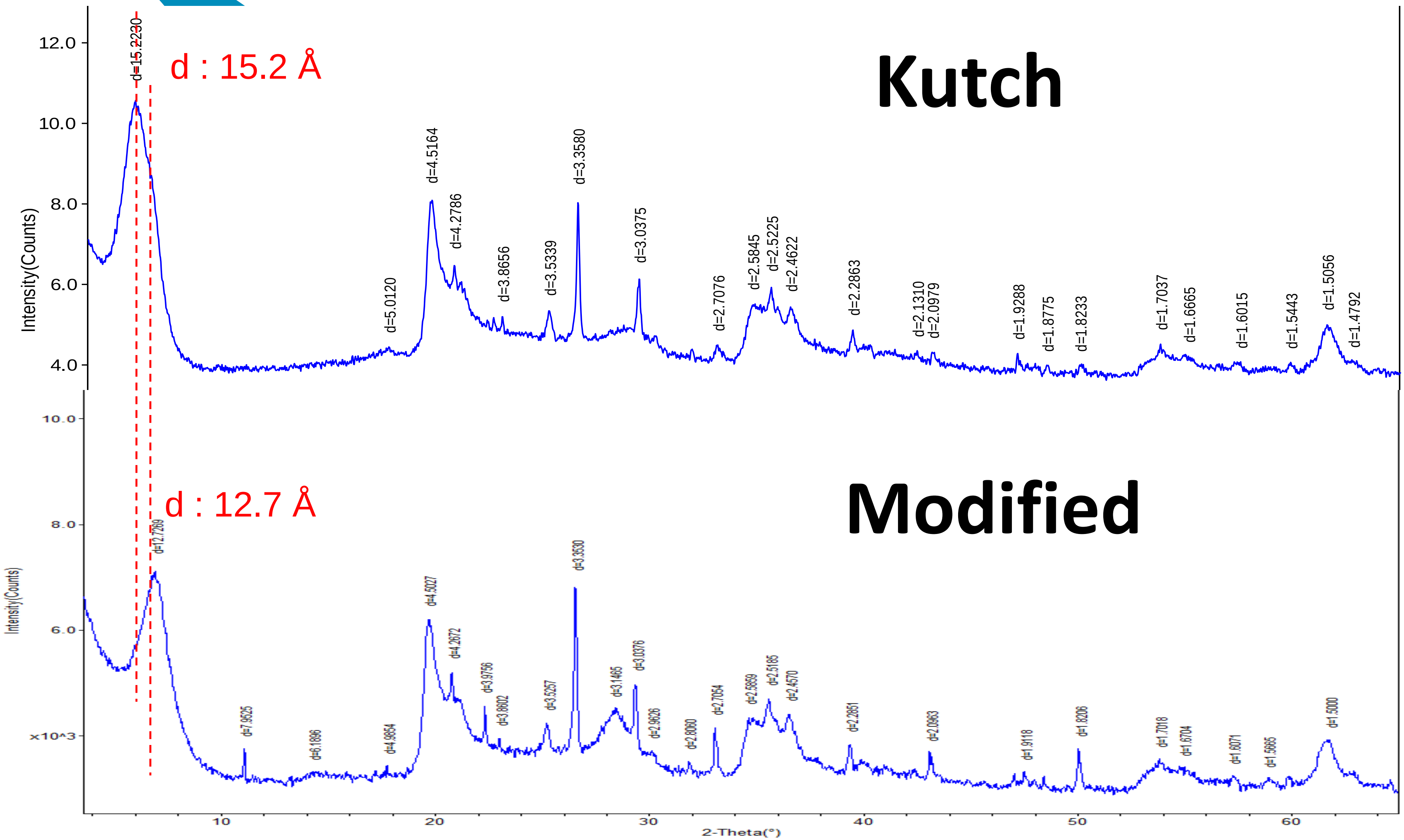


Further studies

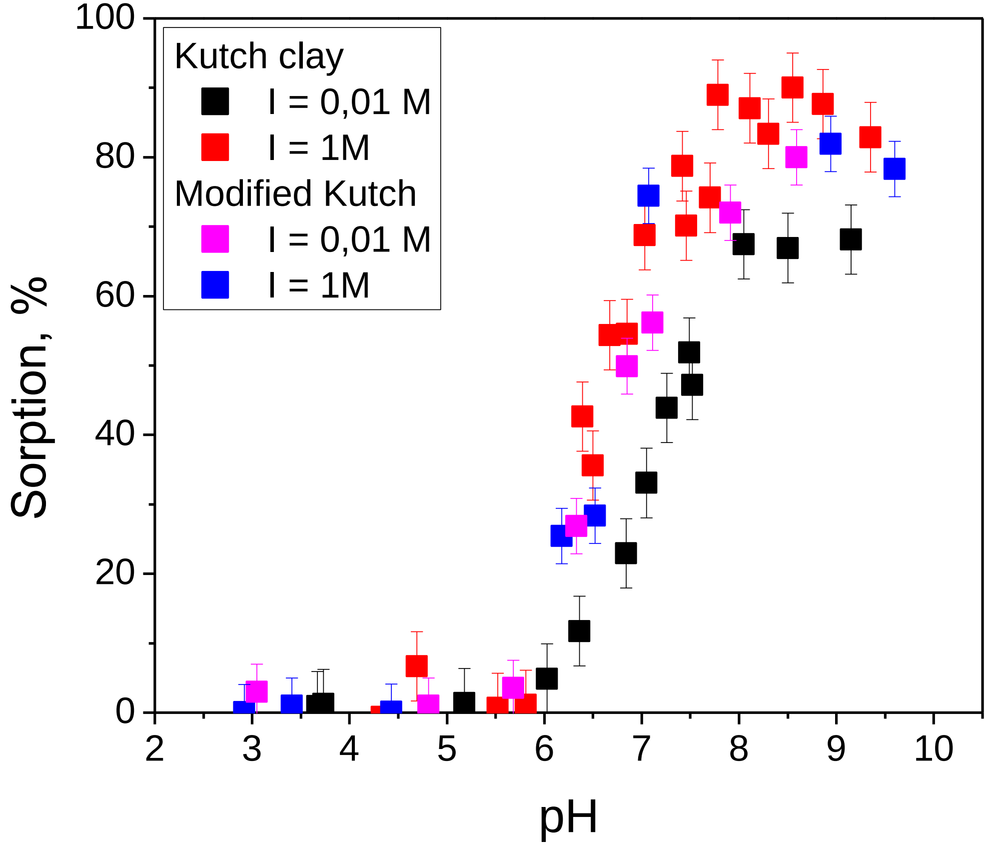
- ❖ Characterization by XRD
- ❖ Np(V) sorption profile



XRD of Kutch and Modified bentonite

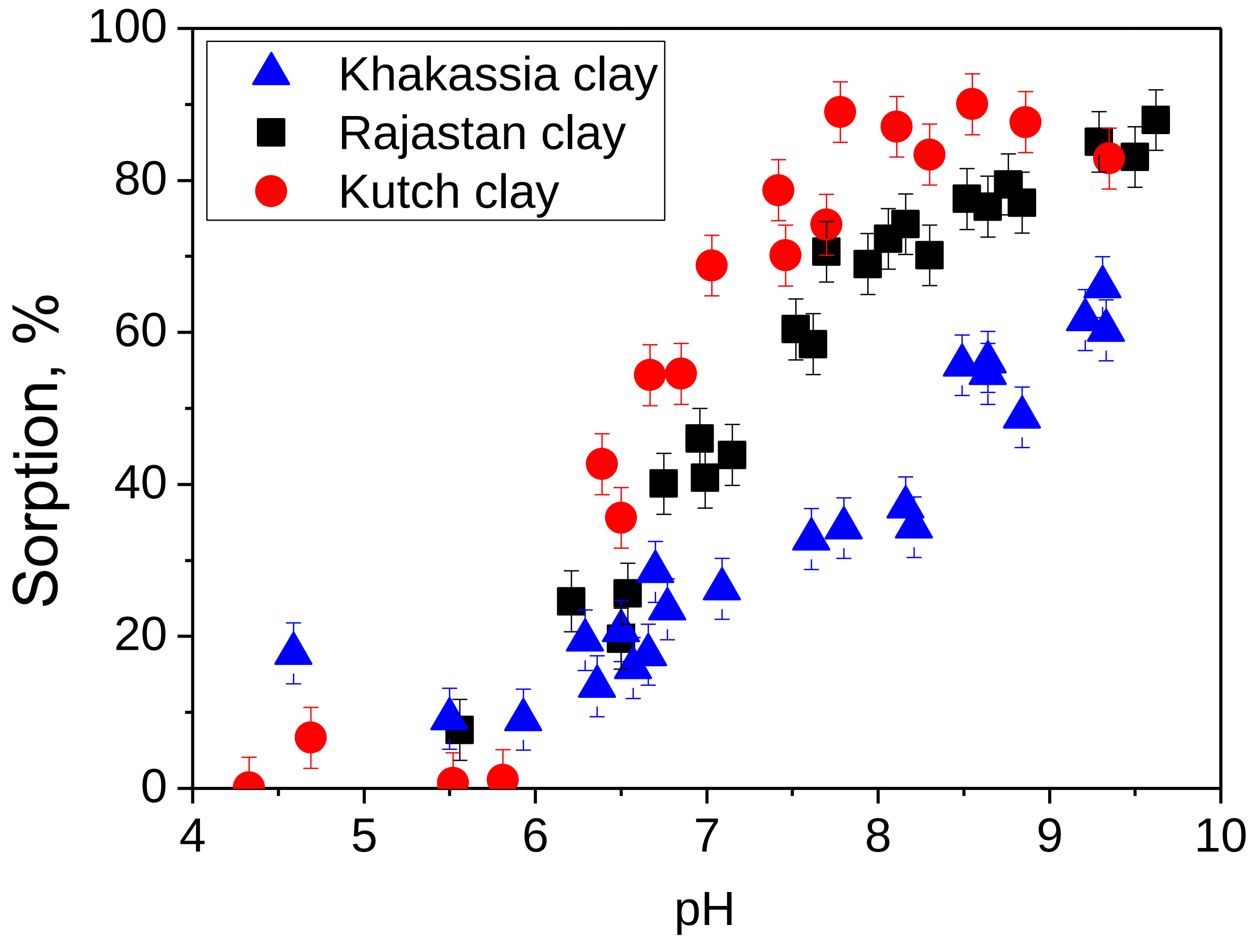


Kutch and Modified bentonite



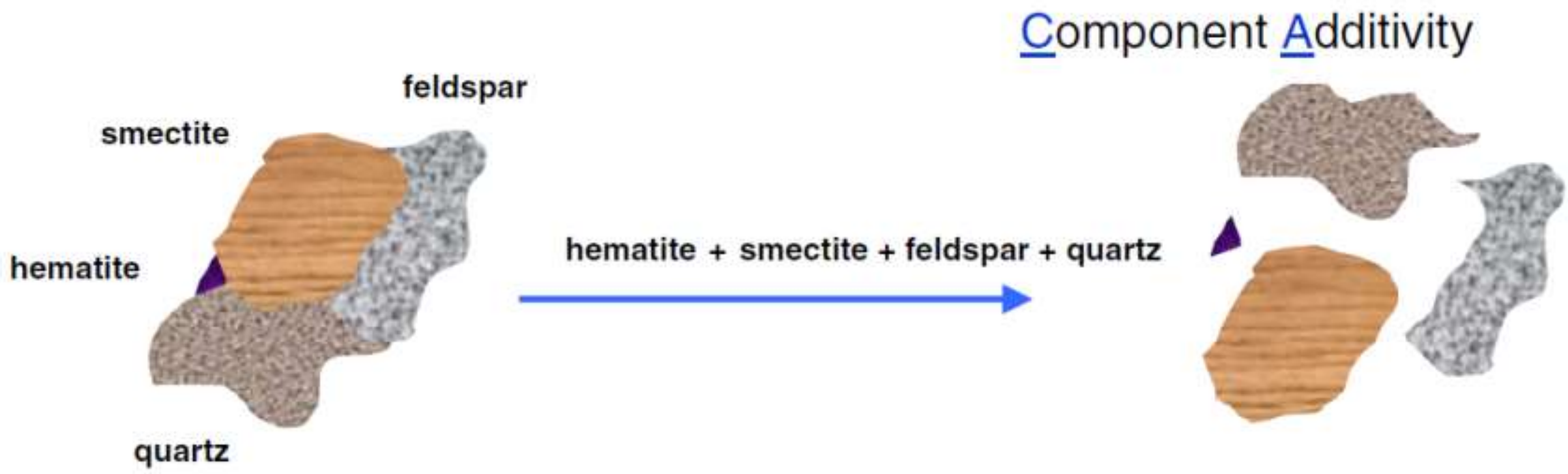
✓Ca-form demonstrate lower sorption

Summary of sorption data



Modeling

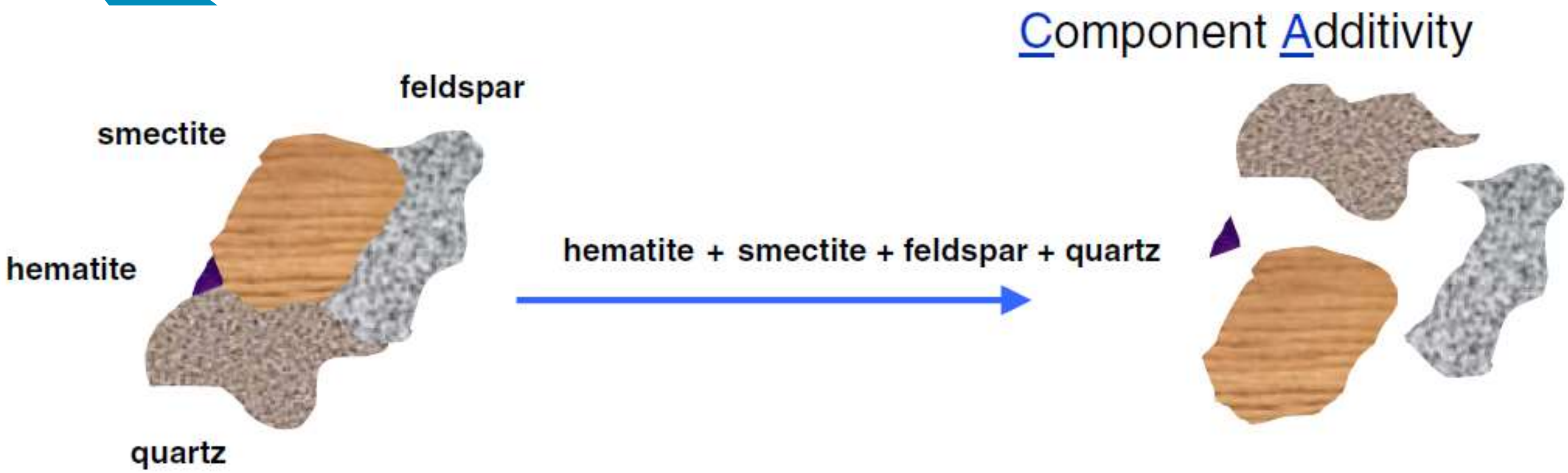
Thermodynamic modeling



- Mineral composition
- Surface properties for each component
- Equilibrium constant for sorption onto pure mineral

NEA Sorption Project Phase II, 2005

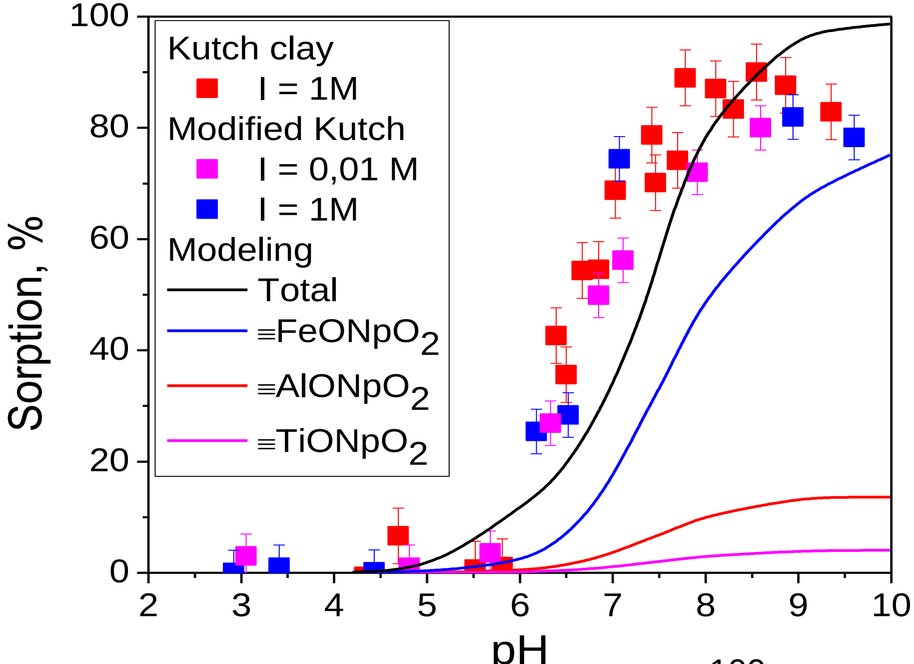
Thermodynamic modeling

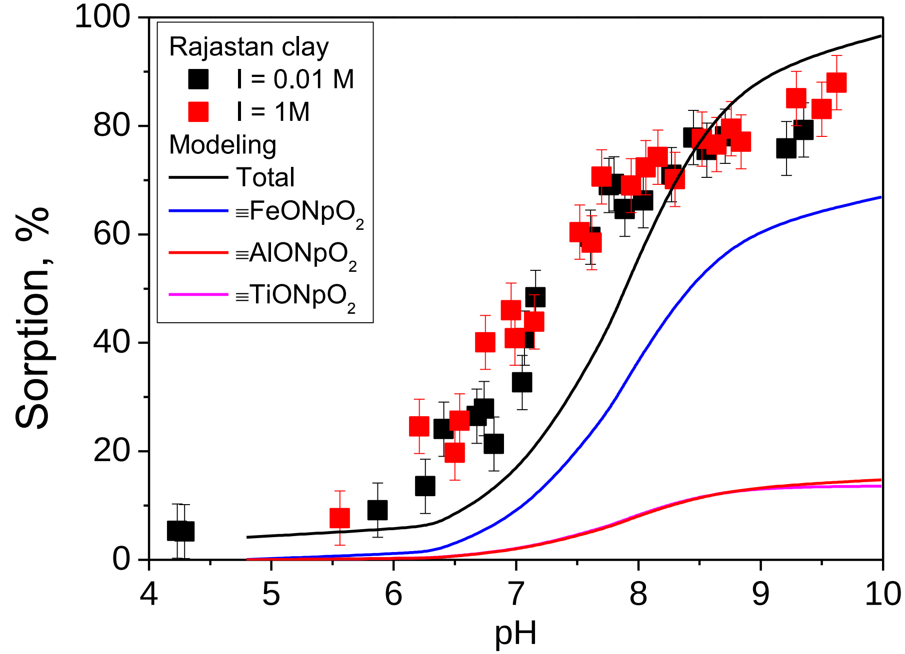


Literature data

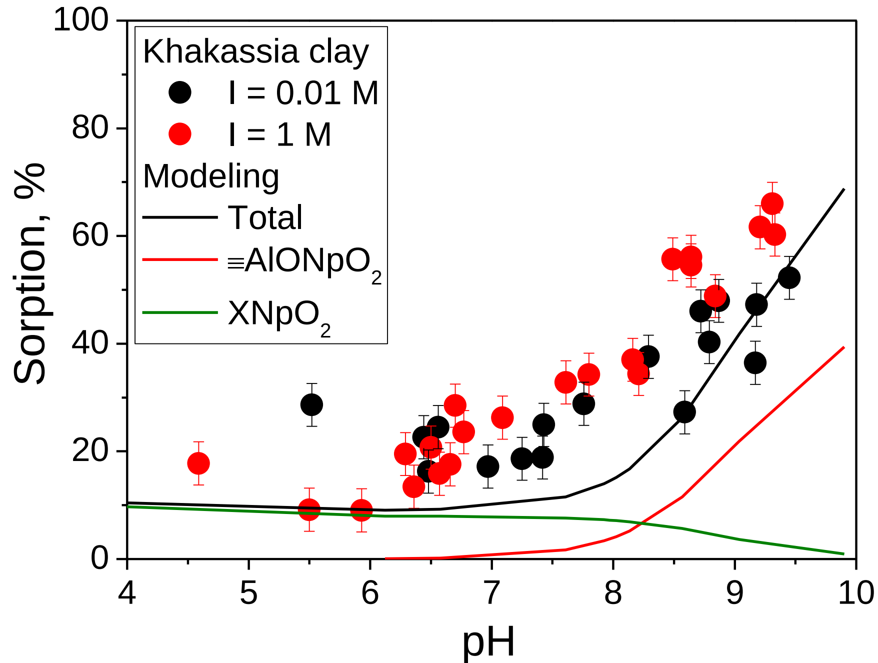
Reaction	log*K*
$\equiv AlOH + NpO_2^+ \rightarrow \equiv AlONpO_2 + H^+$	-4,55
$\equiv AlOH + NpO_2^+ + H_2O \rightarrow \equiv AlONpO_2OH^- + 2H^+$	-13,8
$\equiv FeOH + NpO_2^+ \rightarrow \equiv FeONpO_2 + H^+$	-3,32
$\equiv TiOH + NpO_2^+ \rightarrow \equiv TiONpO_2 + H^+$	-2,89
$NpO_2^+ + X- \rightarrow XNpO_2$	-0.26

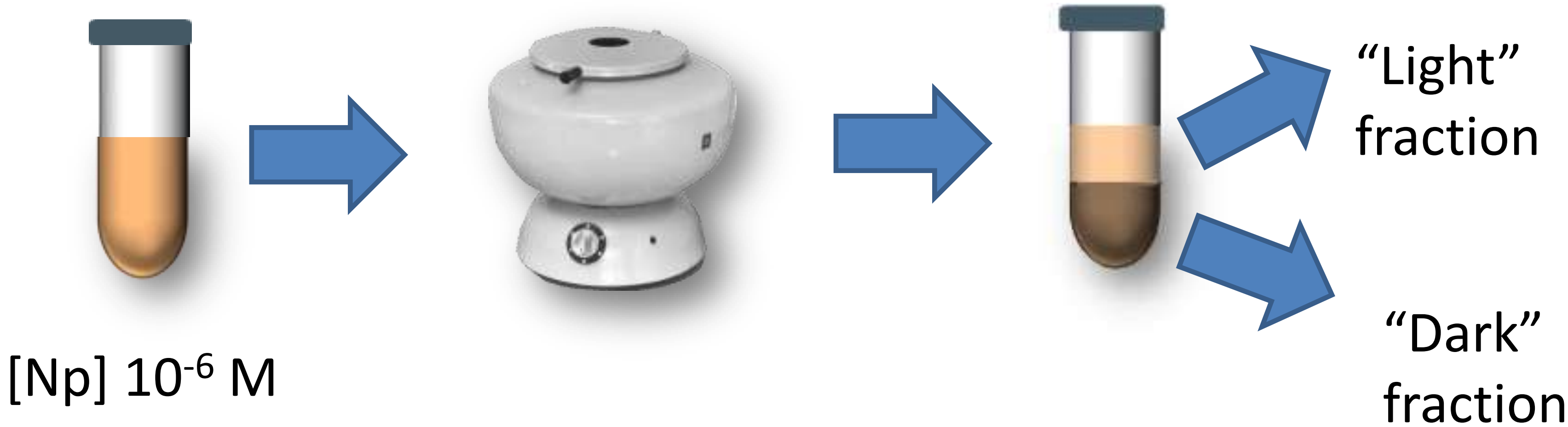
Thermodynamic modeling





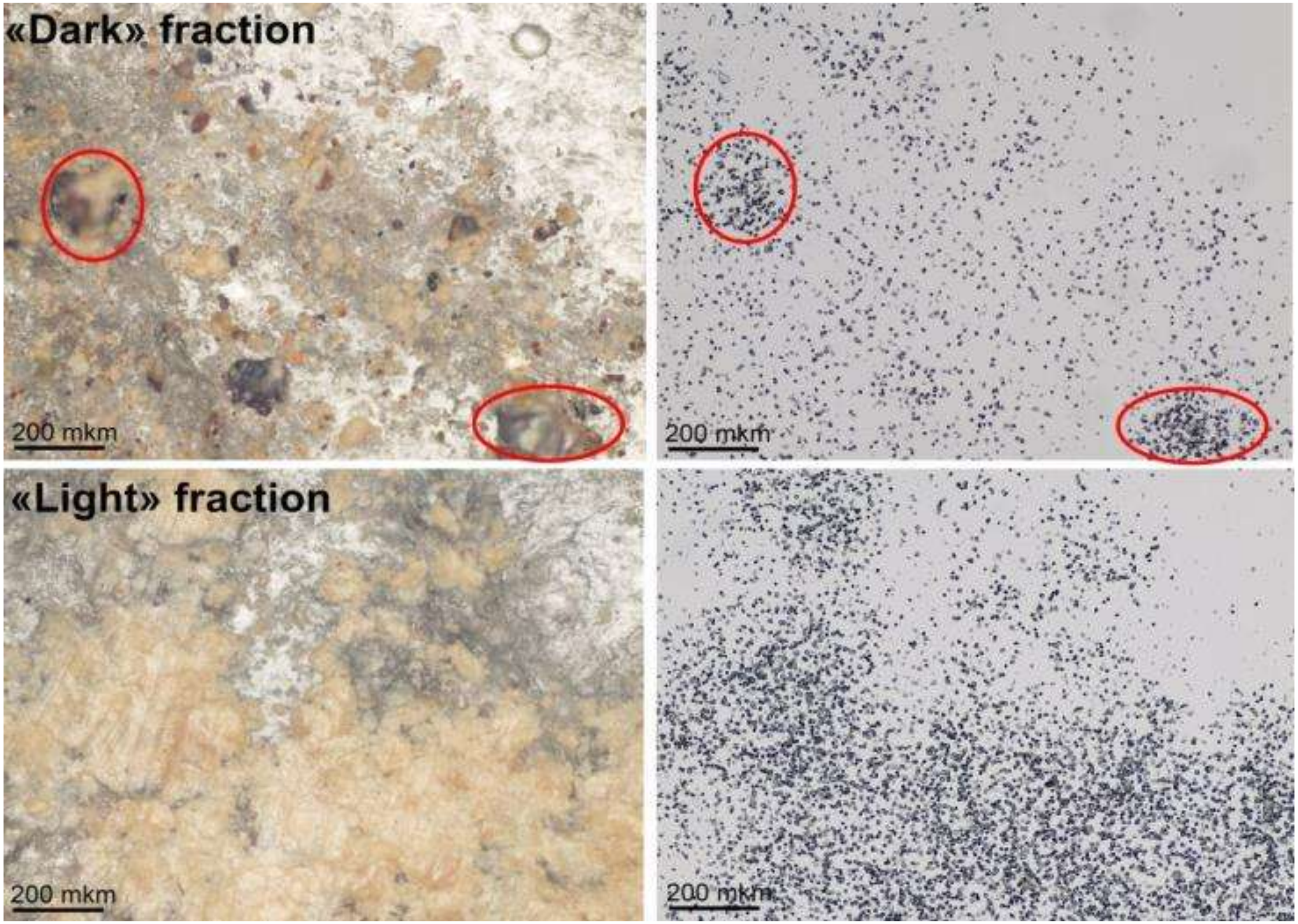
The same set of the equilibrium constants for different clays




[Np] 10^{-6} M
"Light" fraction
"Dark" fraction

α-track analysis images

Rajastan clay



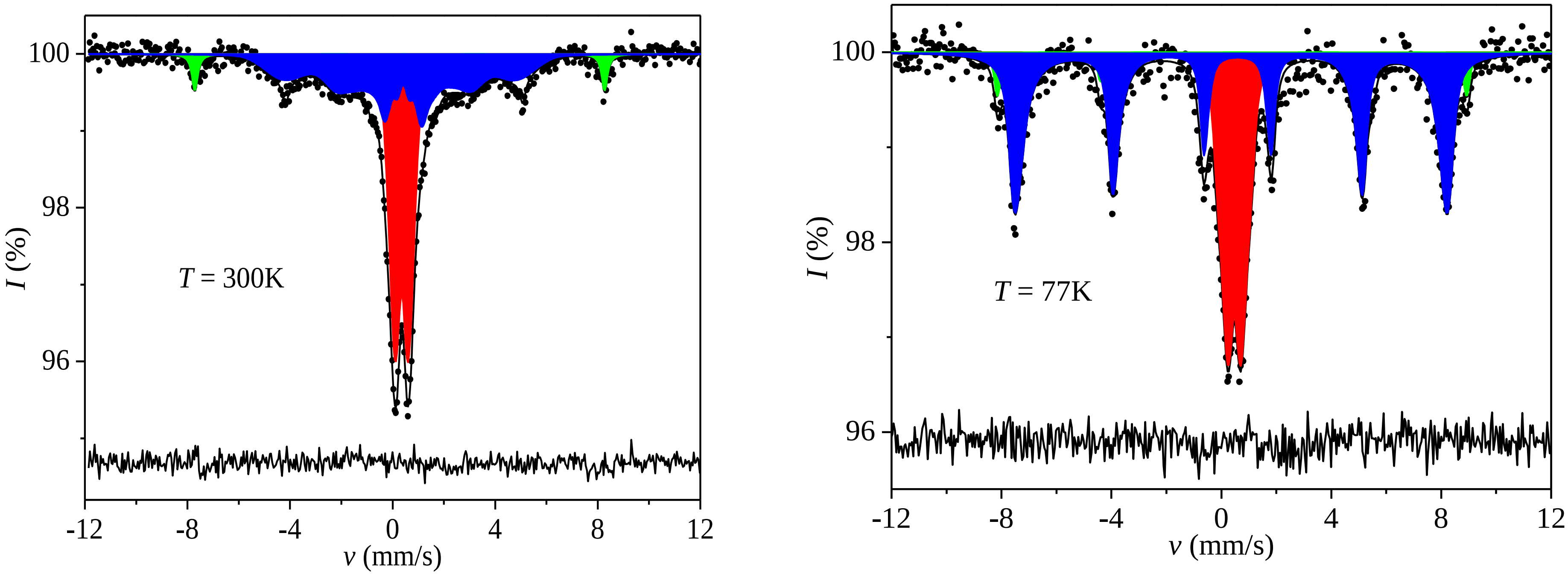
Summary

- Non-clay minerals can dramatically affect on radionuclides sorption onto clay
- Thermodynamic modeling with CA-approach can be used for modeling sorption onto clays

Thank you for your attention!

Mössbauer spectroscopy

Rajastan clay



Study of radionuclides migration through crushed granite in presence of bentonite colloids

Kateřina Kolomá, Radek Červinka

ÚJV Řež, a. s.

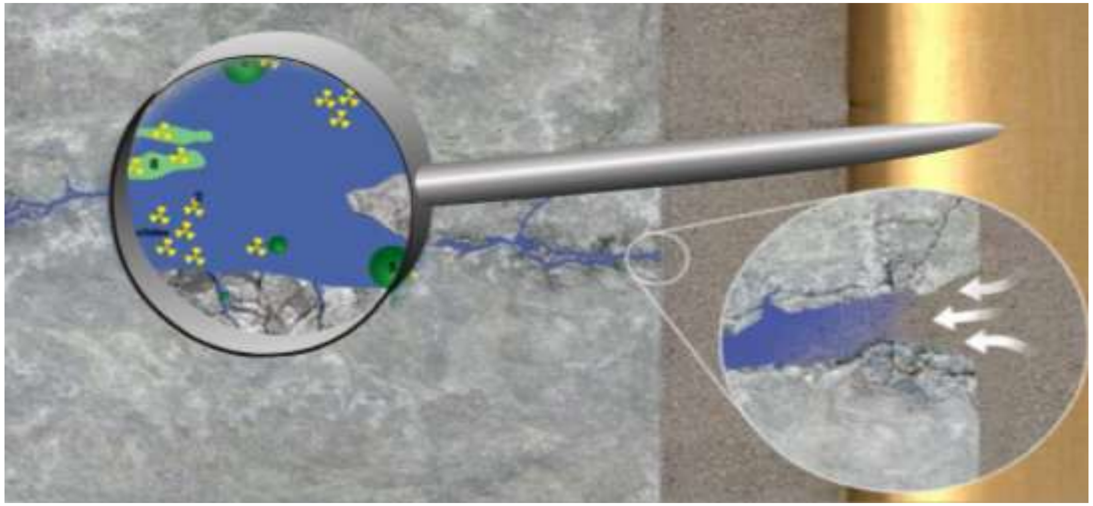
2016

Introduction

- Multibarier system of deep geological repository (DGR)
  - Engineered and natural barirers

www.surao.cz

- Bentonite colloids
  - Formation in engineered barrier system of DGR
  - Generation in contact of bentonite barrier with groundwater
  - Direct impact on repository safety
    - Generation of colloids may degrade the enginerred barrier
    - Colloidal transport of radionuclides may reduce the efficiency of the natural barrier



The goals of experiment

- **Macroscale investigations on colloid mobility in near-natural systems**
  - Study of radionuclide transport in granitic rock
  - Influence of bentonite colloids on radionuclides migration in granite
  - Study of radionuclide, colloid and rock interactions

Experimental background

- Crushed granitic rock → simulation of disturbed granite with fissures network

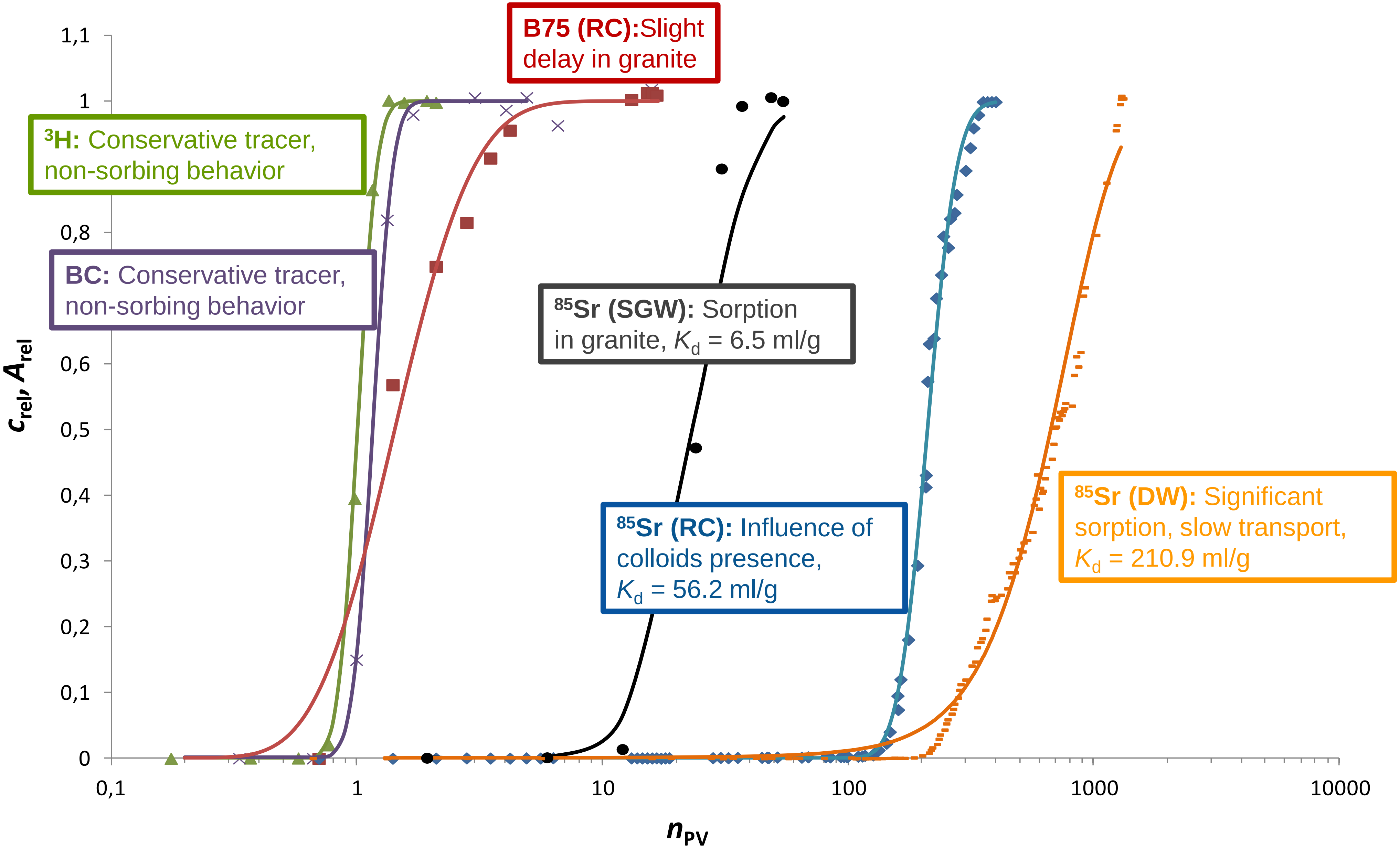
- Bentonite colloids (BC): pure bentonite B75Na^{+}, 400 nm
- Radionuclides
  - ^{3}H
  - ^{85}Sr
  - ^{137}Cs
- Radiocolloids (RC): ^{85}Sr-BC, ^{137}Cs-BC

- Synthetic granitic water (SGW)
- Deionised water (DW)

- Dynamic column experiments
  - Breakthrough curves: transport parameters K_d, R

- The simplified system of:
  - Cationic radionuclides
  - Crushed granite → simulation of disturbed granite (fissure network)

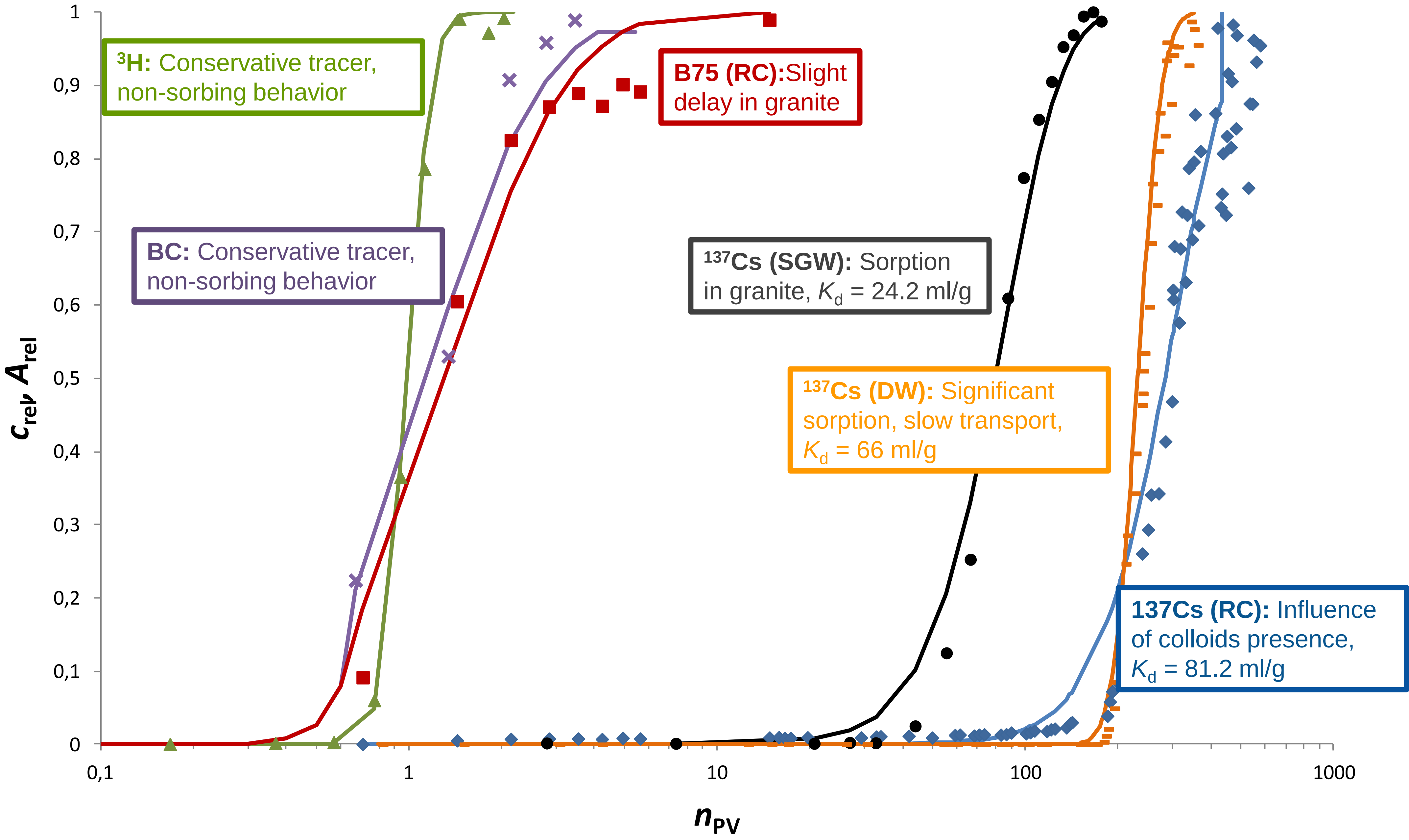
^{85}Sr-bentonite colloids-granite



^{85}Sr-bentonite colloids-granite

- Transport of colloids was fast and comparable with ^{3}H transport.
- Sr transport in SGW was significantly faster than Sr transport in DW.
- After injection of radiocolloids, bentonite colloids without Sr appeared first followed by Sr much more later.
- Sr transport through granite in presence of bentonite colloids in DW was faster than Sr transport in DW.
- Colloids migration in presence of Sr was slightly slower than transport without Sr presence.

^{137}Cs-bentonite colloids-granite



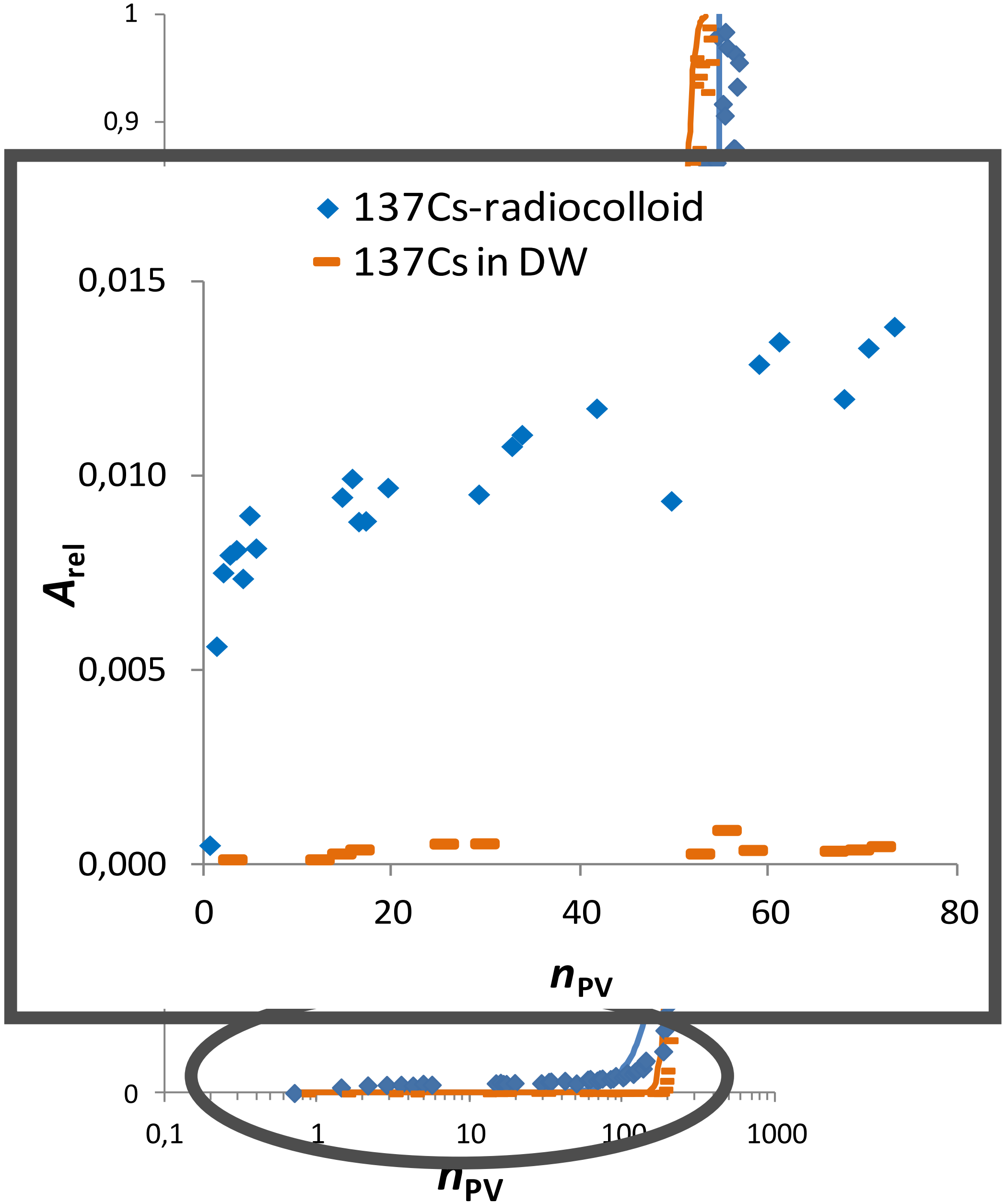
^{137}Cs-bentonite colloids-granite

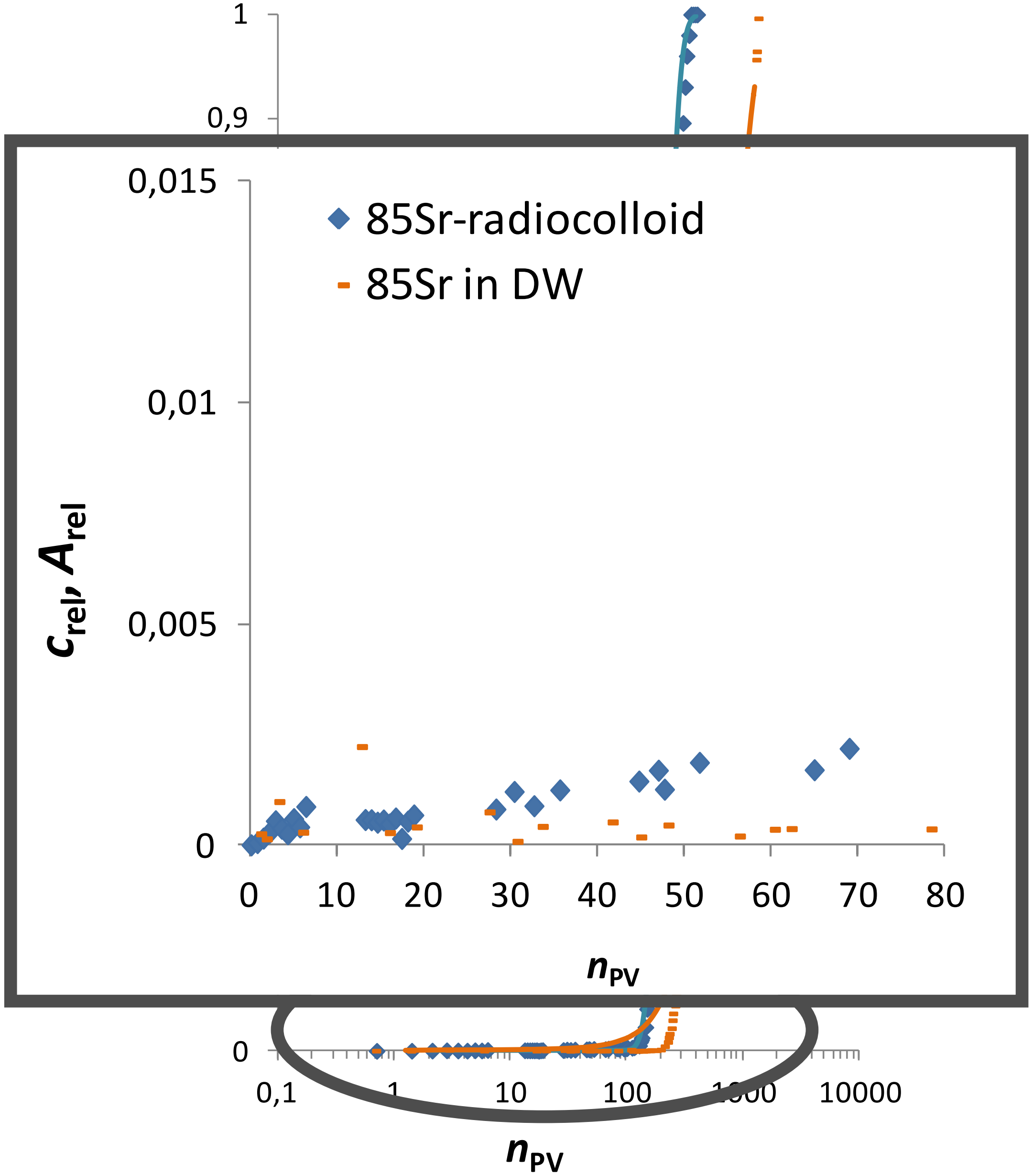
- Transport of colloids was fast and comparable with ^{3}H transport.
- Cs transport in SGW was significantly faster than Cs transport in DW.
- After injection of radiocolloids, bentonite colloids with small part of Cs appeared first followed by Cs much more later.
- Part of Cs passed through granite with bentonite colloids, the most of is sorbed.
- Cs transport through granite in presence of bentonite colloids in DW was not same as Cs transport in DW.

^{137}Cs-bentonite colloids-granite

^{85}Sr-bentonite colloids-granite

- Different behavior of Cs and Sr, even though they are cationic, sorbing RN.





Different mechanism of Cs and Sr sorption on colloid particles

Sorption of cesium

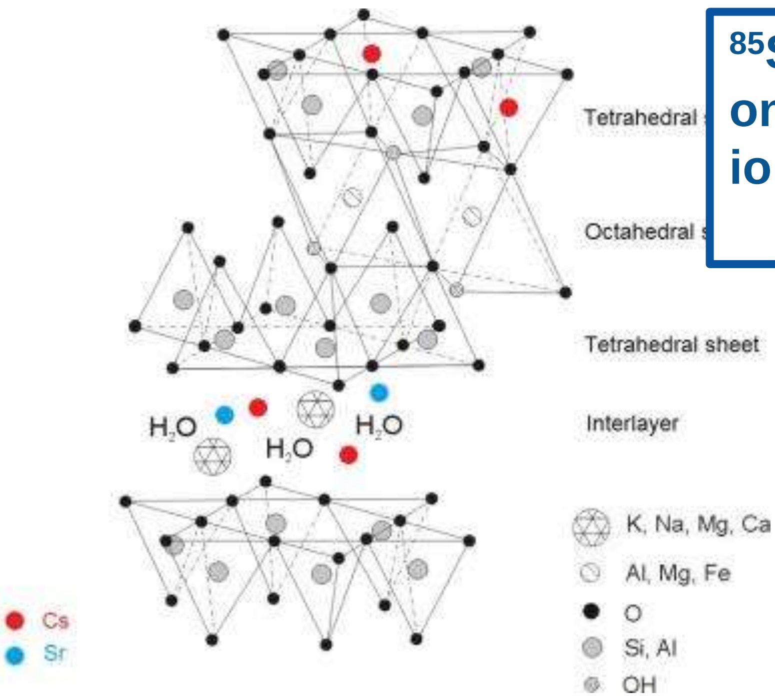
Bentonite structure:

- **Layer sites –** permanent negative charge → cation sorption, weak bond of cesium → desorption of cesium from bentonite and follow sorption on granite.

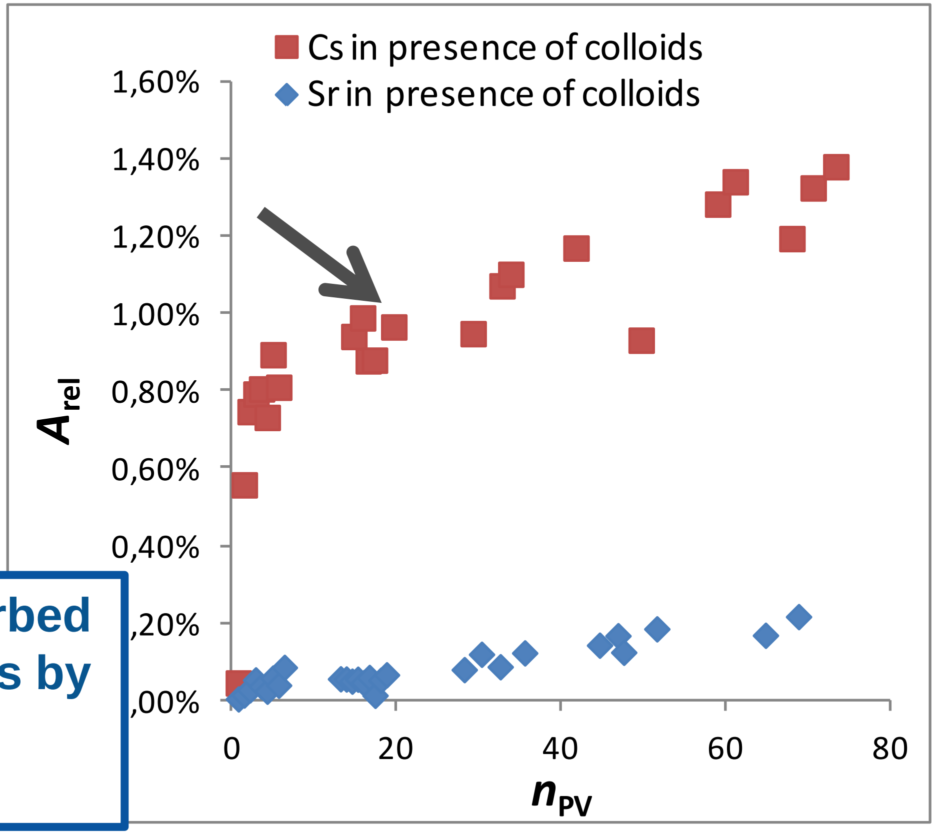
- **Freyed edge sites (FES) –** surface complexation, less available but highly selective sites → strong bond of cesium.

Sorption of strontium

- Sorption by ion-exchange
- Divalent ion → large hydration energy → the freyed edge sites are not accessible for Sr^{2+}.



^{85}Sr is reversible sorbed on bentonite colloids by ion-exchange.



The minor part of ^{137}Cs is strongly sorbed on <u>freyed edge site</u> and passed through granite with colloids.

Most cesium was desorbed from <u>layer sites</u> of montmorillonite on granite.

Different mechanism of Cs and Sr sorption on colloid particles

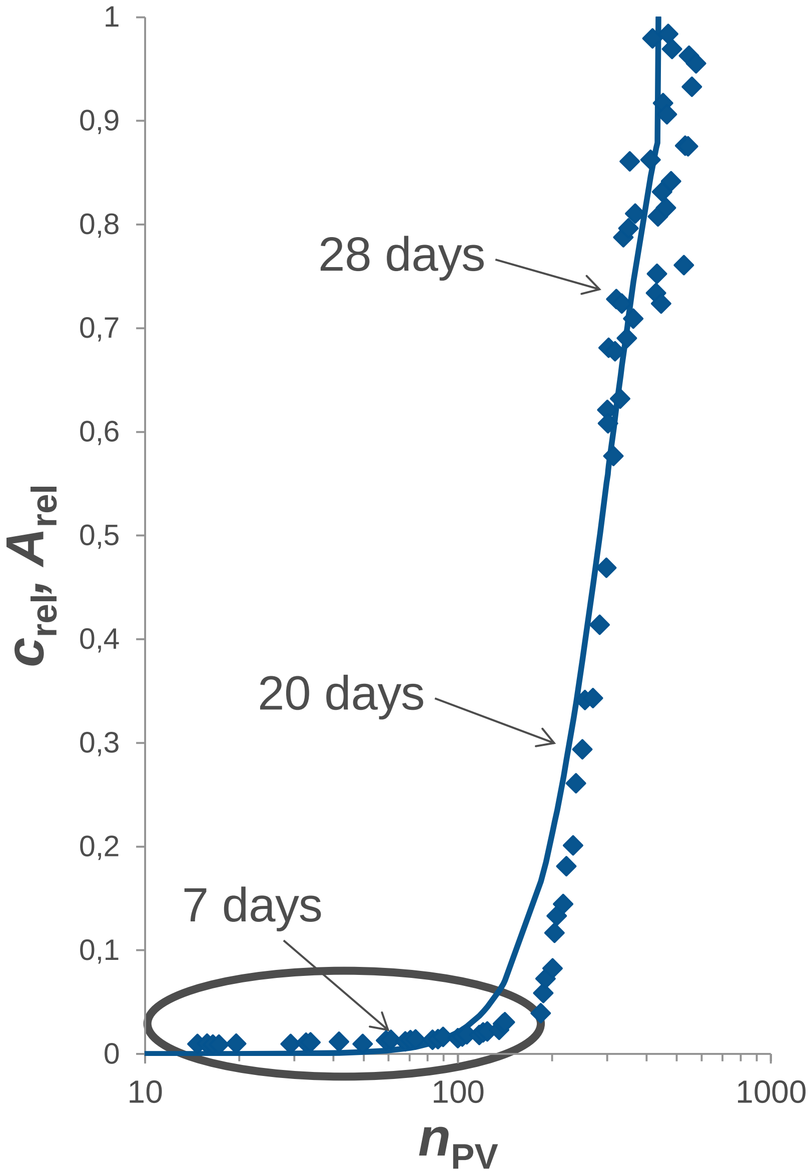
Sorption of cesium

Bentonite structure:

- **Layer sites –** permanent negative charge → cation sorption, weak bond of cesium → desorption of cesium from bentonite and follow sorption on granite.

- **Freyed edge sites** – surface complexation, less available but highly selective sites → strong bond of cesium.

Days	Activity at column outlet		
	A (CPM)	A (%) (liquid phase)	A (%) (solid phase)
7	222	8	92
20	7251	40	60
21	10241	57	43
28	11866	55	45
30	12048	56	44

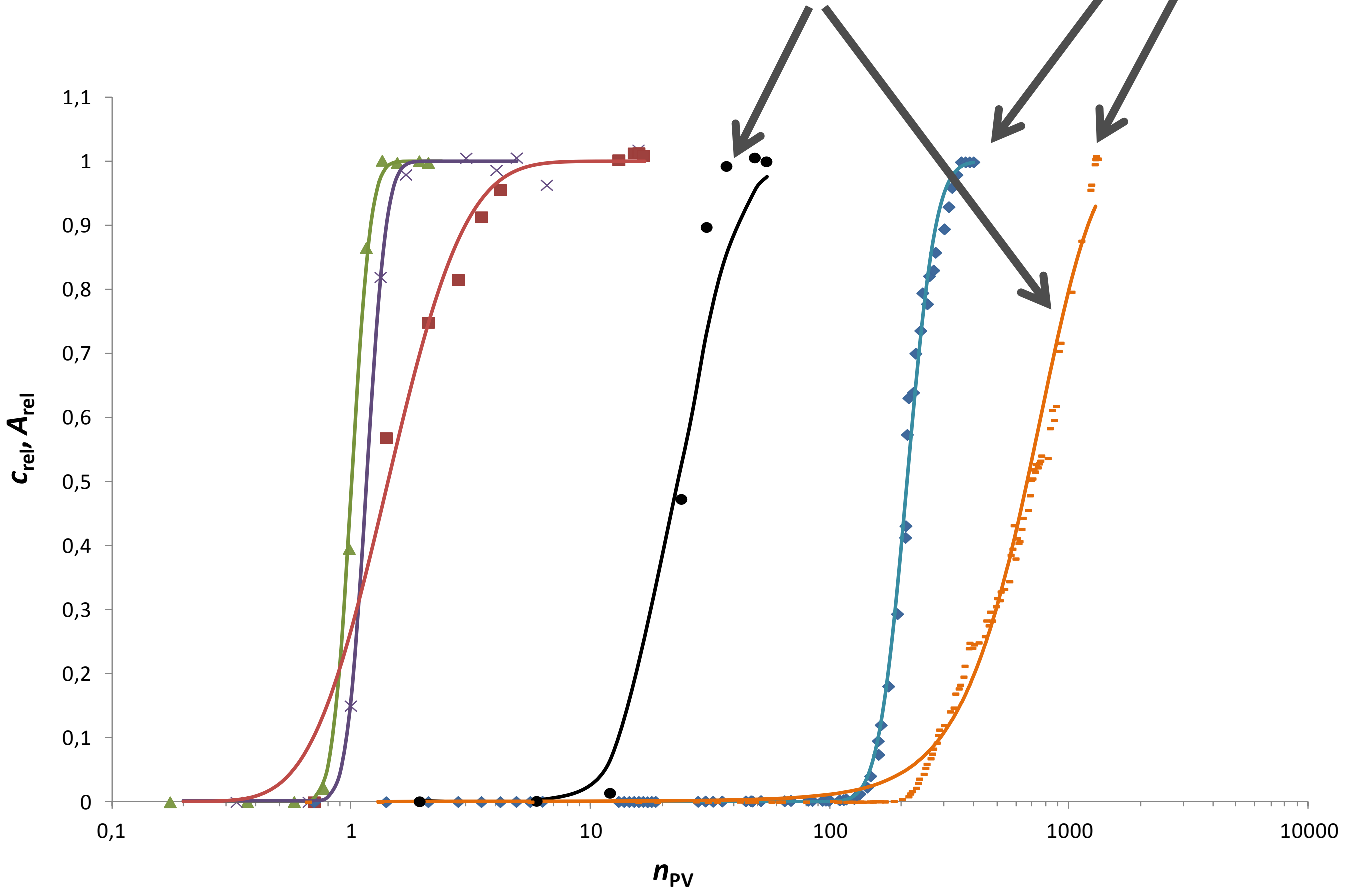


Conclusions

Colloid mobility controlling processes

Clay colloids as radionuclide (RN) carriers?
Is there an upper bound for colloids-mediated transport?

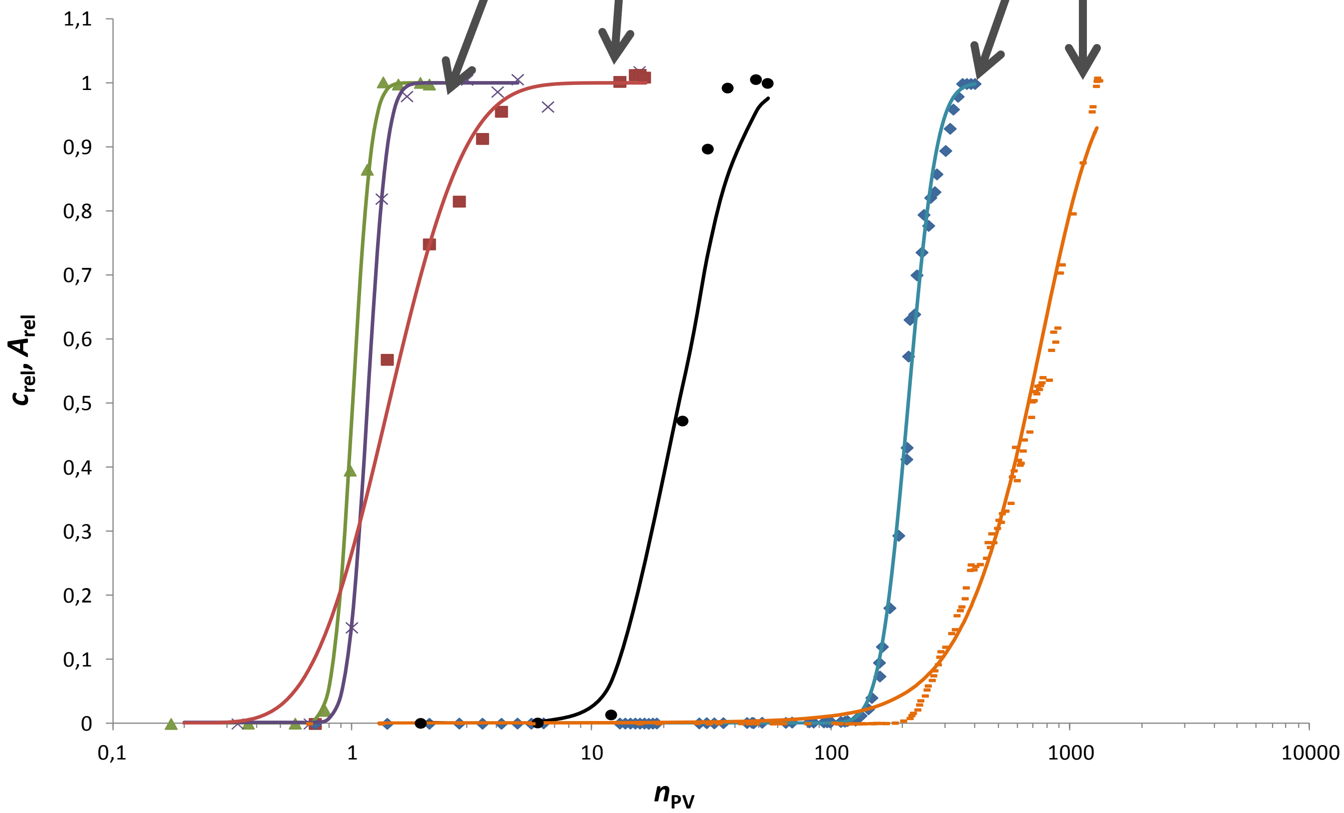
- RN transport through granite in presence of bentonite colloids was faster than RN transport in distilled water without presence of bentonite colloids.
    - Colloids carried RN further in column with earlier breakthrough.
- Influence of liquid phase composition
    - RN transport in SGW is significantly faster than RN tranport in distilled water.
    - Competition of other ions with RN at sorption sites.



Retention processes

Can retardation of colloids in the far field cause the delay of RN arrival in biosphere?

• The colloids migration in presence of RN was slightly slower than transport without presence of RN.
• The delay of RN caused by retardation of colloids in granite was not observed.
• On the contrary, the colloid particles speed up the RN transport in granite.



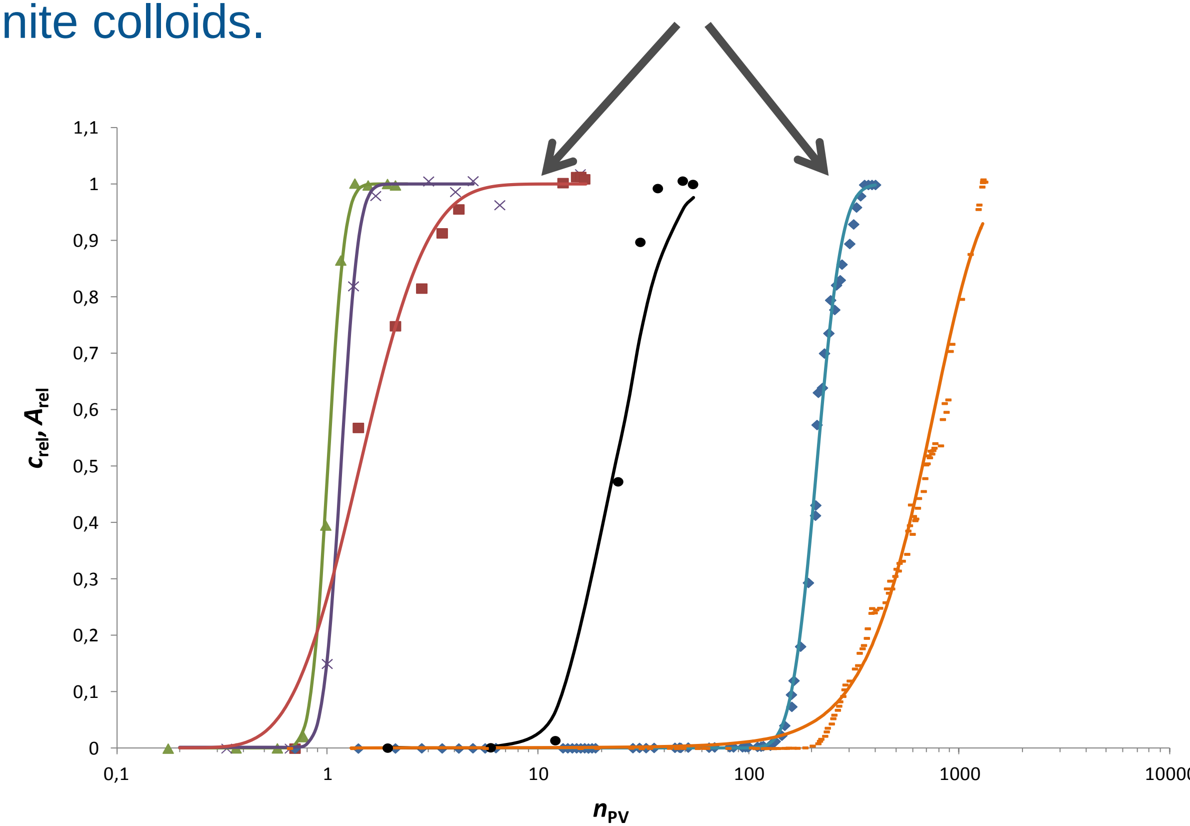
Radionuclide sorption

Equilibrium sorption of radionuclides (RN) onto mobile colloids.
Reversible sorption of radionuclides on colloids?

- The sorption of RN onto mobile colloids was confirmed.
  - Time of equilibration: 7 days
  - V (colloids) : V (RN) = 1:1
  - Separation of phases: centrifugation

  - Sr-colloids: 80% of ^{85}Sr was sorbed on bentonite colloids
  - Cs-colloids: 75% of ^{137}Cs was sorbed on bentonite colloids

  - Reversible sorption: The RN affinity towards the granite was higher than toward the bentonite colloids.



Acknowledgement

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no295487, the BELBaR project.

References

Videnská K., Červinka R. (2015) Study of ^{85}Sr transport through a column filled with crushed granite in presence of bentonite colloids. Clay Conference Brussels 2015, March 23-26, 2015, Brussels, Belgium.

Berlin, 4 February 2015

RADIONUCLIDE (RN) TRANSPORT IN THE PRESENCE OF BENTONITE COLLOIDS (BC): SUMMARY OF THE STUDIES CARRIED OUT AT CIEMAT

Tiziana Missana, Miguel García-Gutiérrez,
Ursula Alonso, Manuel Mingarro

Physico-chemistry of Actinides and
Fission Products Unit

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD
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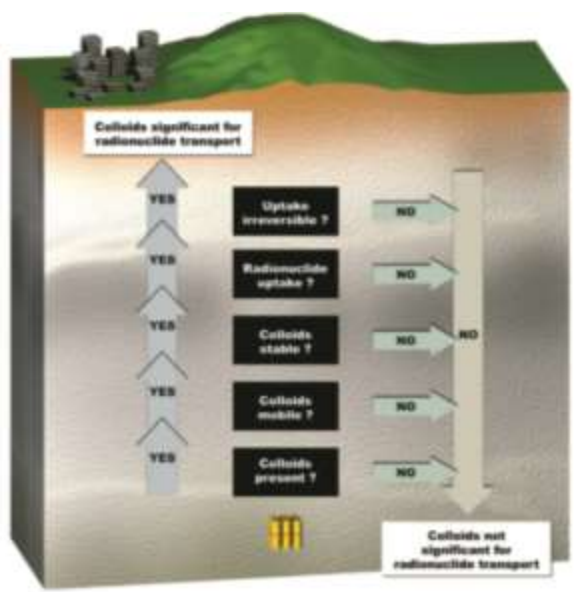
What have we learnt on BC & RN transport in granite ?

- Based on BELBAR and previous studies with FEBEX clay.
- Examples of radionuclides of different type (Eu, Sr, U and Cs).
- Examples of very different scenarios from a chemical point of view (Grimsel and Äspo).



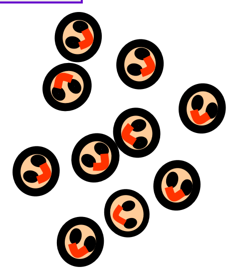
<u>First of all:</u> transport experiments must be included in a wider context, in which studies related to the "colloid ladder" questions have been considered.

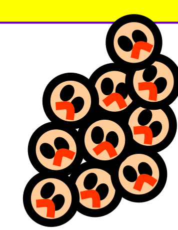
Information on chemistry of the <u>scenario</u>;

- Stability of colloids;
- Mobility of colloids;
- Adsorption of the radionuclide on colloids.

BENTONITE COLLOID STABILITY

GRIMSEL	$NaClO_4$	ÄSPÖ
BC conditioned to Grimsel Water (pH=9; I=1E-03)	Purified Na-FEBEX BC in $NaClO_4$ 5E-04 M	BC in Äspö Water (pH=8, I=0.01 M)
STABLE	STABLE	NOT STABLE





Initial size by PCS, around 300 nm: if “STABLE” no significant size increase observed with time.

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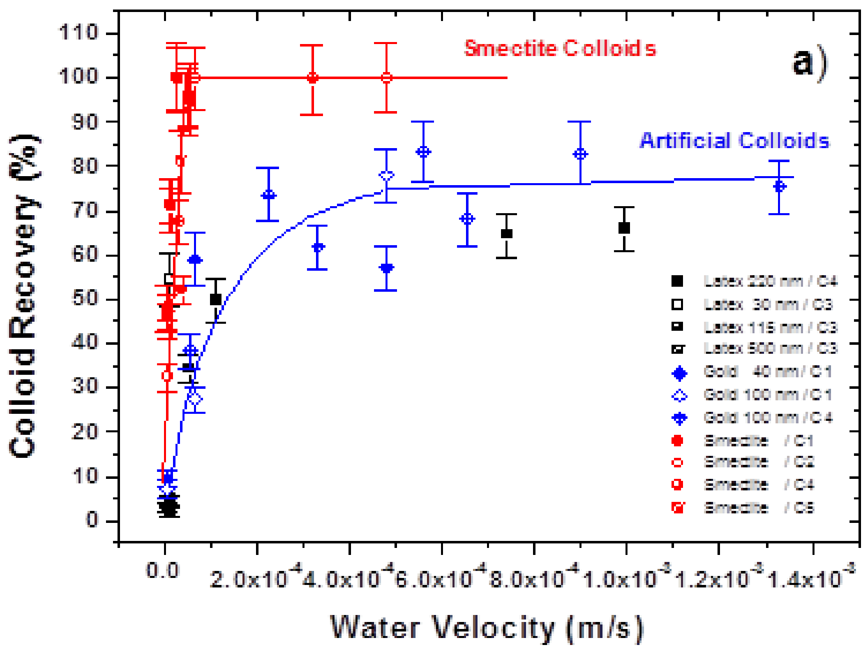
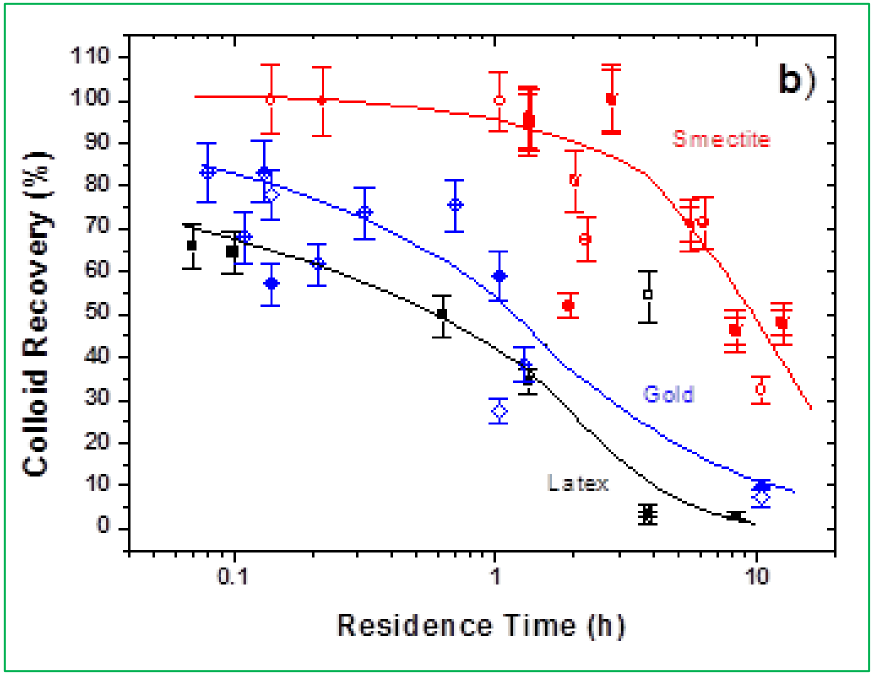
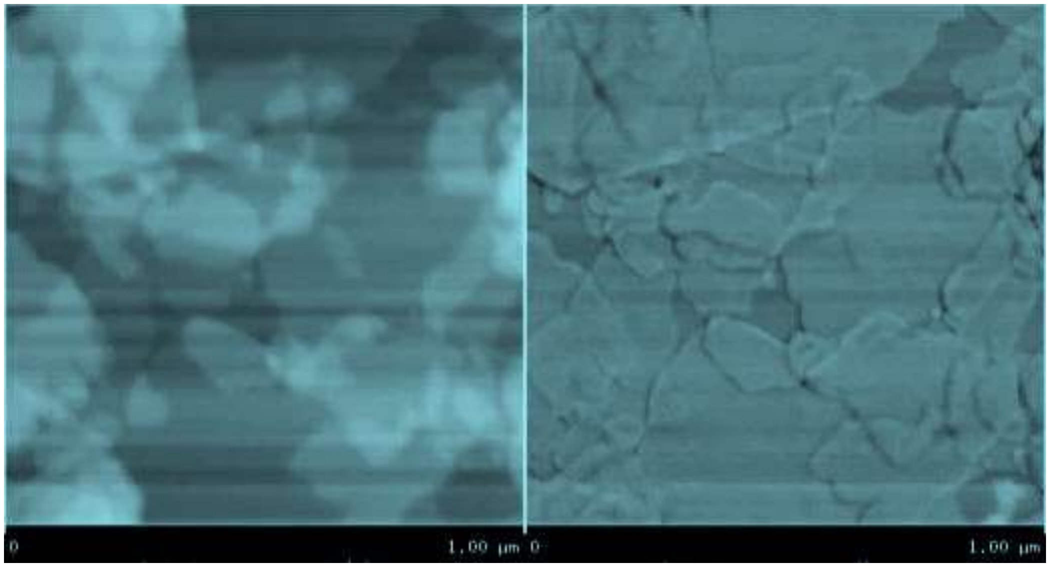
BENTONITE COLLOID MOBILITY



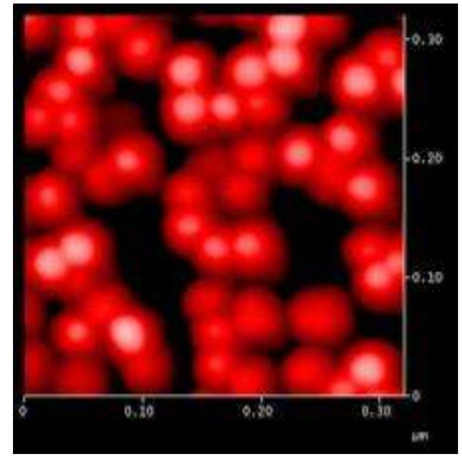


BC recovery in granite fractures strongly depends on (a) the water flow rate (or (b) the residence time). The lower the water flow, the less the recovery. FILTRATION OCCURS !!

COLLOIDS

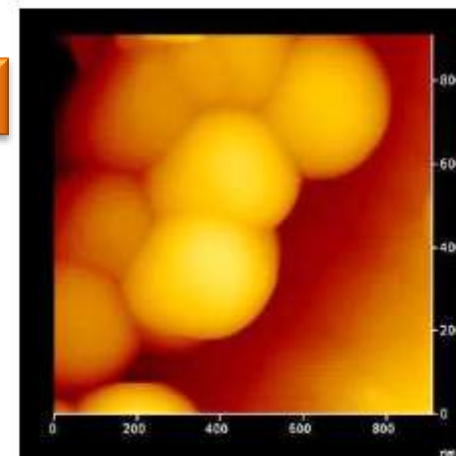


FEBEX



Gold

Latex



Different recovery & FILTRATION behaviour as a function of morphology, charge, size. Fracture roughness.

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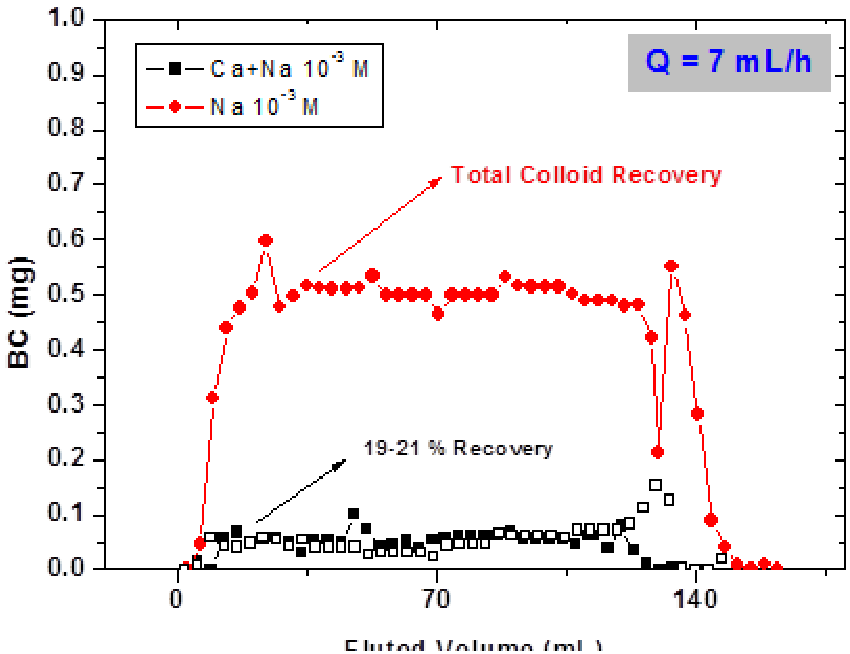
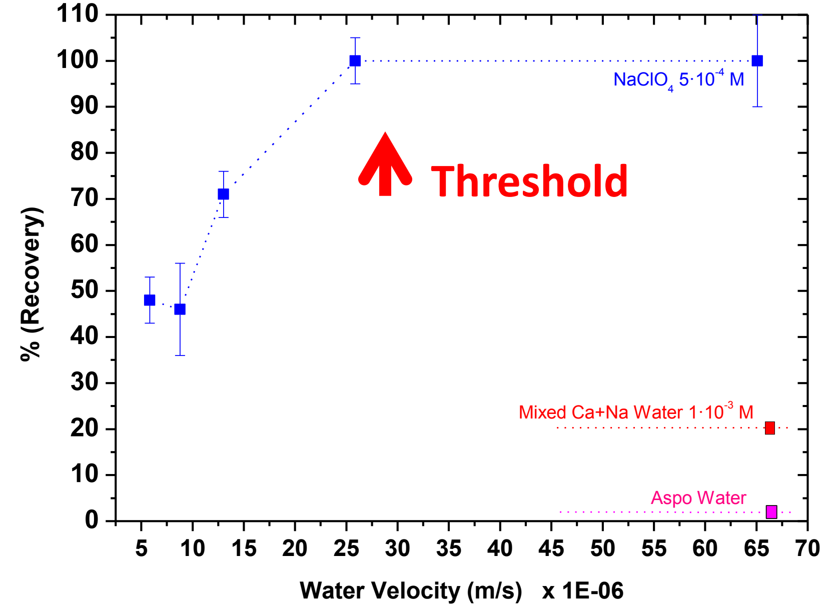
BENTONITE COLLOID MOBILITY





BC recovery in granite fractures strongly depends on the chemistry of the water. The threshold water flow for the total recovery of BC depends on the chemistry.

BENTONITE COLLOID MOBILITY

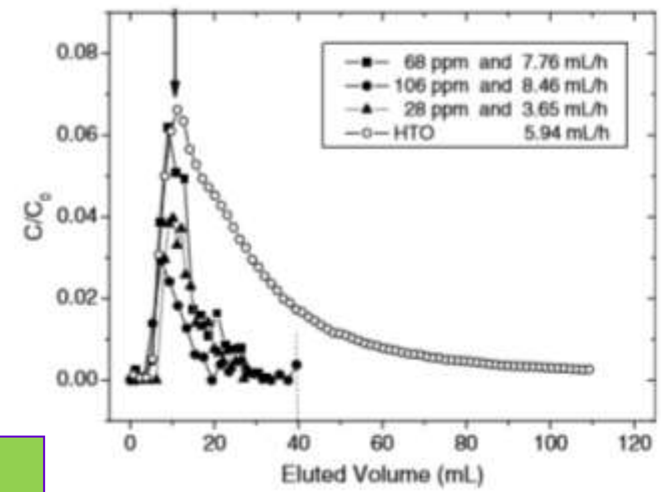
Retained by filtration in the fracture ⟷ Eluted

NOT MOBILE FRACTION

Eluted

MOBILE FRACTION

ALWAYS PRESENTED "CONSERVATIVE" TRANPORT BEHAVIOUR (NOT RETARDED)



Effects of BC on RN transport will depend on the predominance of one or the other fraction.

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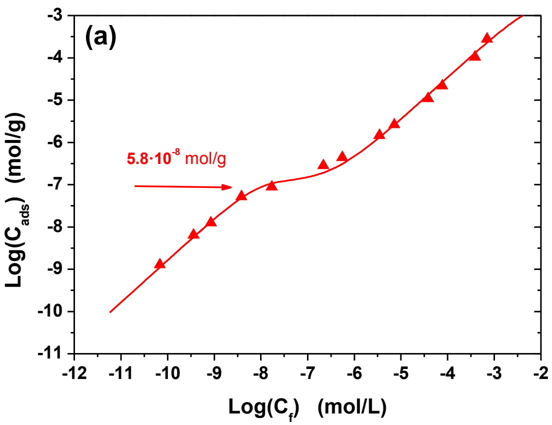
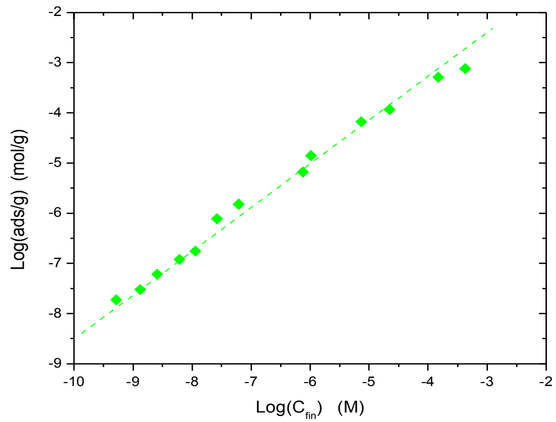
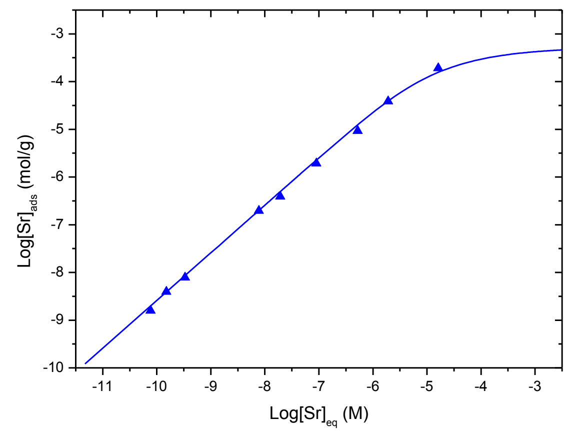
RN SORPTION ON BENTONITE COLLOID







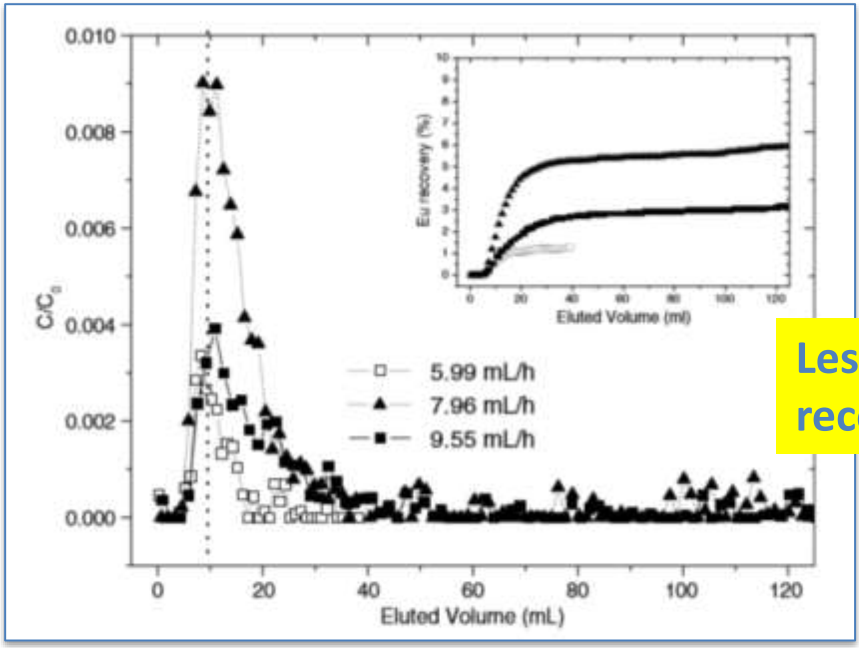
Cs
- Cation exchange
- **Non-linear**

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

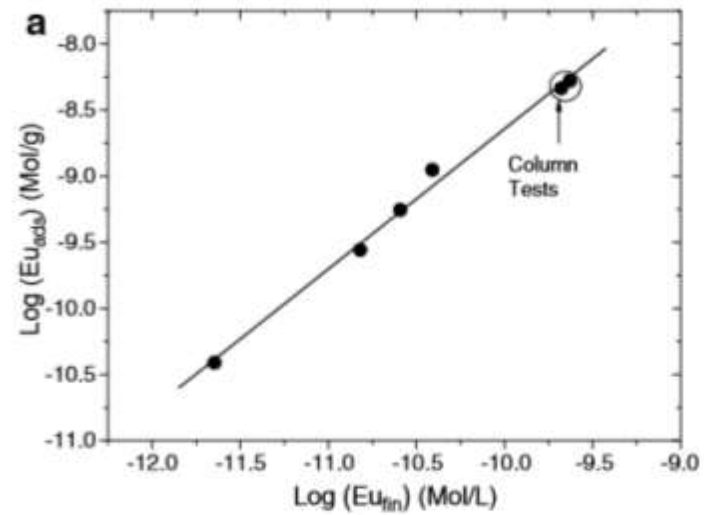
Sr
- Cation exchange (& I.S. surface complex)
- **Linear**

Not entering here in details, just mentioning that, in general, sorption behaviour of the RN on BC, was previously analysed, to identify the main retention mechanisms and to quantify retention under the specific conditions of transport experiments.

Europium Transport (Natural Fracture, GRIMSEL)



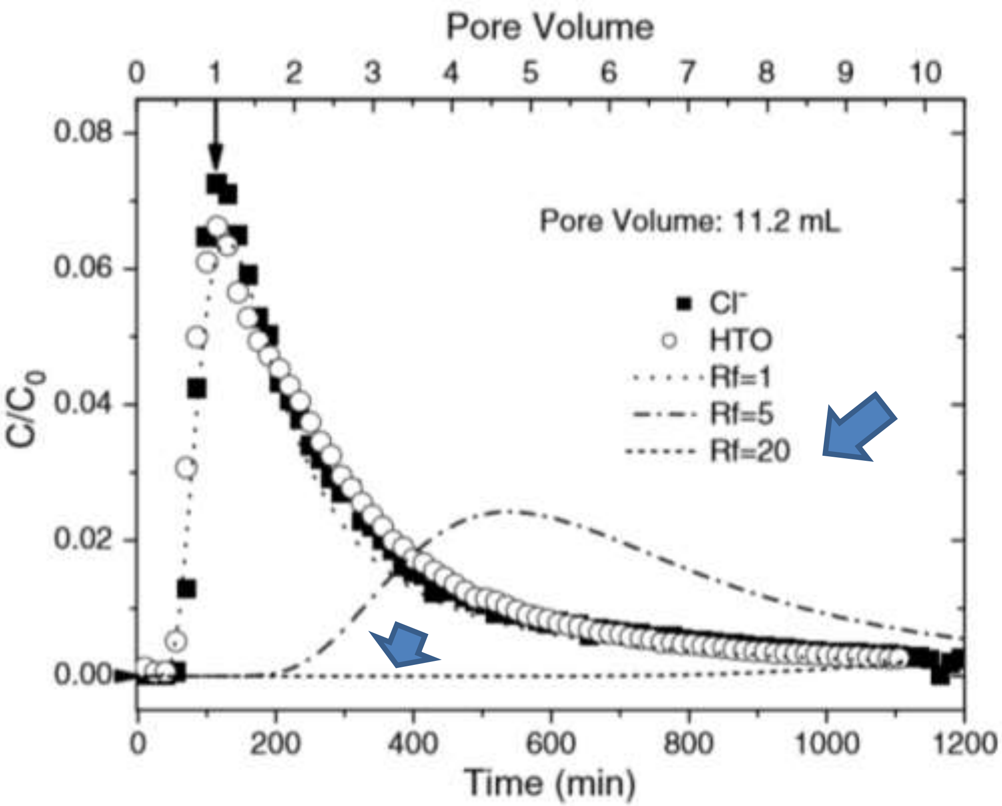
Less 7% recovered



80-85 % Initially sorbed

Europium activity detected with a retardation factor of approximately 1. Less activity then the expected, considered the colloid elution at the given flow rates and the RN initially sorbed. No Eu detected later.

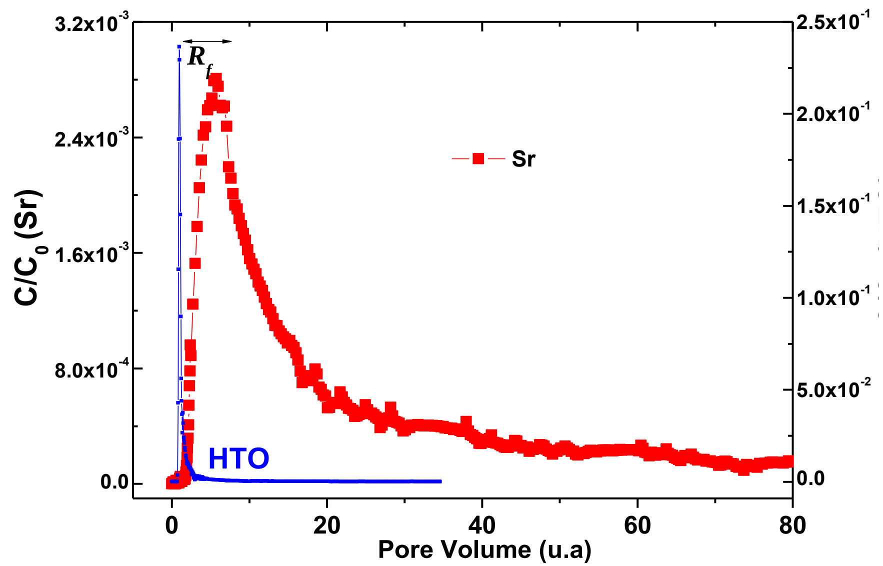
Europium Transport (Natural Fracture, GRIMSEL)

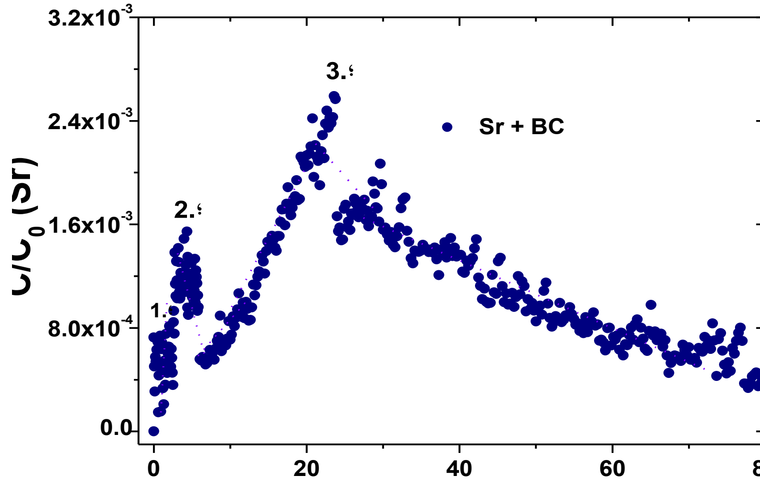


1. Eu desorbed from BC;

2. Solute Eu, retarded by (high) sorption in granite would appear much later than conservative tracers. It did not.

Strontium Transport (Artificial Fracture, $NaClO_4$)



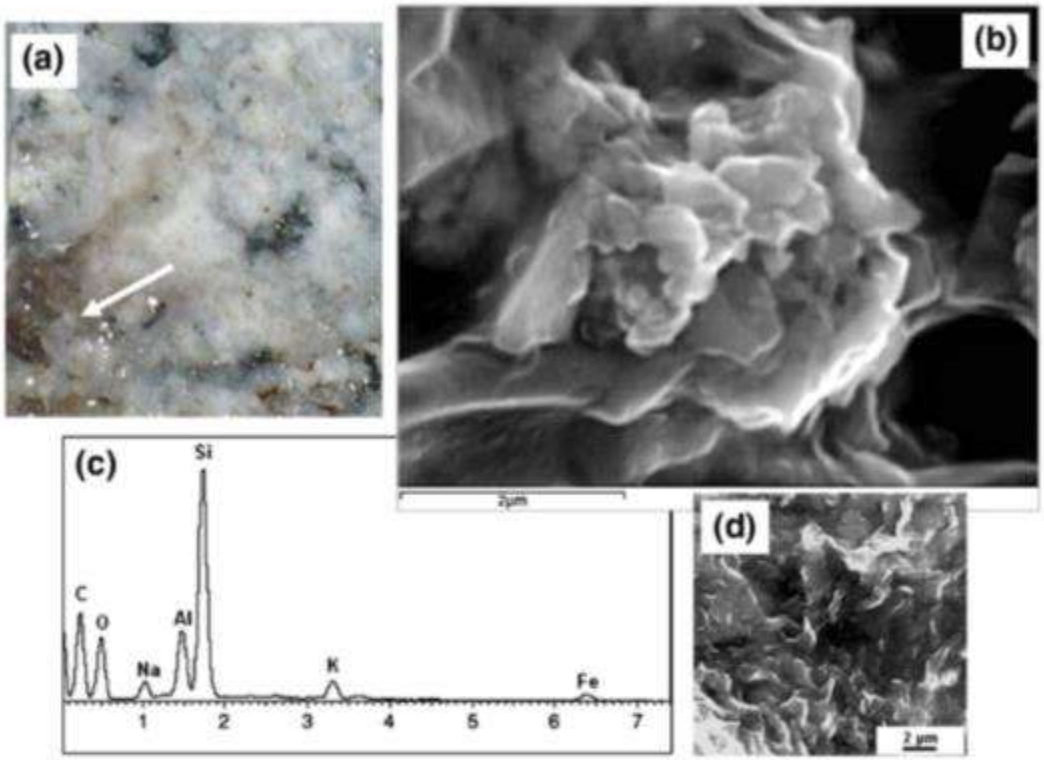


90 % Initially adsorbed, only 1.7 % recovered with colloids

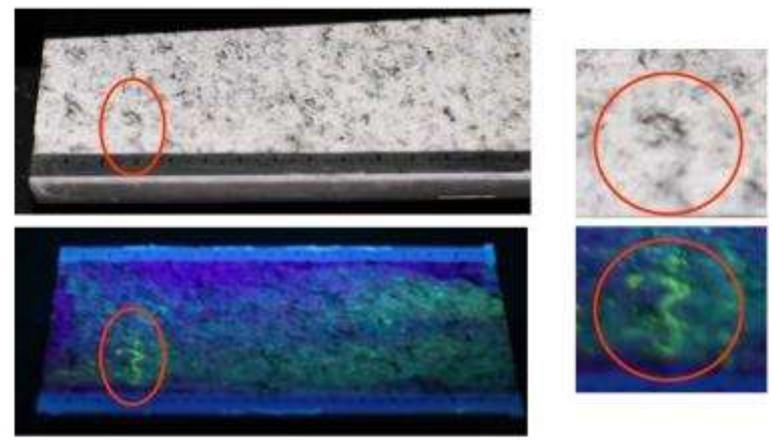
1. Sr desorbed from BC;
2. Breakthrough curve different (with and without colloids): 3 peaks
3. Hypothesis: Colloid retained in the fracture modify sorption properties of the granite surface. Dynamic interactions / slight effect on retardation (increase).

BC Retention (Artificial Fracture, $NaClO_4$)

N. Albarran et al. / Journal of Contaminant Hydrology 122 (2011) 76–85



Retained bentonite



Columna "Corta"

Retained fluorescent latex

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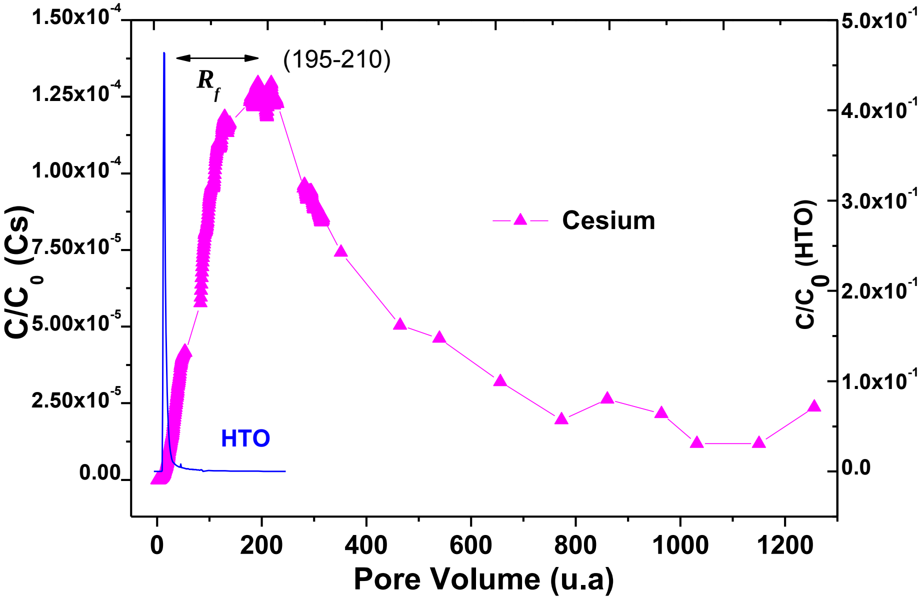
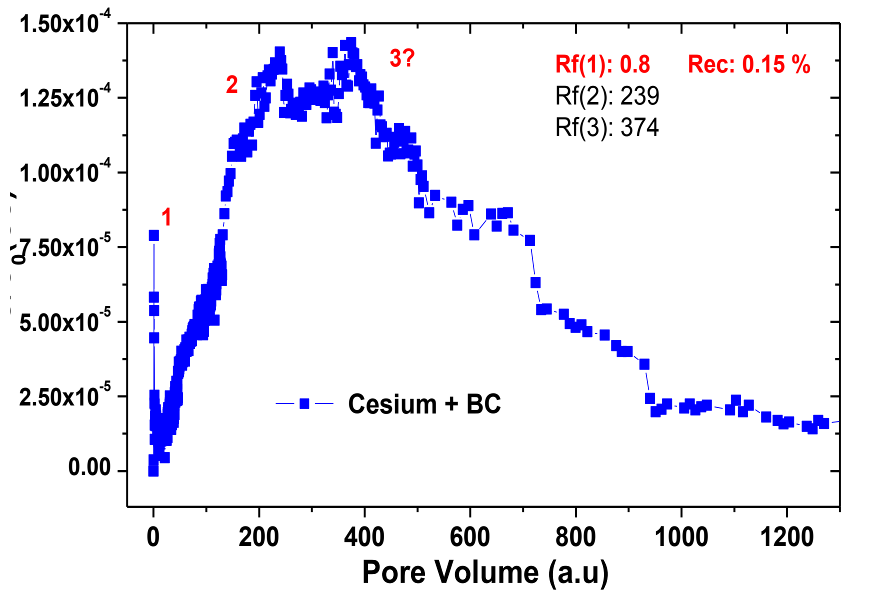
Cesium Transport (Artificial Fracture, NaClO4)

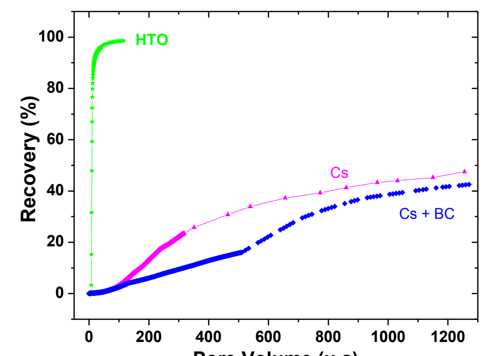




1. Cs desorbed from BC; Initial 80, with BC <1 %

2. Breakthrough curve different (with and without colloids): 3 peaks (as Sr).

3. No significant effect of BC on recovery.



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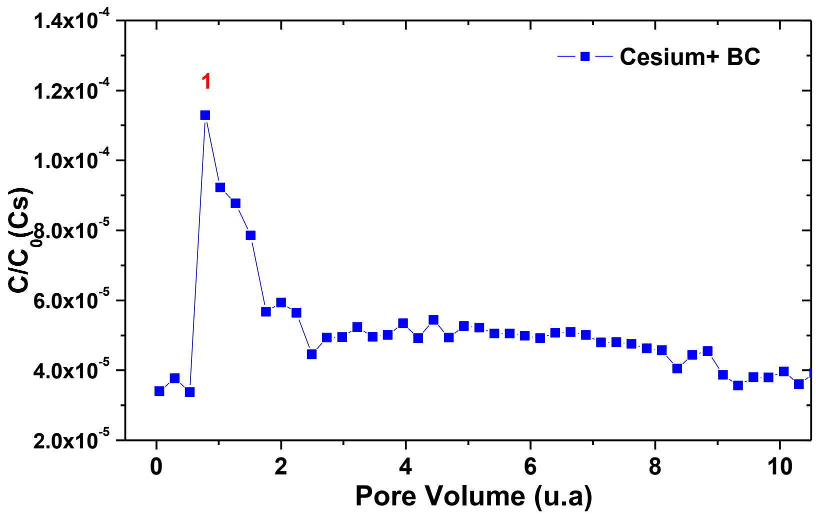
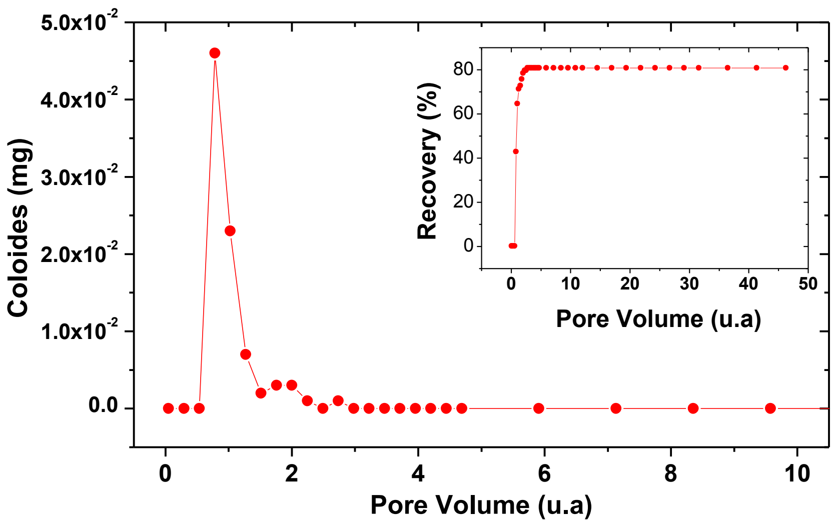
COLLOID CONCENTRATION AND ACTIVITY MEASURED IN THE SAME SAMPLES

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

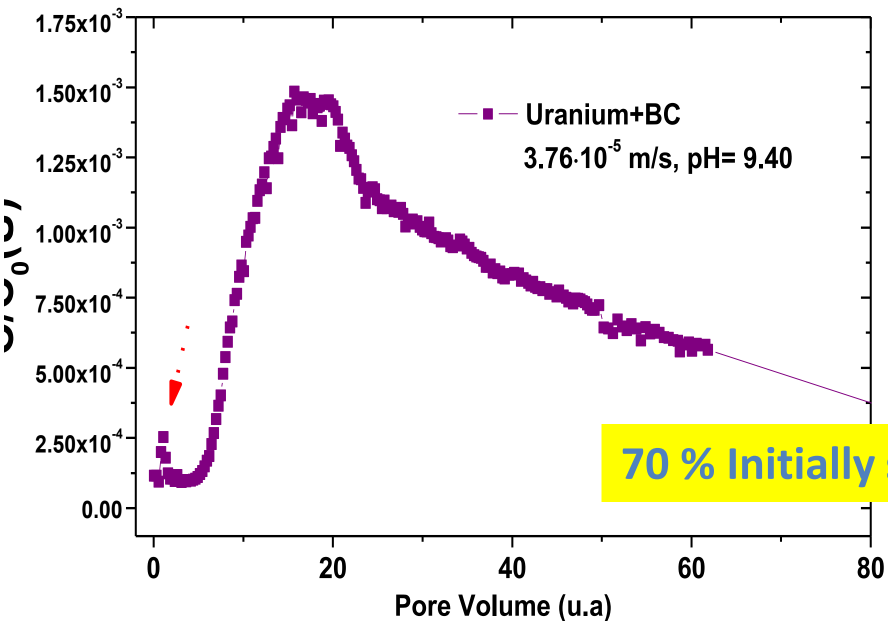
Cs Elution (with colloid)



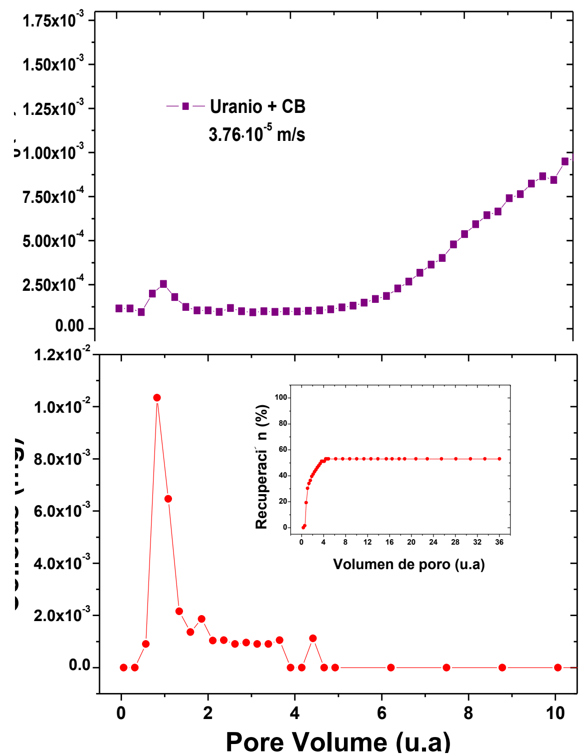
Colloid Elution



Uranium Transport (Artificial Fracture, $NaClO_4$)



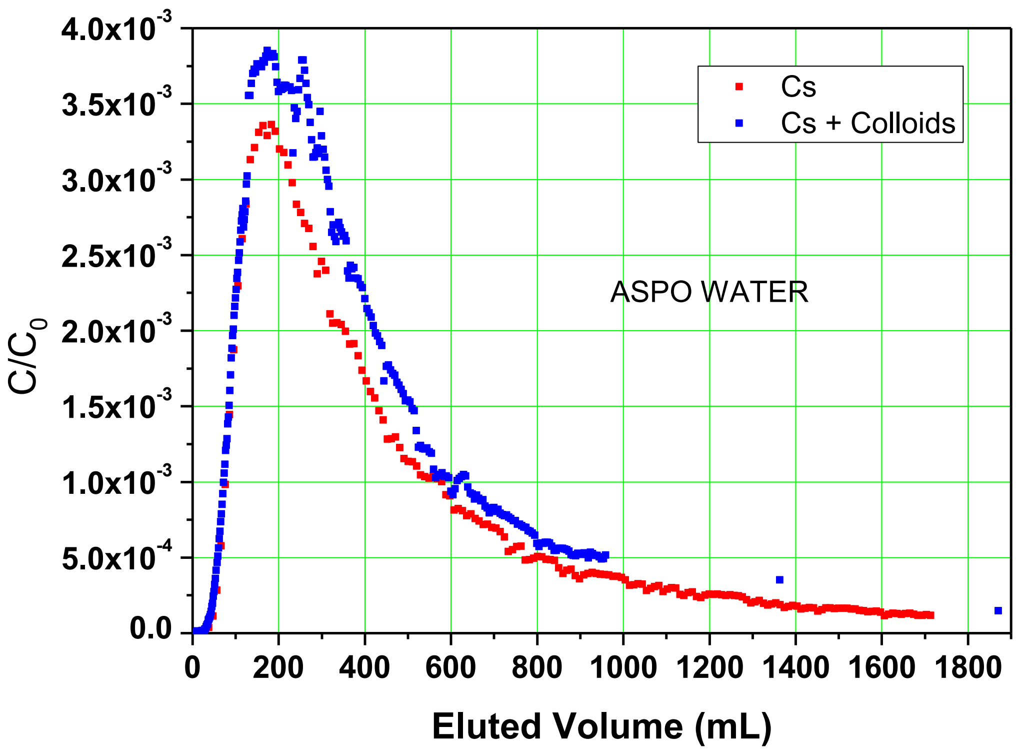
70 % Initially sorbed



Less than 1 % recovered with colloids

- In that case, several experiments as a function of pH where made. Different BT curves (sorption properties) but regarding to BC effects…
- similar characteristics also in this case. (U desorption & not very different recovery)

Cesium Transport (Artificial Fracture, Äspo)



Similar (even no identical) breakthrough curves

No BC recovered !!

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CONCLUSIONS

- Transport experiments were carried out under different conditions and RN;
- The recovery of the bentonite colloids depends on the water flow rate and the physico-chemistry of the systems. (Water, fracture, colloids characteristics)
- The mobile fraction of BC moves always un-retarded with respect to the conservative tracer (Rf=1).
- Different RN presented different degree of sorption under the conditions of the experiments but, in all the cases
- RN transported by colloid was always detected in condition of BC "stability"
- The quantity of RN measured with the mobile BC was lower than the expected, considering the initial adsorption on BC and colloid recovery.
- In the case of Cs in Äspö (not stable), the effect of the colloid presence was negligible.

CONCLUSIONS

- In the case of Sr and Cs, the BT curves with and without colloids were clearly different.
- Filtration of bentonite colloids (above all at low water flow rates) and their deposition modifies the sorption properties of the granite fracture surface.
- In most of the cases, the presence of bentonite colloids did not significantly enhance radionuclide transport in the medium, but rather produced a slight increase in the overall retardation in the fracture. Only in the case of very highly sorbing radionuclides like Eu, for which elution was not expected, small elution (less then 7% of the initially adsorbed) was observed and clearly attributable to the presence of the mobile colloidal particles.

Thanks for your attention

This work was supported by the EU FP7/2007-2011 program, under the EC-BELBAR project (Nº 295487).

MODELLING BENTONITE EROSION

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Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement n° 295487

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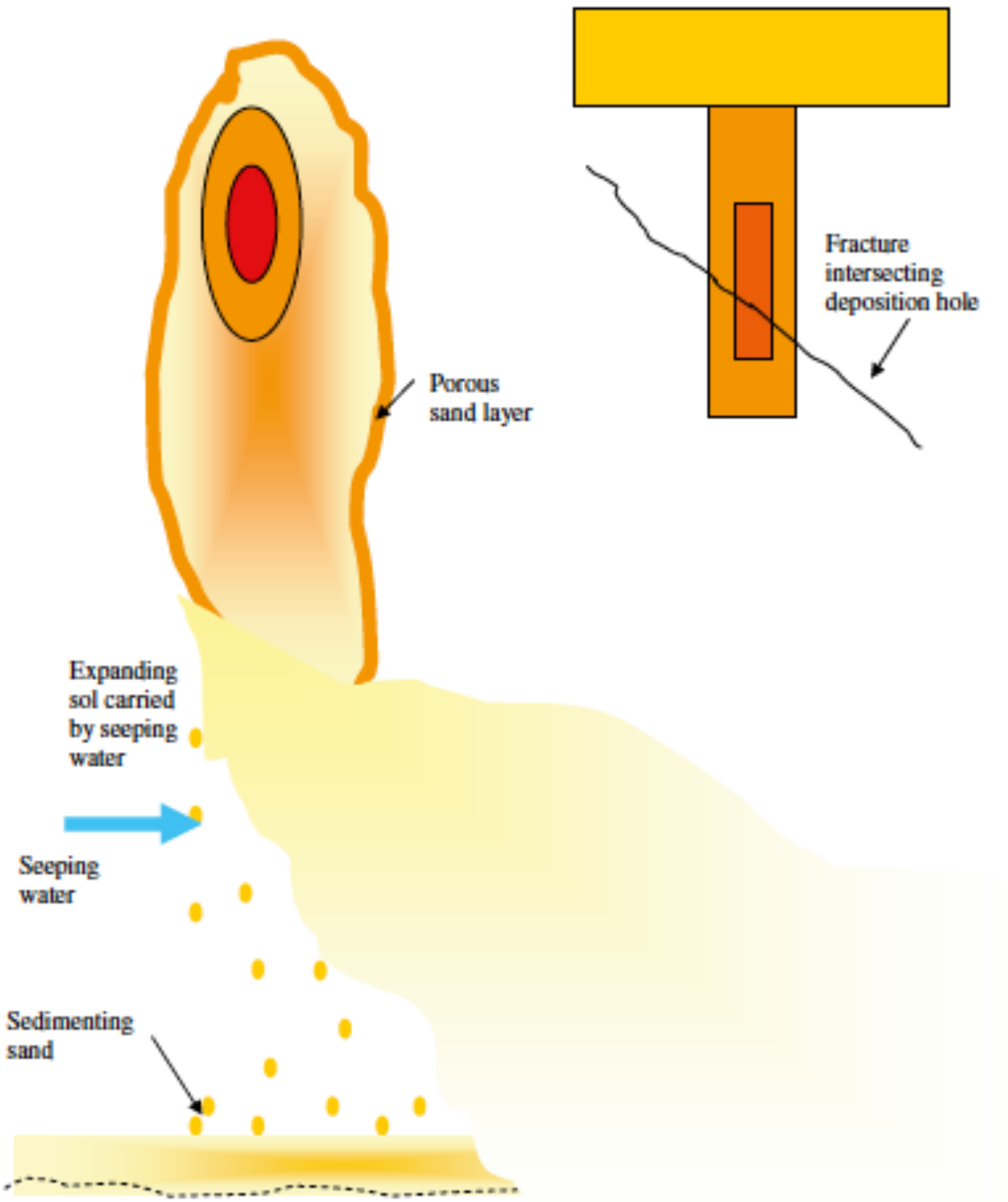
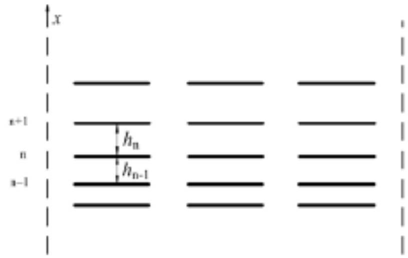


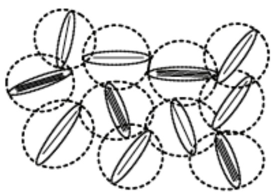
Concepts 207

Figure 3-3. Cartoon of how a sand region could develop in the fracture around a deposition hole and that it may be breached and sediment away in the lower parts of the fracture.

Dynamic model: Summary of processes

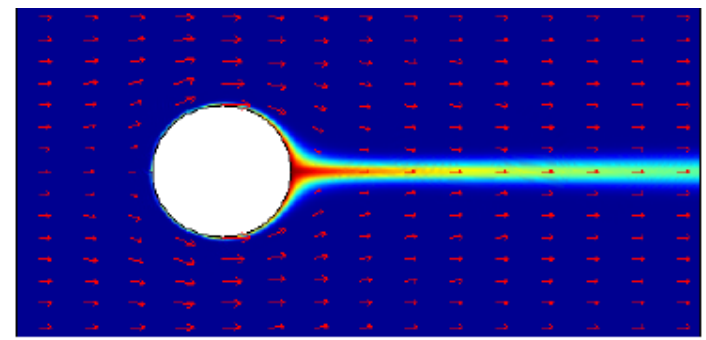


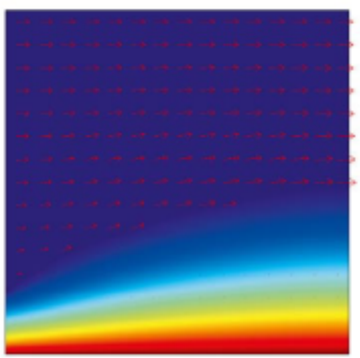
Expansion of
bentonite paste.
Viscosity “ infinite



Large diffuse double
layer, co-volumes overlap

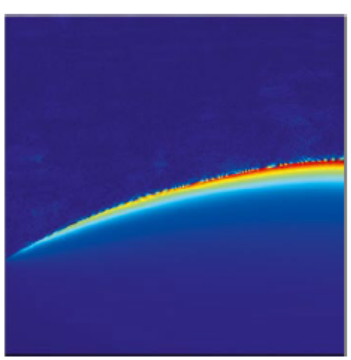
Starting rotation.
Viscosity of sol
drops, Sol flows





Colloidal particles
diffuse into seeping
water.
Concentration
Picture of rim zone

Viscosity of sol drops
from 10* water to
water in rim zone



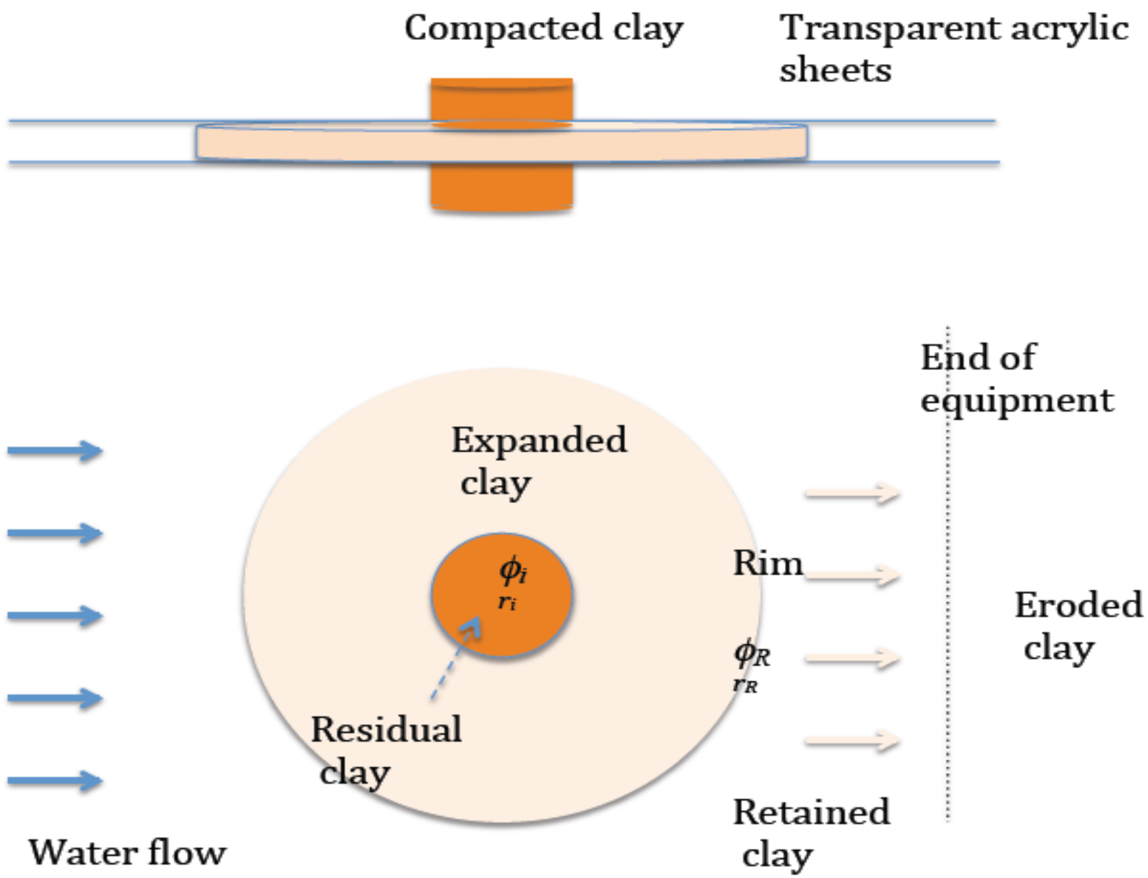
Most flux in thin zone

Interface to rigid gel

Sol flows.
Flux picture
of rim zone

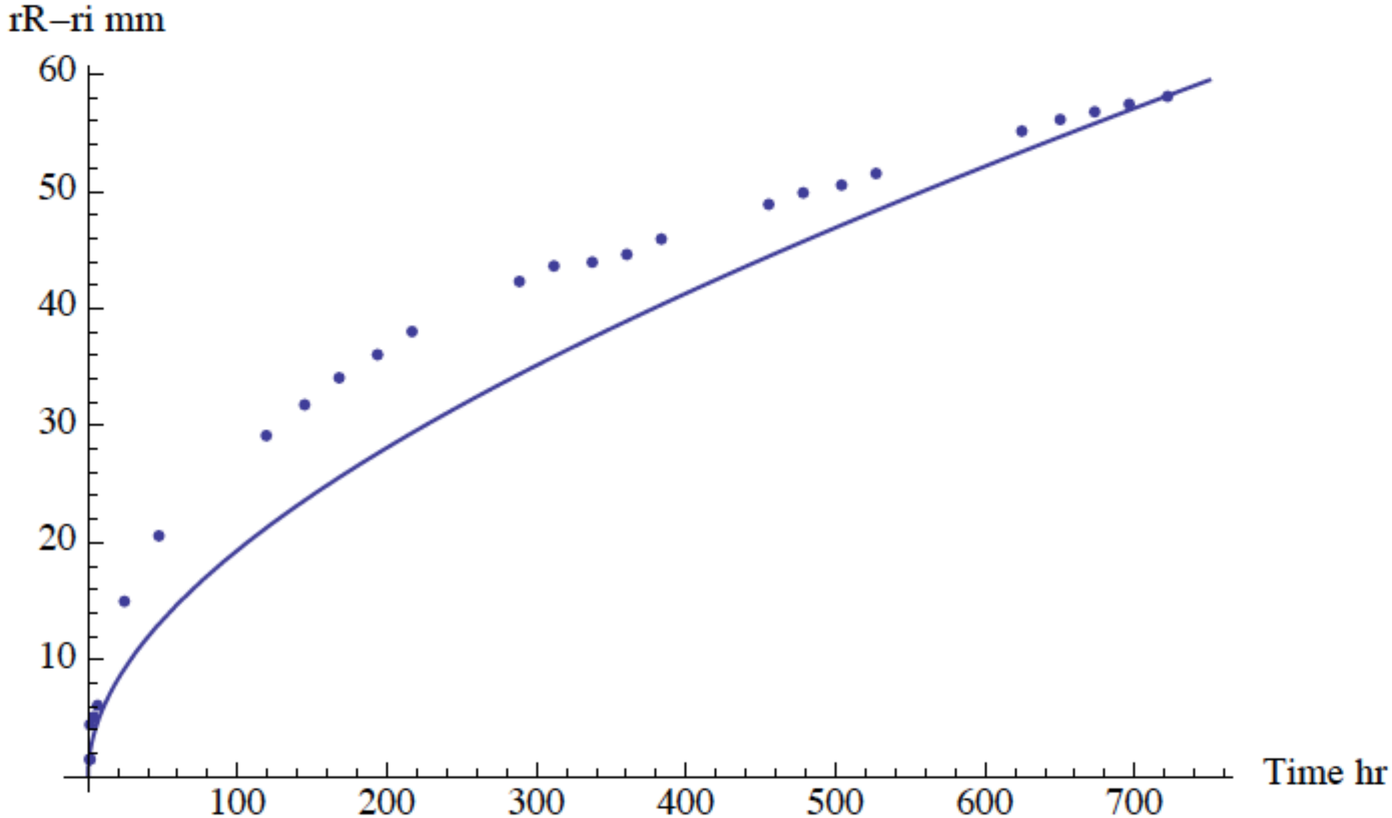
Comparison w. experiments

Schatz et al. (2012) experiments

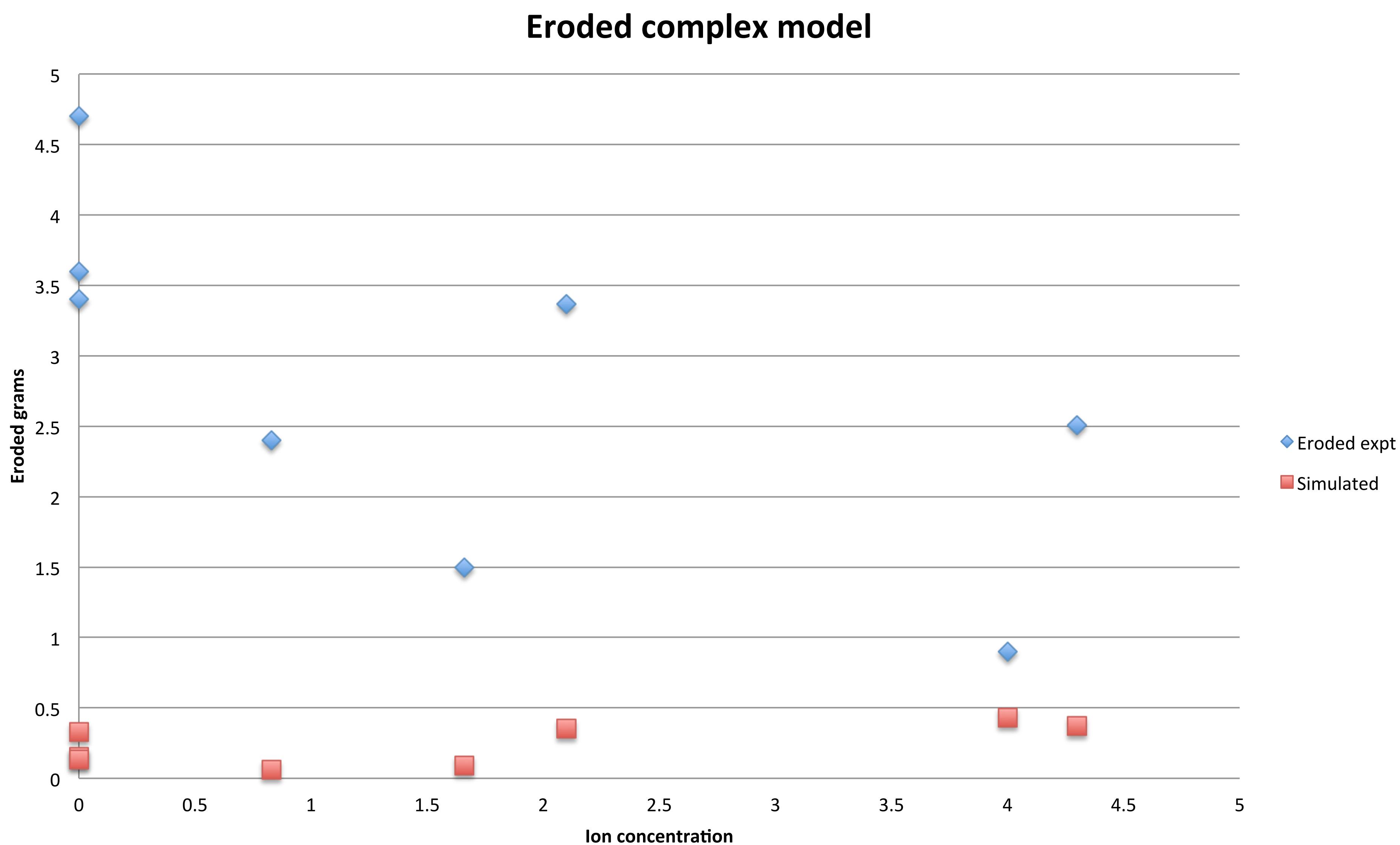


Schatz, T., Kanerva, N., Martikainen, J., Sane, P., Olin, M., Seppälä, A and Koskinen, K., 2012, Buffer Erosion in Dilute Groundwater. Posiva Report 2012-44 (2012).

Just expansion no flow, DI water- Fairly good prediction



Predicted erosion with 2-region model



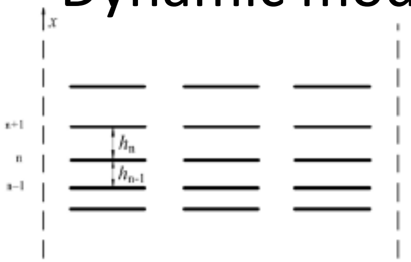
Obviously this is not a good prediction

Model is wrong or model does not account for some mechanism(s)

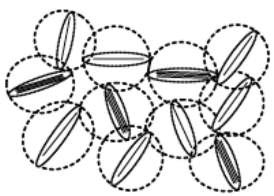
Agglomeration to flocs, Low ionic strength water

Schatz et al. (2012), Buffer Erosion in Dilute Groundwater. Posiva Report 2012-44.

Dynamic model

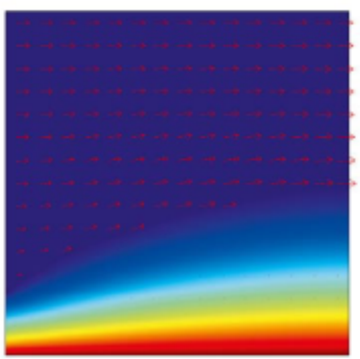


Expansion of
rigid gel.
Viscosity “
infinite

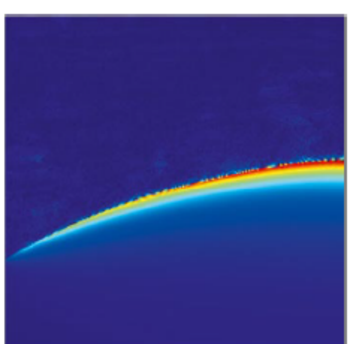


Large diffuse double
layer, co-volumes overlap

Starting
rotation.
Viscosity of
sol drops



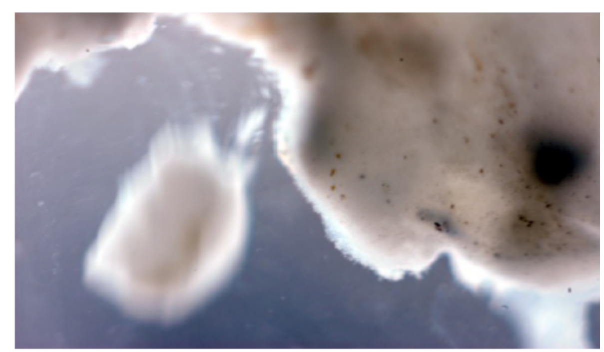
Colloidal particles
diffuse into
seeping water.
Concentration
Picture of rim
zone



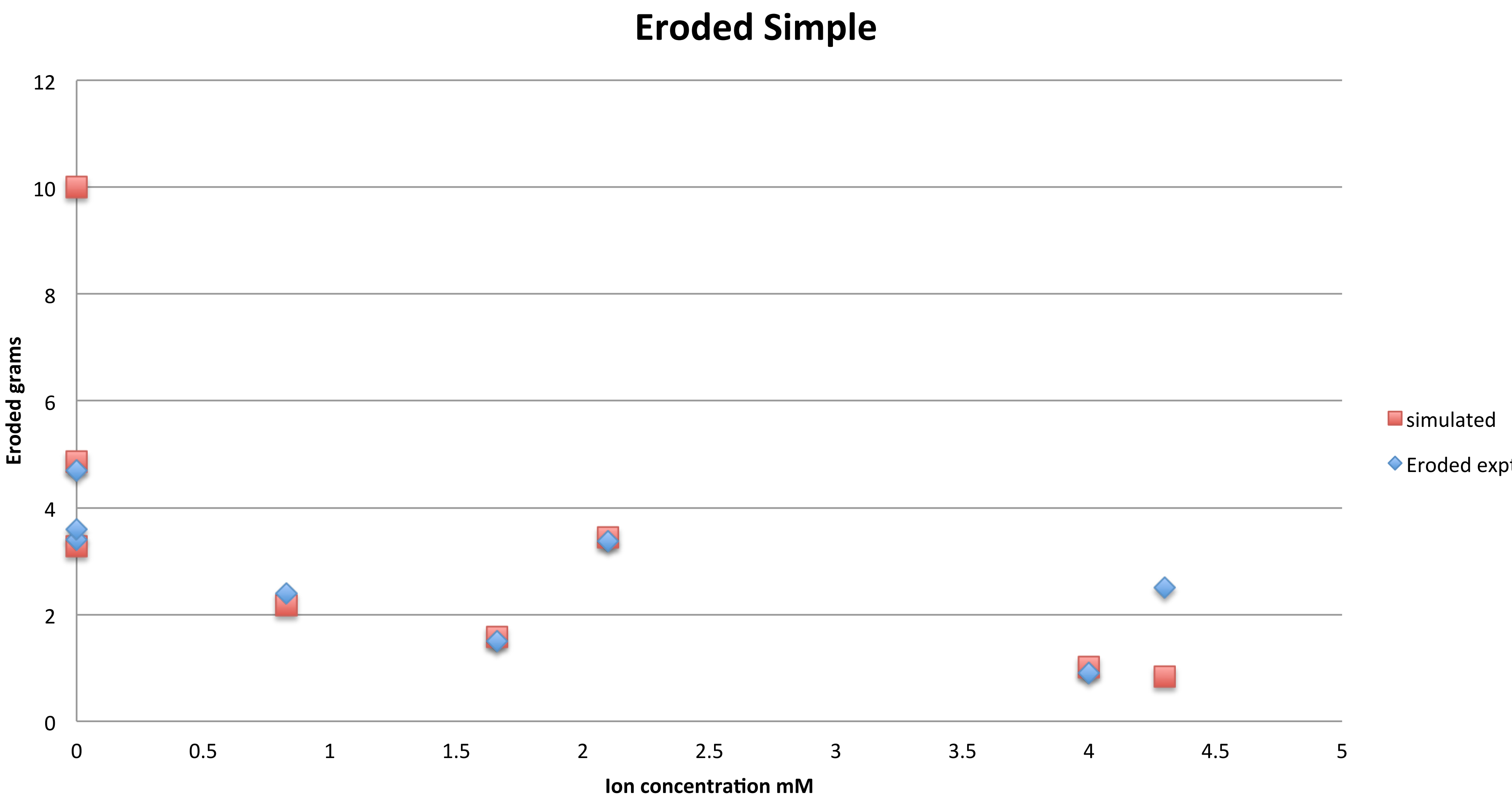
Sol flows.
Flux picture
Of rim zone

Dynamic model with floc formation

Flocs form. Can
sediment.
Floc slurry viscosity
near water.



Simulated erosion with Simple 2-region model ϕ_R=0.015

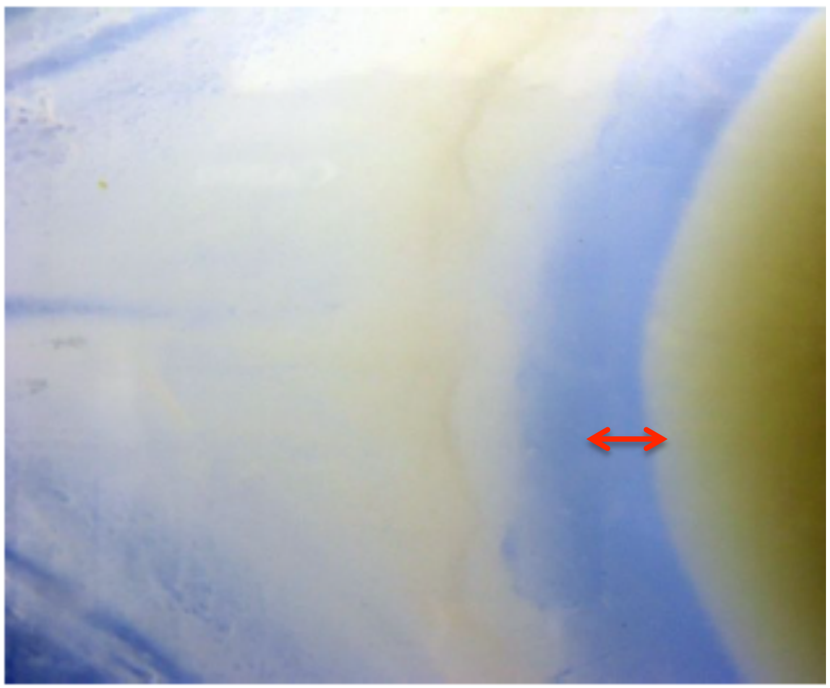


Loss of smectite by sedimentation

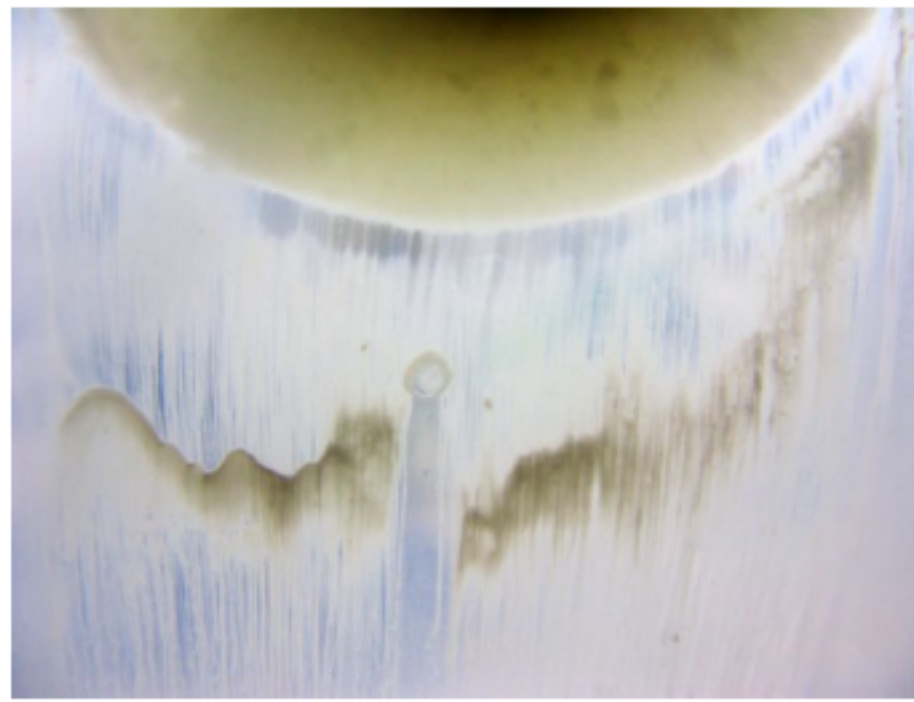
Schatz et al. (2012) erosion experiments

50/50 calcium/sodium montmorillonite in Di

Formation of flocs



Gravity pulling off flocs when slit is vertical

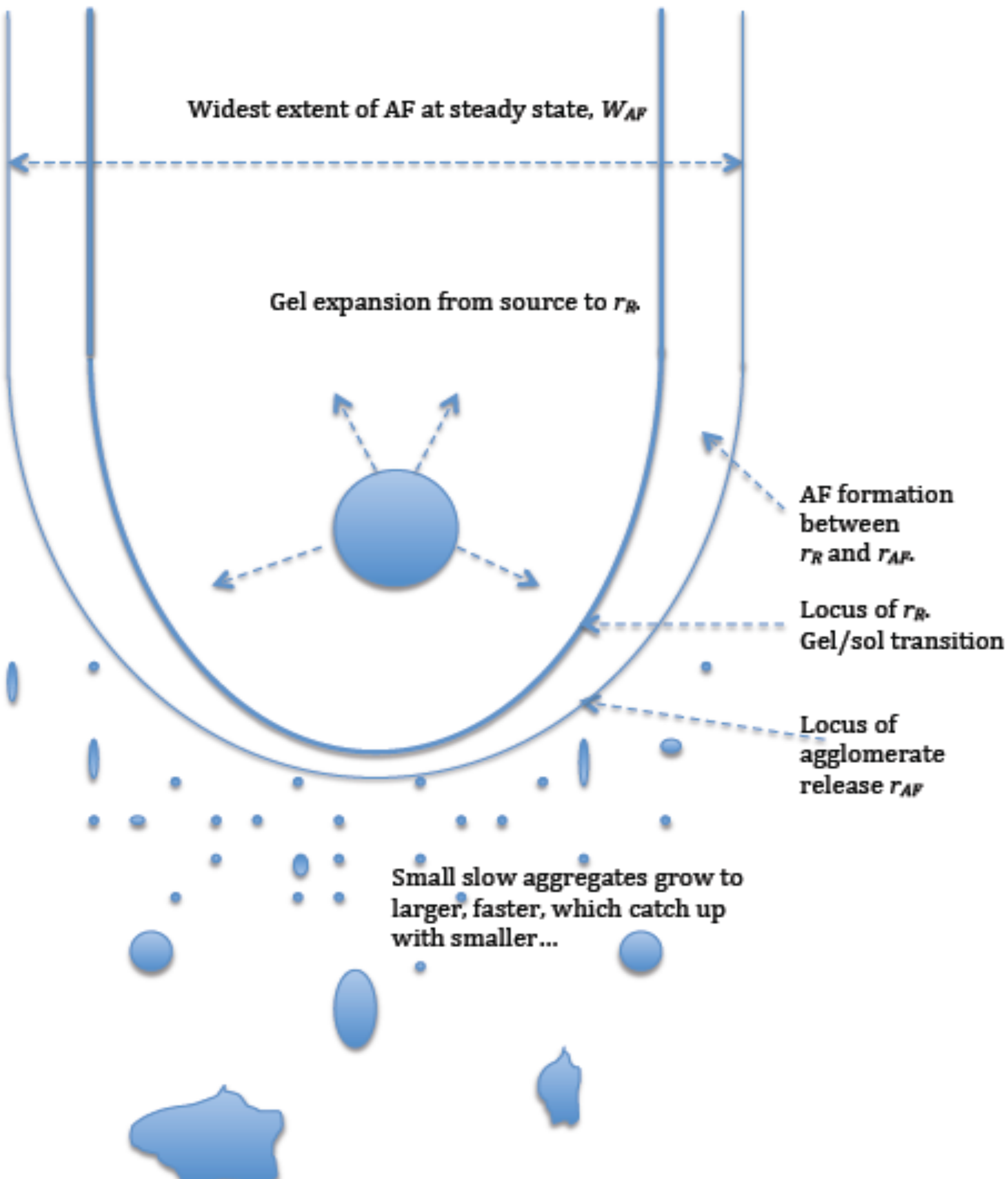


Schatz, T., Kanerva, N., Martikainen, J., Sane, P., Olin, M., Seppälä, A and Koskinen, K., 2012, Buffer Erosion in Dilute Groundwater. Posiva Report 2012-44 (2012).

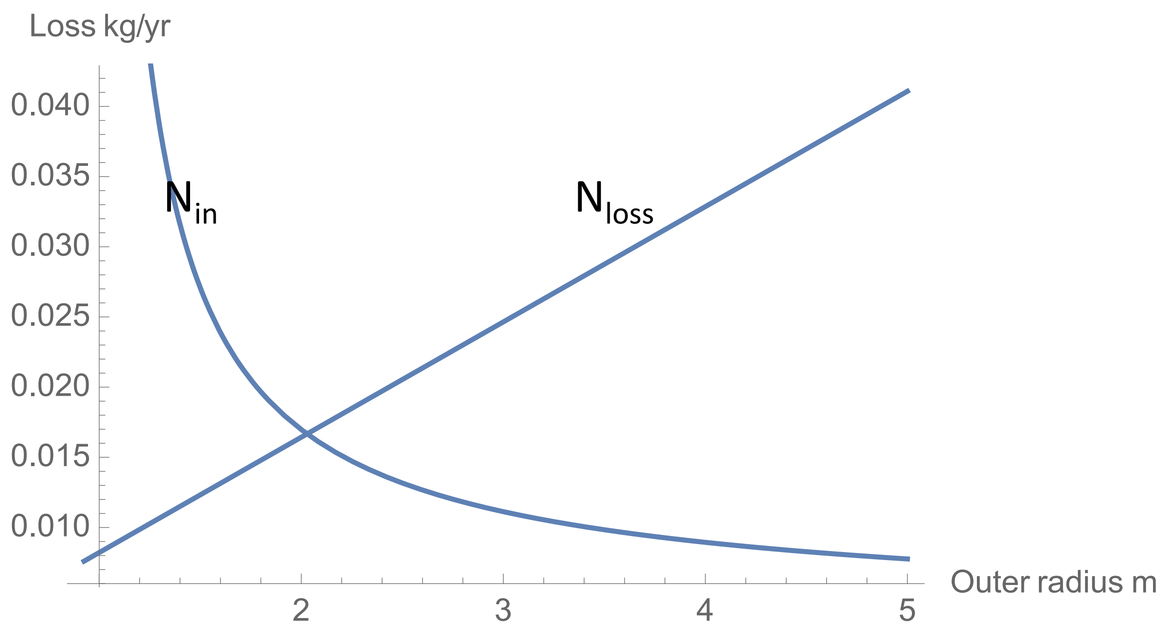
Maximum loss is set by maximum sedimentation flux

- Free sedimentation of small flocs
  - Modeled by Stokes law
- Larger flocs have friction against fracture walls
  - Modeled by flow in slot (fracture) driven by gravity

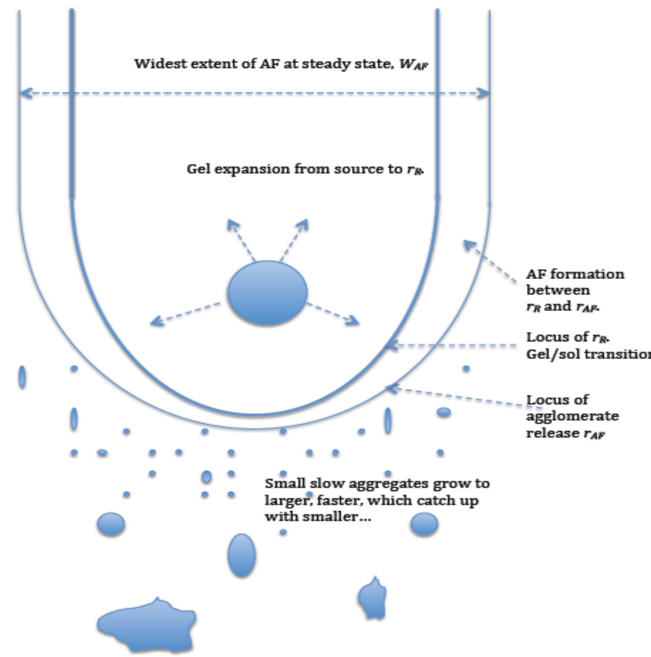
Loss of smectite by floc sedimentation



Stabilisation of width of expansion



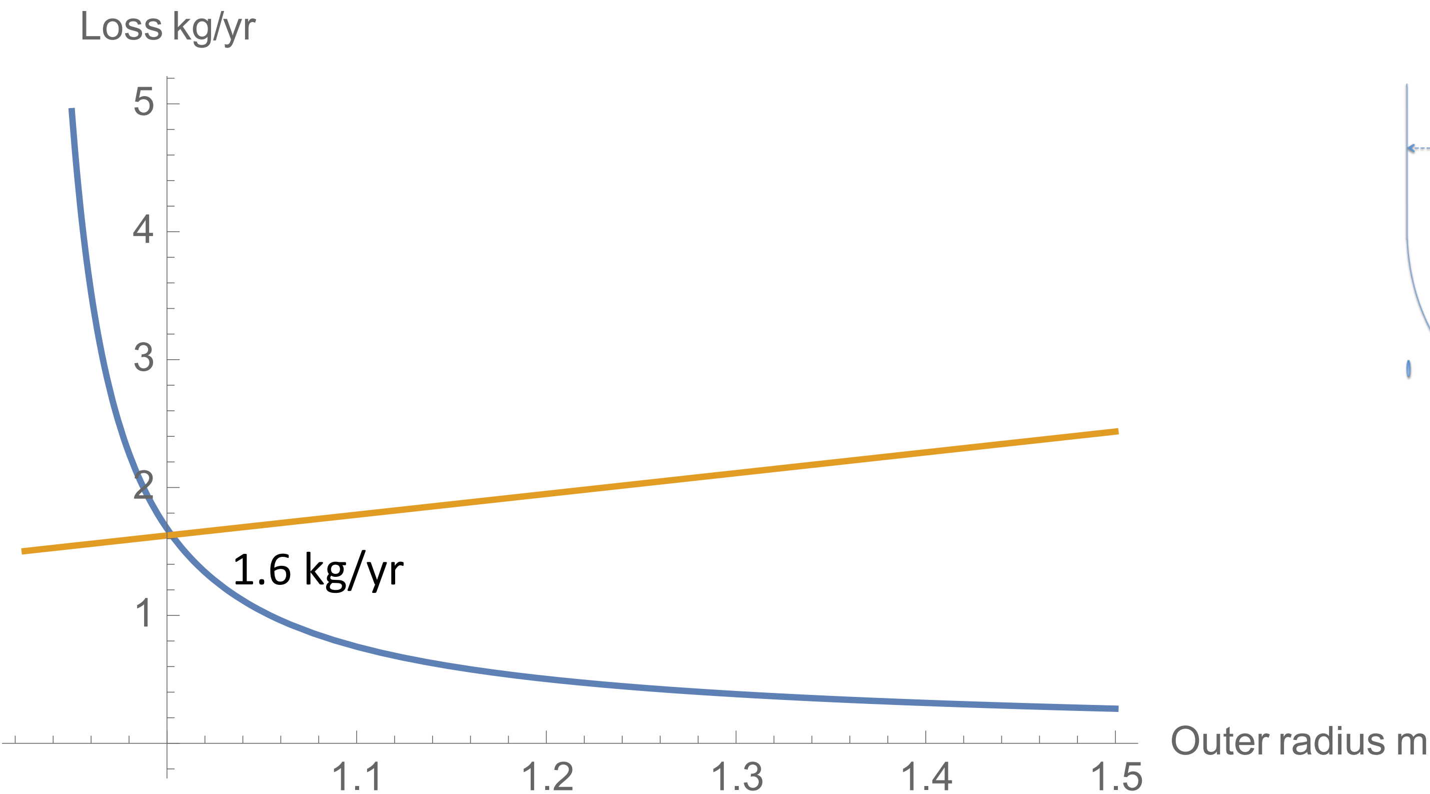
Aperture 0.1 mm, fr=0.01

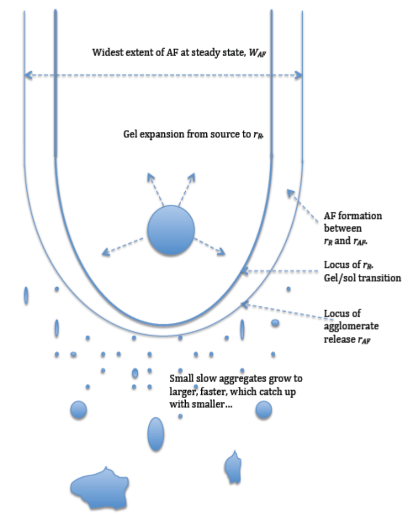


Rate of loss from deposition hole N_{PSS} (curved line) and rate of loss by sedimentation N_{smec} (straight line) as function of the radius to the rim

Aperture 1 mm, no restriction on release rate at rim.

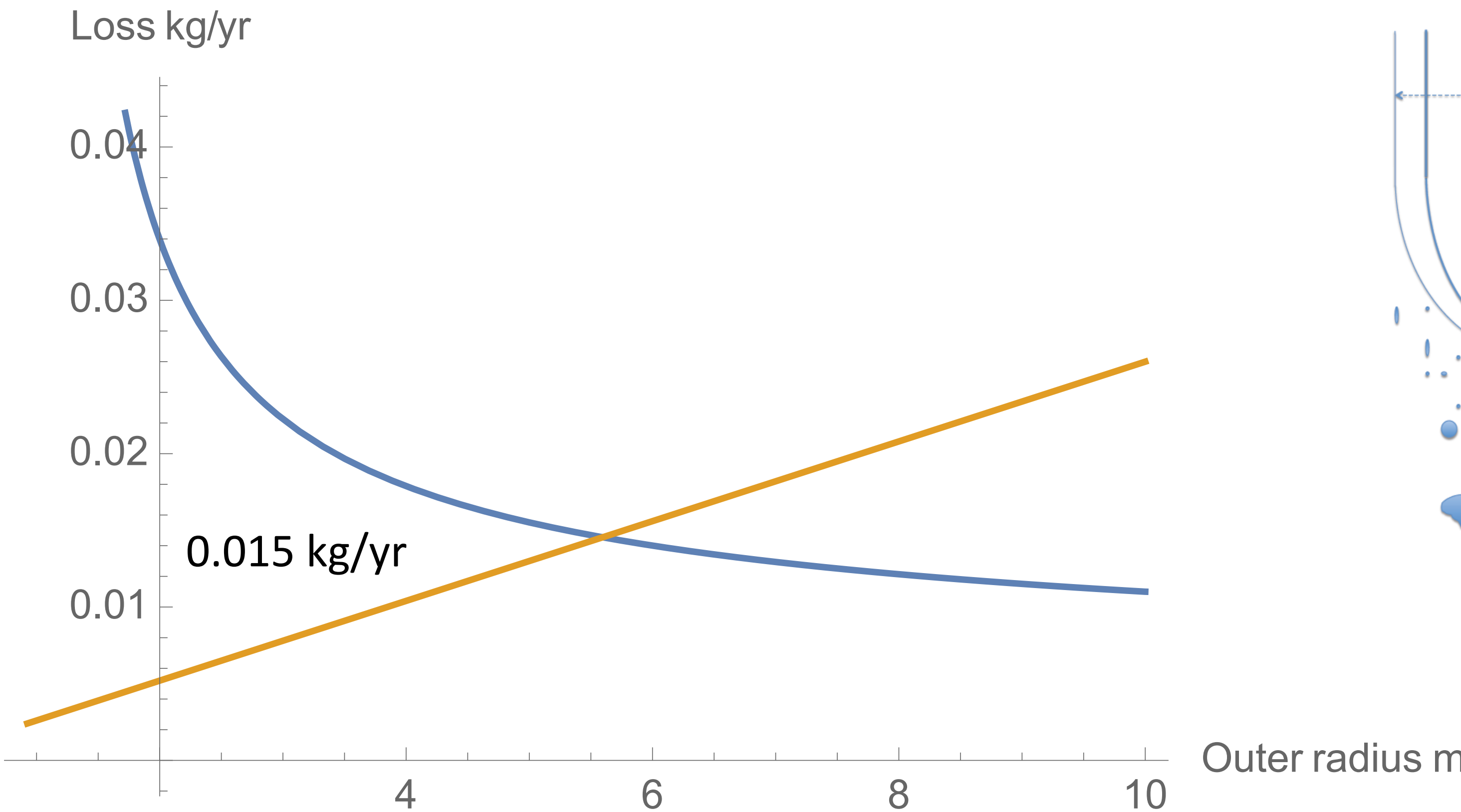
In the range of measured values!

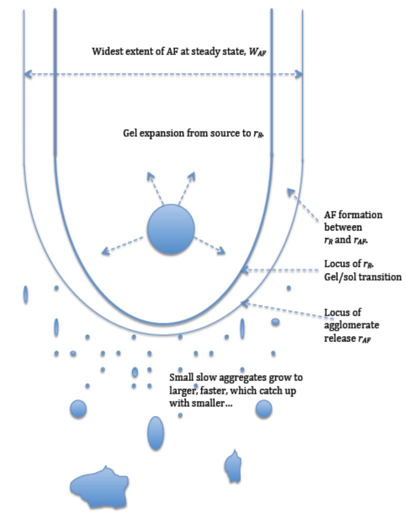




Rate of loss from deposition hole N_{PSS} (curved line) and rate of loss by sedimentation N_{smec} (straight line) as function of the radius to the rim

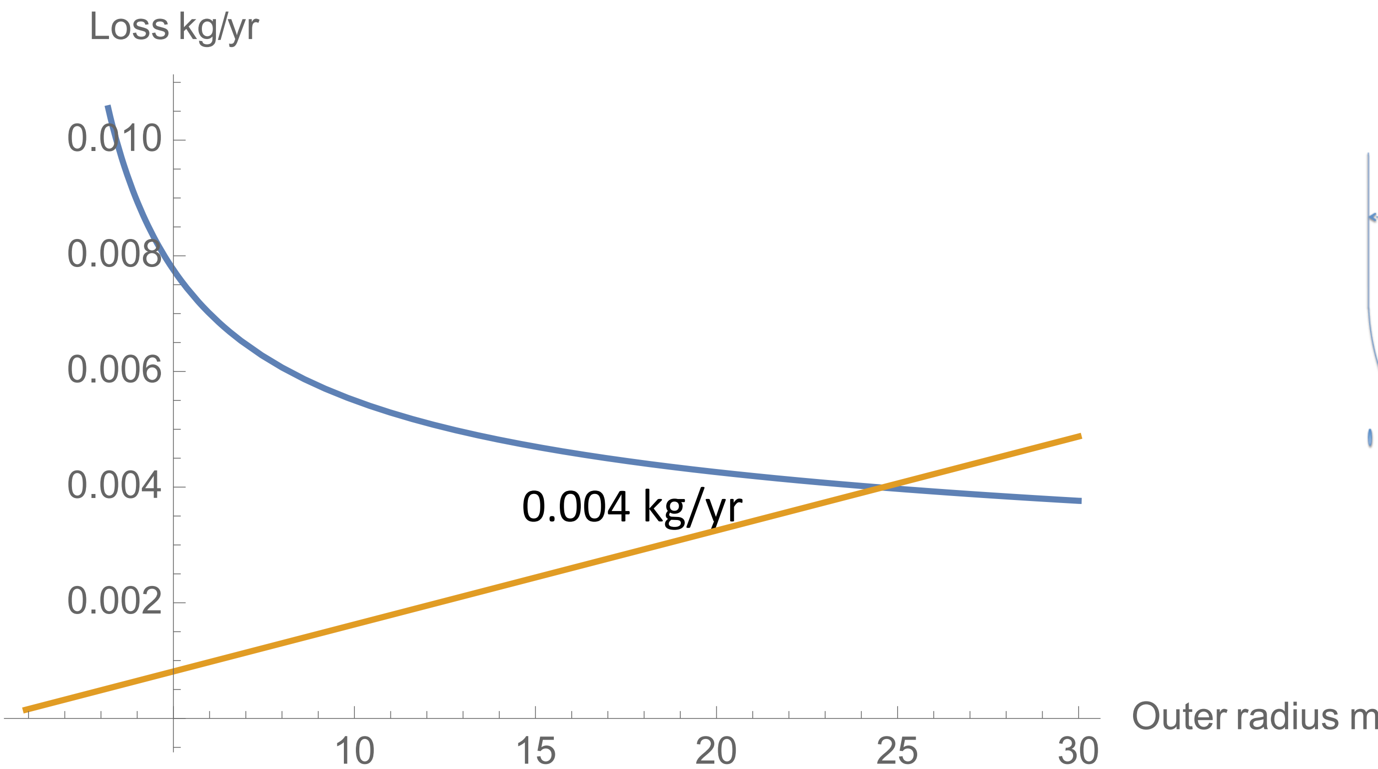
Aperture 0.2 mm. Considerable expansion of clay in fracture

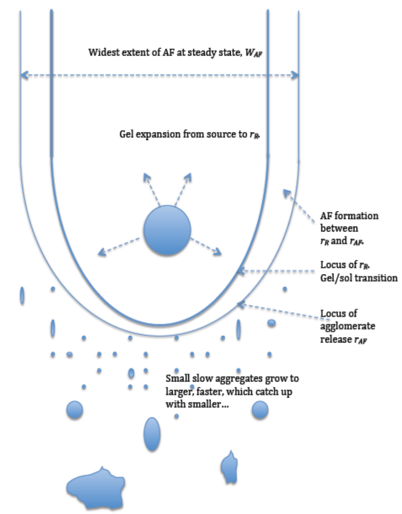




Rate of loss from deposition hole N_{PSS} (curved line) and rate of loss by sedimentation N_{smec} (straight line) as function of the radius to the rim

Aperture 0.1 mm. Considerable expansion of clay in fracture





Rate of loss from deposition hole N_{PSS} (curved line) and rate of loss by sedimentation N_{smec} (straight line) as function of the radius to the rim

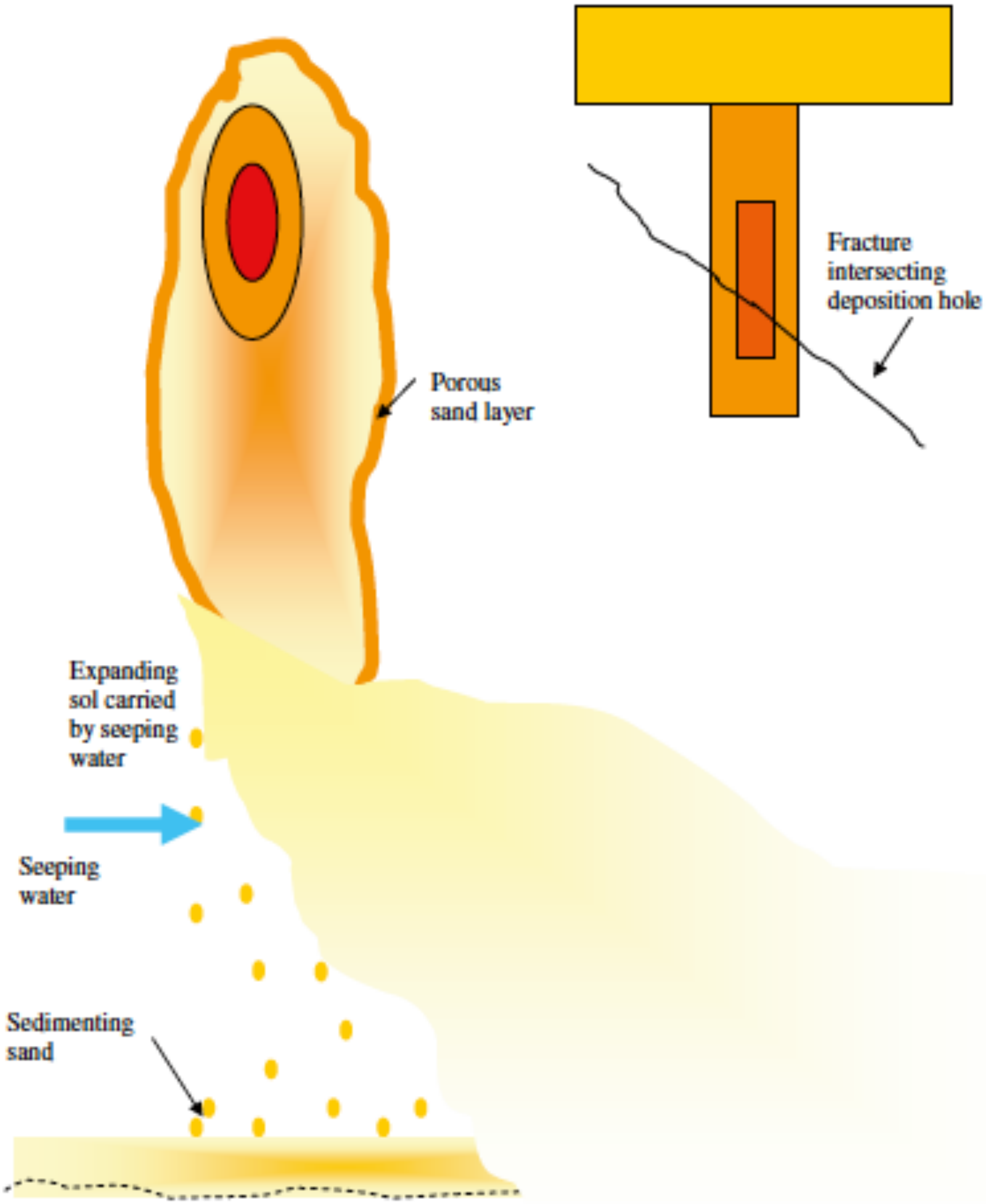


Figure 3-3. Cartoon of how a sand region could develop in the fracture around a deposition hole and that it may be breached and sediment away in the lower parts of the fracture.

Concepts 2007

Still OK and

Flocculation now added

But

Detritus fate of not accounted for

Some queries I

Where does the bentonite end up?

Example 100 kg bentonite loss

Agglomerate volume fraction of bentonite= 0.01

Rock porosity of fractures 10^{-4}

Fills 38 000 m^3 rock

A cube with 34 m sides

Could this be used as an argument against large loss?

Some queries II

- What does the detritus do to the loss of smectite?
- Where does the detritus end up?

Suggestions

- More experiments in narrow slots
- Develop a model for detritus migration in variable aperture fractures
  - Movement of small particles pushed by expanding
  - Movement of particles pulled by gravity in Buildup of filters for smectite
  - Smectite filtering

Richards T., Neretnieks I., 2010, Filtering of clay colloids in bentonite detritus material. Chem. Eng. Technol., 33, No 8, 1303-1310

Some references on erosion modelling and background reports

SKB reports can be freely downloaded from www.SKB.se
Posiva reports can be freely downloaded from www.Posiva.fi
The reports marked yellow summarise modelling approaches

Liu, L., 2010. Permeability and expansibility of sodium bentonite in dilute solutions. Colloids Surf. A: Physicochem. Eng. Aspects 358 (1–3), 68–78.

Liu L. Neretnieks I., Moreno L., Permeability and expansibility of natural bentonite MX-80 in distilled water, Physics and Chemistry of the Earth 36 (2011) 1783–1791

Liu L., 2011, A model for the viscosity of dilute smectite gels, Physics and chemistry of the earth, 36, p 1792-1798

Liu L., 2013, Prediction of swelling pressures of different types of bentonite in dilute solutions, Colloids and Surfaces A: Physicochem. Eng. Aspects 434 (2013) 303– 318

Liu, L., Moreno, L., Neretnieks, I., 2009a. A Dynamic force balance model for colloidal expansion and its DLVO-based application. Langmuir 25 (2), 679–687.

Liu, L., Moreno, L., Neretnieks, I., 2009b. A novel approach to determine the critical coagulation concentration of a colloidal dispersion with plate-like particles. Langmuir 25 (2), 688–697.

Liu L., Neretnieks I., Moreno L., 2011, Permeability and expandability of natural bentonite MX-80 in distilled water. Physics and Chemistry of the Earth, 36, p 1783-1791

Moreno L., Neretnieks I., Liu L., 2010, modelling of bentonite erosion SKB TR-10-64.

Moreno L., Neretnieks I., Liu L., 2011, Erosion of sodium bentonite by flow and colloid diffusion, Physics and chemistry of the earth, 36, p 1600-1606

Neretnieks, I., Liu, L., Moreno, L., 2009. Mechanisms and Models for Bentonite Erosion. Swedish Nuclear Fuel and Waste management Co., Technical report, SKB TR-09-35

Neretnieks I., Liu L., Moreno, L., 2010, Mass transfer between waste canister and water seeping in rock fractures. Revisiting the Q-equivalent model, Swedish Nuclear Fuel and Waste management Co., Technical report, SKB TR-10-42

Schatz, T., Kanerva, N., Martikainen, J., Sane, P., Olin, M., Seppälä, A and Koskinen, K., 2012, Buffer Erosion in Dilute Groundwater. Posiva Report 2012-44 (2012).

Richards T., Neretnieks I., 2010, Filtering of clay colloids in bentonite detritus material. Chem. Eng. Technol., 33, No 8, 1303-1310

Reports submitted to BELBaR 2015

1) Bentonite expansion and erosion- Development of a two-region model by Ivars Neretnieks, Luis Moreno and Longcheng Liu
2) Evaluation of some erosion experiments by the two-region model by Ivars Neretnieks, Luis Moreno and Longcheng Liu
3) Release and sedimentation of smectite agglomerates from bentonite gel/sol by Ivars Neretnieks

Thank you for your attention

Scaling of erosion from laboratory experiments to temporal and spatial extent of a repository

Clay Colloids in Aqueous Systems
3-4 February 2016, Berlin, Germany

Markus Olin
Veli-Matti Pulkkanen, Michał Matusewicz

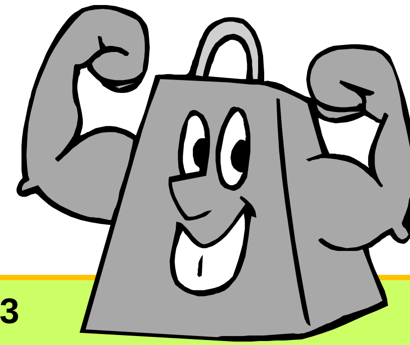
The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement n°295487, the BELBaR project.

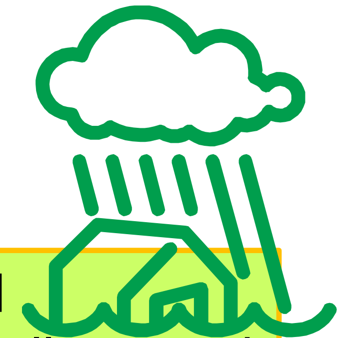
CONTENT

- Introduction
- General observations
  - Why different scales?
  - Quantum mechanics and molecular dynamics
  - Micro experiments and measurements
  - Macro experiments
  - Macro modelling
  - Full scale modelling
- Some results
- Discussion
- Conclusions

Introduction

Thermodynamics of bentonite in KBS3 method





Thermodynamic variables

- Temperature, *T*
- Pressure, *P*
- Chemical composition
  - Saturation, *S*
  - Density, *ρ*
  - Ionic strength, *I*

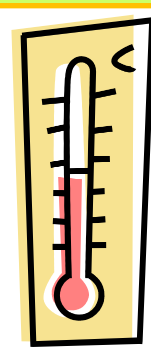
ρ: 1…1 700 kg/m³
Montmorillonite, exchangeable cations, accessory minerals

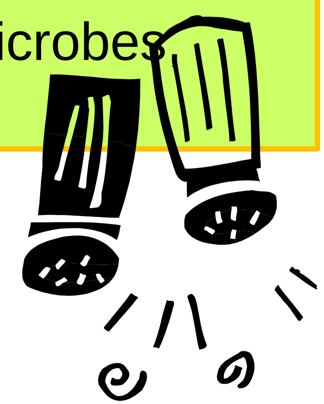
***S*: 0.3…1**
Dry to totally wetted

***T*: -10…100 ºC**

***P*: 0.1…4 MPa +** ice cover

***I*: 0.01 mM…1 M**
1 mg/L…100 g/L
Na-Ca-Cl + other ions, microbes, colloids

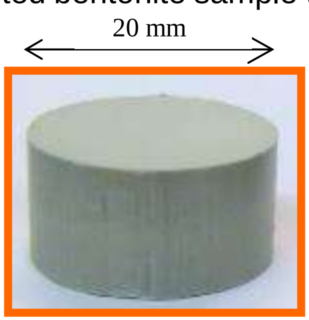


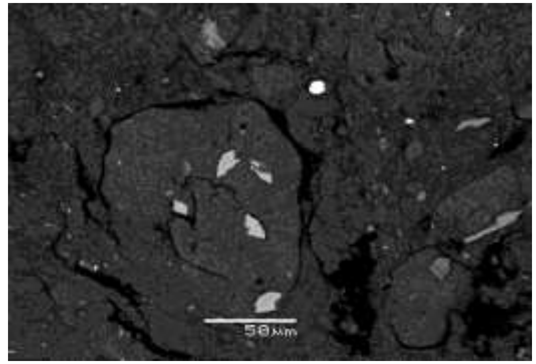


Scales, properties of bentonite and water phase

- **Spatial scales**
  - Colloidal size
  - Pore size
  - Laboratory
  - Small scale
  - Pilot scale
  - Repository scale
- **Time scales**
  - Nanoseconds in molecular dynamics
  - Lab = days to years
  - Repository = years to millennia

Compacted bentonite sample (JyU)



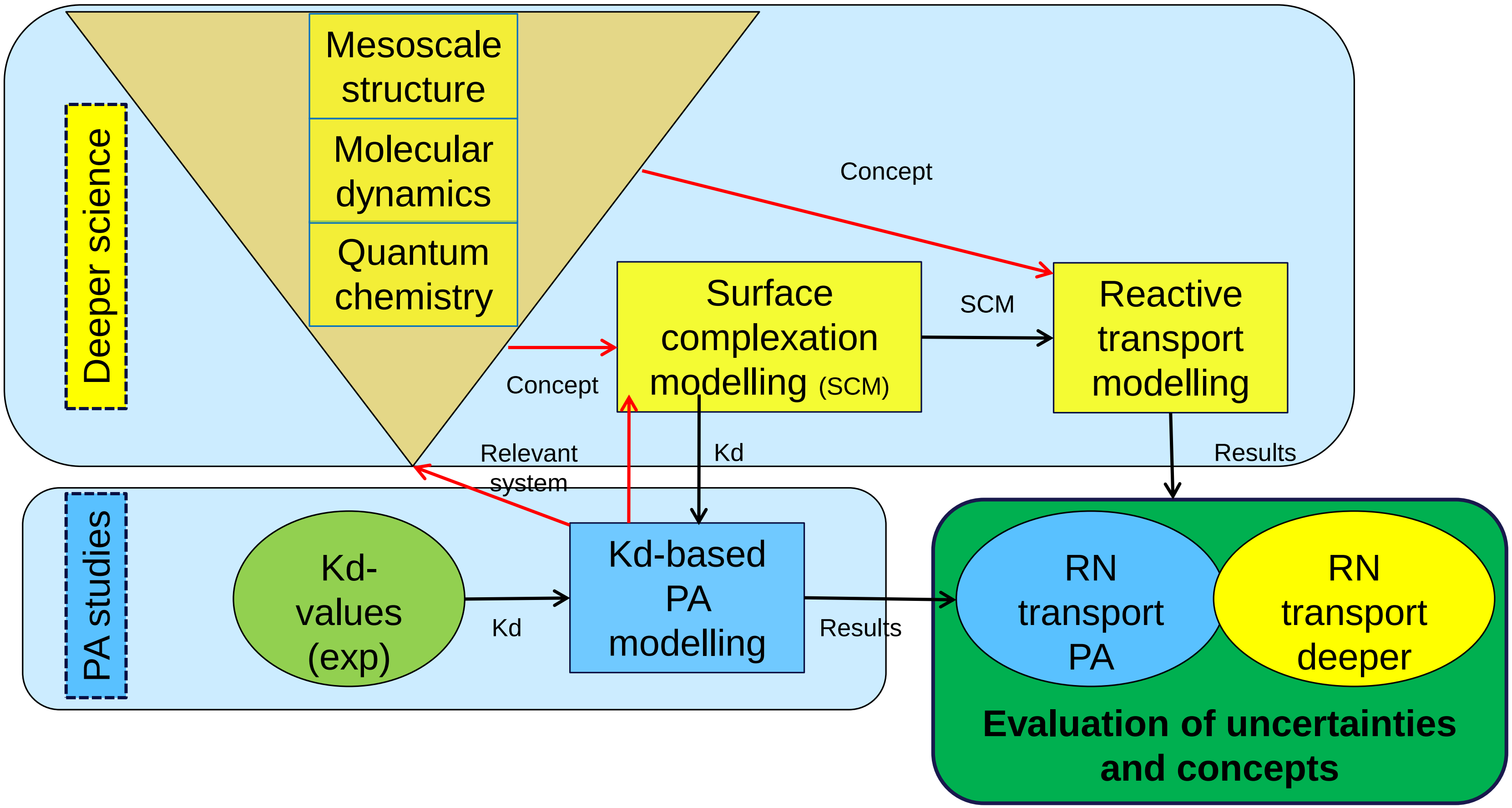


- **Bentonite properties**
  - Relative amount of montmorillonite
  - Cationic form of montmorillonite
  - Accessory minerals
  - Grain size
  - Initial water content
  - “History” of the samples
    - Production
    - Transport
    - Processing

- Water
  - Humidity or saturation
  - Composition
    - Electrolyte
    - Groundwater simulant
  - Gases
  - Colloids
  - Microbes

Loose bentonite sample (HYRL)

Hierarchy of both models and nature itself

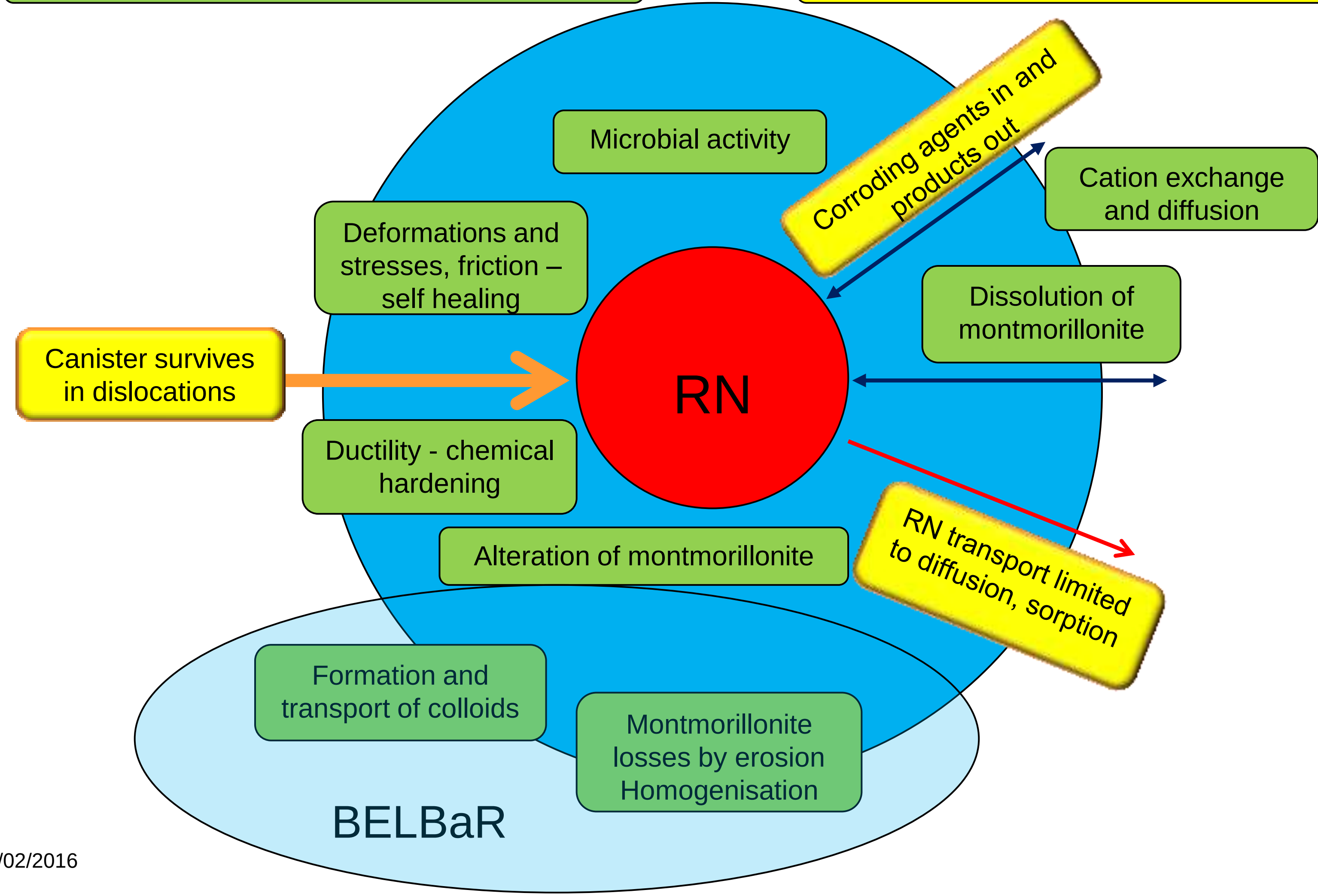


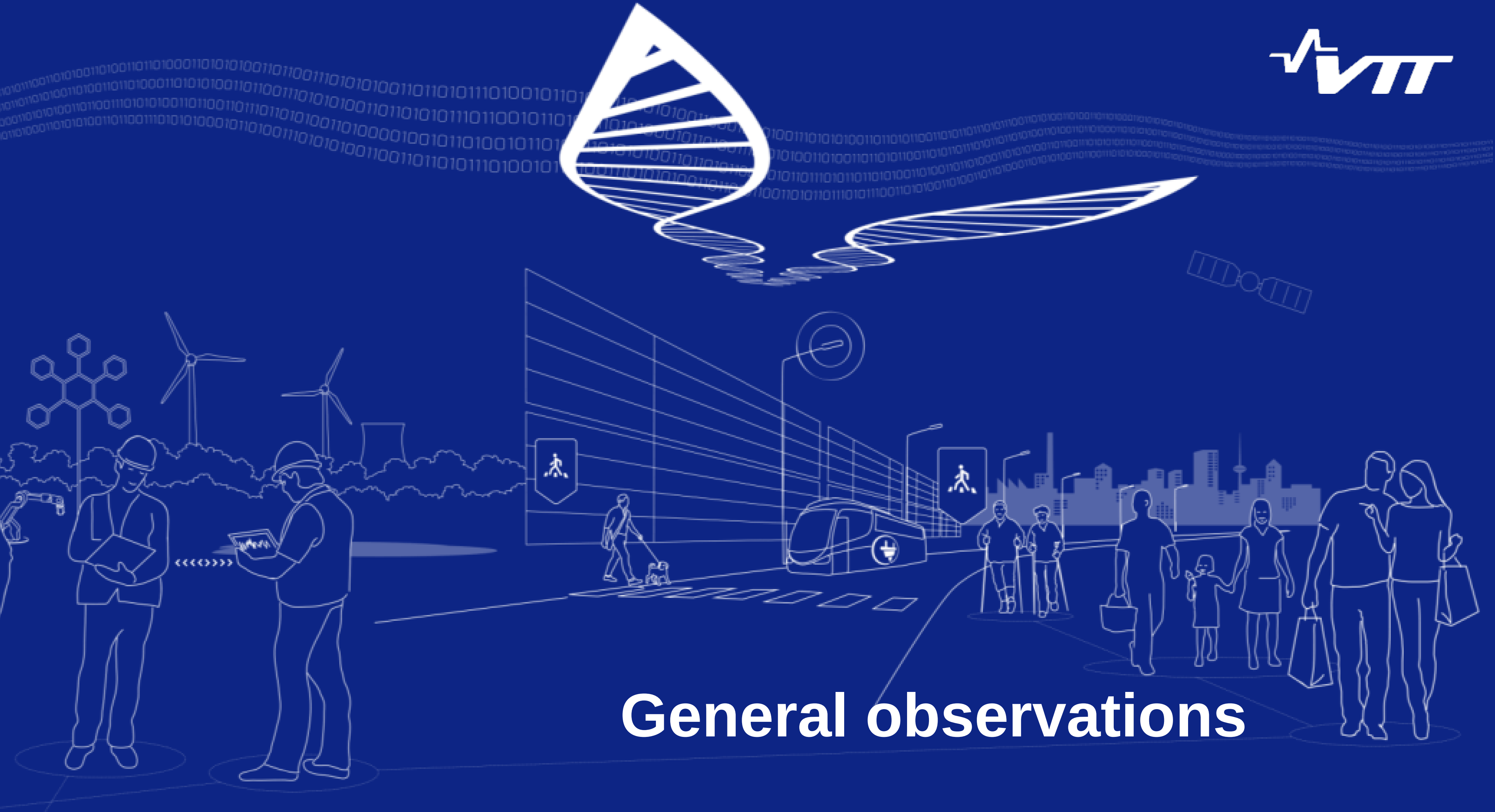
- **Not only models, but reactions are also taking place on different scales**
- **Absence of know-how of reactions does not guarantee absence of those reactions**
- “Doctors most commonly get mixed up between absence of evidence and evidence of abense” — Nassim Nicholas Taleb

Safety functions: protect canister, and limit and delay release of RN
Processes related to these shown below

Boxes of green colour = important issues

Boxes of yellow colour = safety functions





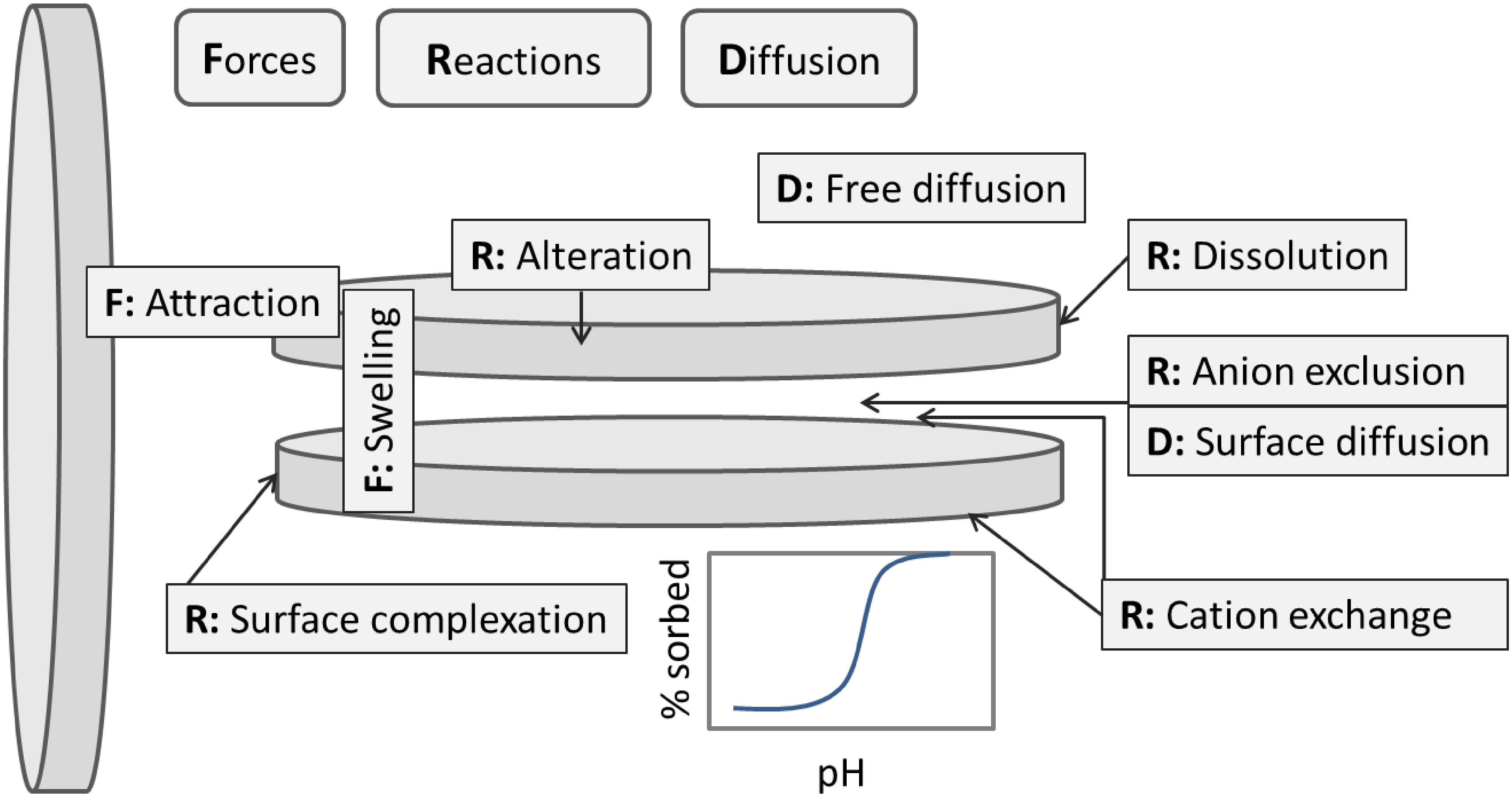
General observations

Why different scales?

- Essentially all beneficial properties of bentonite are based on nano-level reactions, which
  - can be directly modelled by present quantum mechanics and molecular dynamics tools (not much in BELBaR).
  - can be studied by some experimental methods like SAXS, NMR and
  - by many kinds of diffusion and sorption (exclusion) studies.
- However, all practical modelling must be done by macroscopic models
  - Macroscopic model is the only working option for full scale predictive work

Quantum mechanics and molecular dynamics

- By modern tools of quantum mechanics and molecular dynamics it is possible to study montmorillonite on nano-level
- However, these type of studies were not included in BELBaR (?)
- Typical results:
  - Distances between montmorillonite layers at different conditions (possible to measure, too, see previous slide)
  - Distribution of ions both in interlamellar space and elsewhere
  - Computation of forces between layers -> swelling pressure
- Impact
  - Proper approach for nano-level phenomena compared to continuum models applied earlier
  - May change even the very basic thinking of montmorillonite
  - May offer by proper upscaling better basis for macroscale modelling


Forces
Reactions
Diffusion
D: Free diffusion
R: Alteration
R: Dissolution
F: Attraction
F: Swelling
R: Anion exclusion
D: Surface diffusion
R: Surface complexation
% sorbed
pH
R: Cation exchange

Micro experiments and measurements

- BELBaR/VTT/Matusewicz (poster)
- Many methods to study microstructure down to nanolevel
  - SAXS, NMR, IE, diffusion
  - Problems in sample preparation
- Results
  - Aperture (distribution) of interlamellar space (SAXS)
    - Porosity fractions by simple calculations
  - Fraction of interlamellar space (NMR, IE)
- Impact
    - Evaluation of bentonite will be based on macroscopic studies.
    - Almost all properties of bentonite are based on the microscopic properties
    - How macroscopic properties relate to microscopic ones: properties of both scales before and after the experiments.
    - Otherwise, apparently similar macroscopic bentonite samples may be totally different at the microscopic scale.
    - At least some of the observed controversial experimental results may be caused by these types of differences.

Macro experiments

- In BELBaR much work in macro experimenting
- It has appeared possible to experimentally simulate erosion in dilute water systems
  - Very useful results obtained
  - Scaling issues
    - Full scale experiments are “impossible”
    - Effects of bentonite ageing (some studies available about microstructural changes)
- Both sorption and erosion experiments
  - Applying both results in modelling?

Macro modelling

- BELBaR/VTT/Pulkkanen (poster)
  - Initial state for bentonite erosion is prepared by compaction and wetting -> one way to know the initial state is by model including wetting
  - Bentonite model should therefore include also wetting in addition of mechanistic phenomena, and chemical interaction which the driving force for swelling
- Principle: same basic model for (almost) all phenomena in bentonite
- It is possible develop models
  - Mathematical tools for inclusion of large deformations (elastic and plastic) and chemistry are available
  - Thermodynamic limitations
  - Finally much systematic lab work needed

Full scale modelling

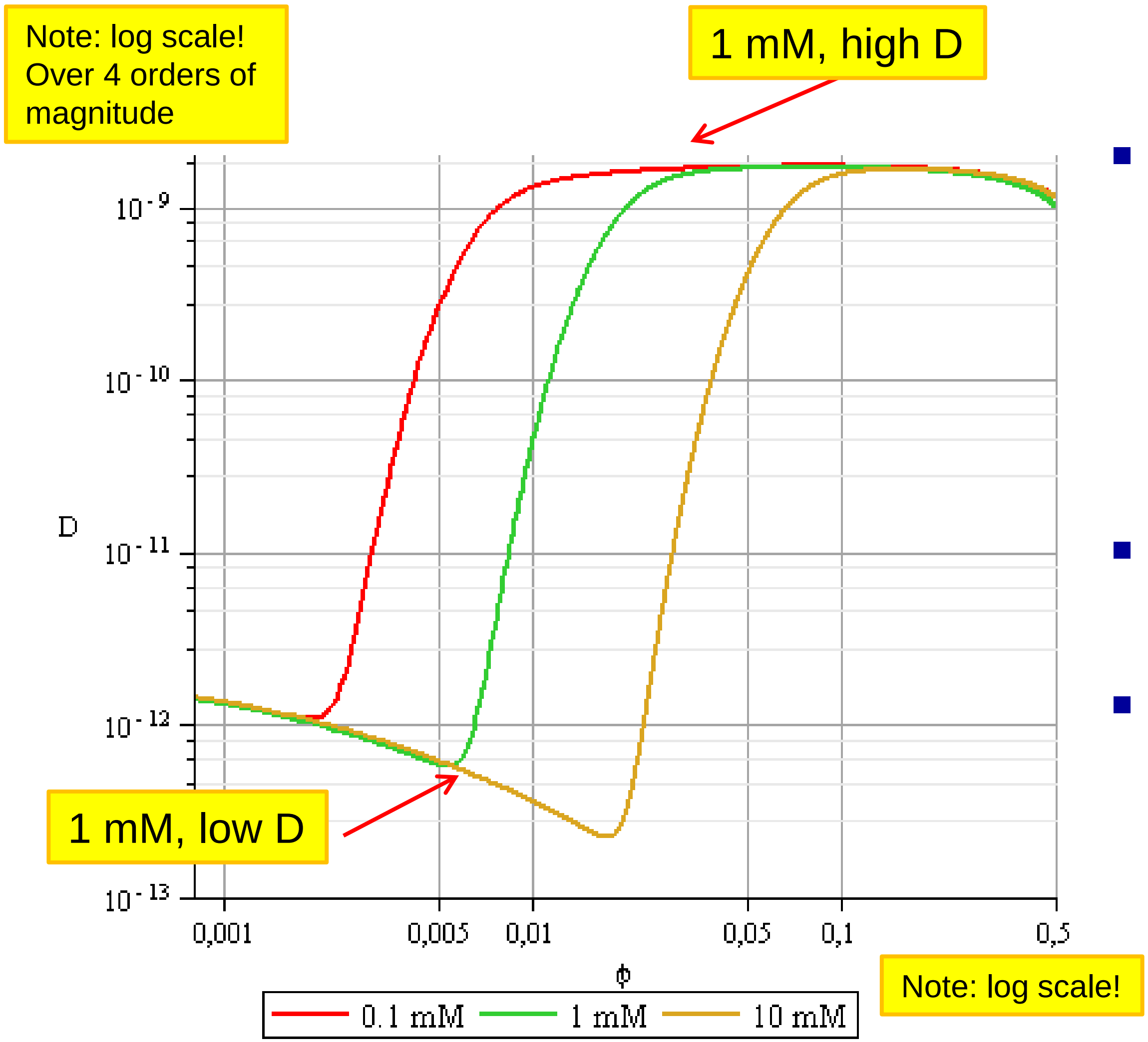
- KTH (Ivars') model based on
  - Nano-level forces
  - Some structural properties
- Model has appeared difficult to apply
  - VTT has applied simplified version
  - Can be claimed to be verified to certain extent
- Validation has appeared demanding
  - Lab experiments done anyway in different conditions than full scale is assumed to happen

Some macroscopic scaling results

Some results of macroscopic scaling by modelling

- Simplified version of Ivars' (KTH) model
- Observables:
  - Flux (or flux density), *Q*, and
  - Penetration depth, *L*
- Parameters
  - Boundary value, φ_b
  - Salinity, *c*,
  - Geometry, radius *R*
  - Diffusivities, *D*
  - Velocity, *v*
- Simple dimensional analysis (Péclet number = *Pe*)
  - $Q=Q(\varphi_b,c,R,D,v)=Q_0\times F(R\times v/D)\times G(\varphi,c)\approx F(Pe)$
- Computed by varying *R* and *v*, and in some cases *c*

Bentonite expands by non-linear "diffusion"



- Non-linear: diffusivity of bentonite depends on volume fraction of bentonite (or montmorillonite), ϕ
- At 1 mM solution
  1. High diffusivity (like ions in free water) above $\phi \approx 0.040$
  2. Low (more than three orders of magnitude, like colloids) diffusivity below $\phi \approx 0.006$
- By decreasing salinity dropdown changes to lower values of ϕ
- However, at low ϕ values groundwater flow starts to be an important transport mechanism → erosion of bentonite

- When ϕ high, D_F high (h)
- When ϕ low, D_F low (l)
- At very low volume fraction colloidal diffusivity (c)
- Turning point as a function of volume fraction varies as a function of salinity

Trial functions

$$D_F(\phi,c) = D_F^l \cdot \left(\frac{D_F^h}{D_F^l}\right)^{\alpha(\phi,c)} + D_F^c$$

$$\alpha = \alpha(\phi,c) = \left(1 + \left(\frac{\ln\phi}{\ln\phi_{\text{critical}}}\right)^n\right)^{-1}$$

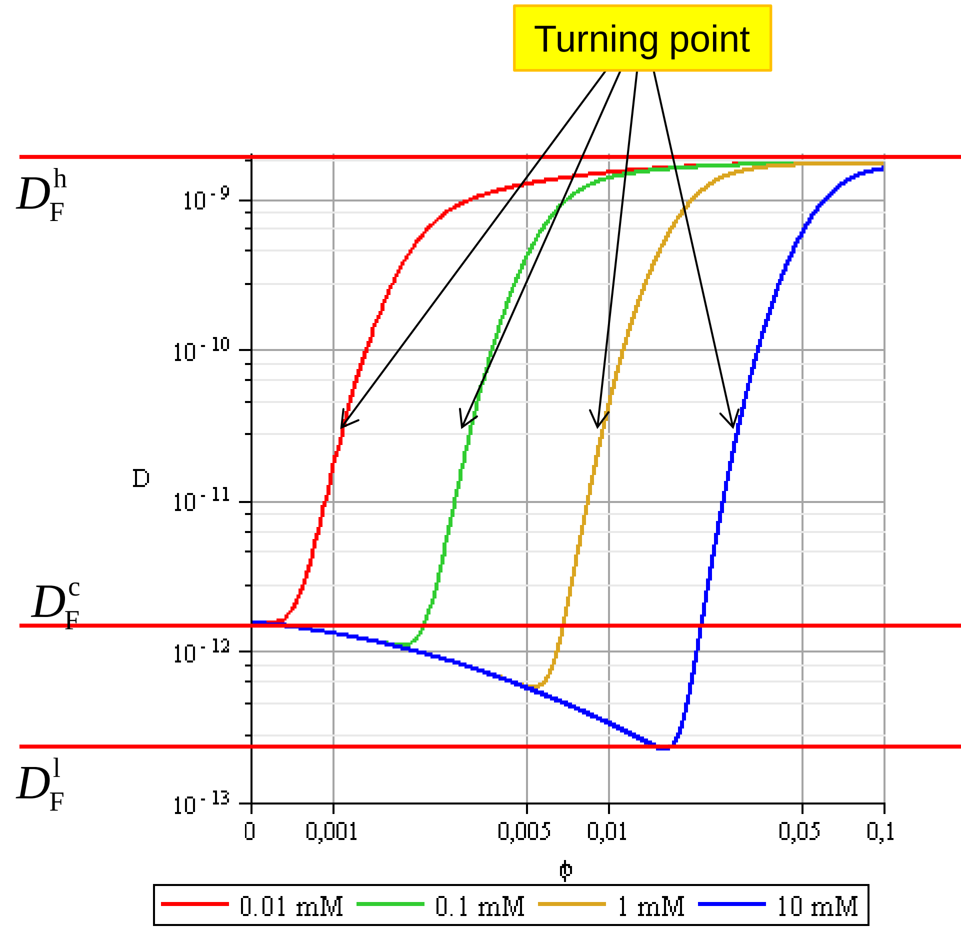
$$\phi = 1, \alpha = 1$$

$$\phi \to 0, \alpha \to 0$$

$$\phi_{\text{turning}} = Ac^b \cong 0.01\sqrt{c}$$

$$\alpha = \alpha(\phi,c) = \left(1 + \left(\frac{\ln\phi}{\ln A + b\ln c}\right)^n\right)^{-1}$$

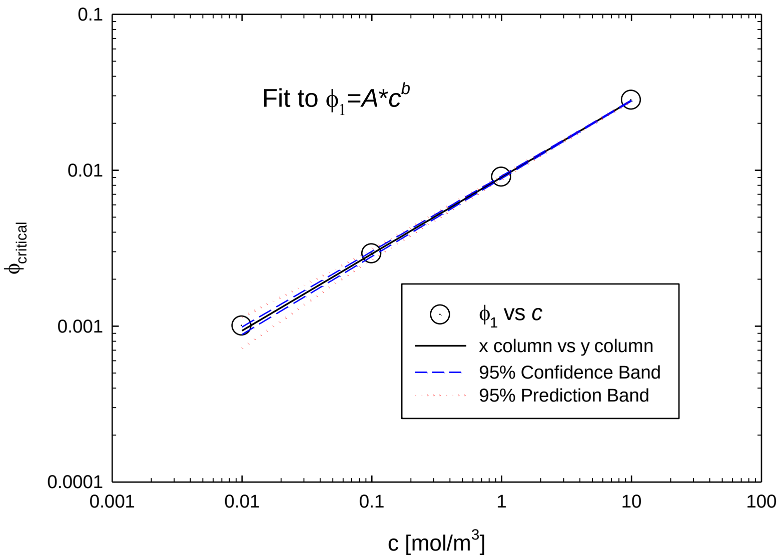
For testing purposes mainly: an analytic expression for D_F



Fitting parameters and goodness of fitting

- Parameters in Table and fitting in Figures

Parameter	Value	Unit
n	16	-
A	0.009± 3.90E-005	-
b	0.492± 0.0020	-
D_F^h	1.6e-9	m^2/s
D_F^l	1e-13	m^2/s
D_F^c	1.9e-12	m^2/s



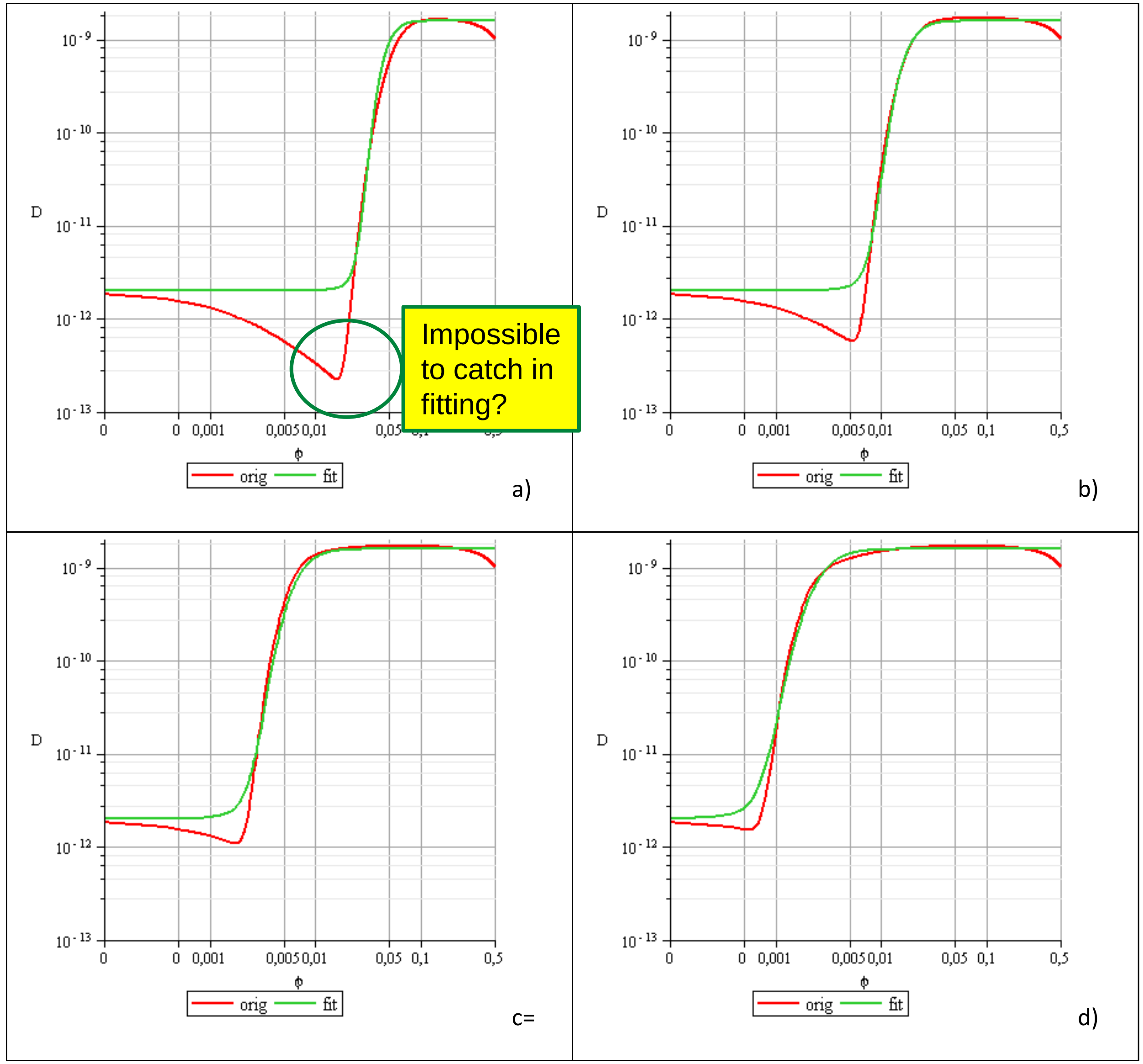
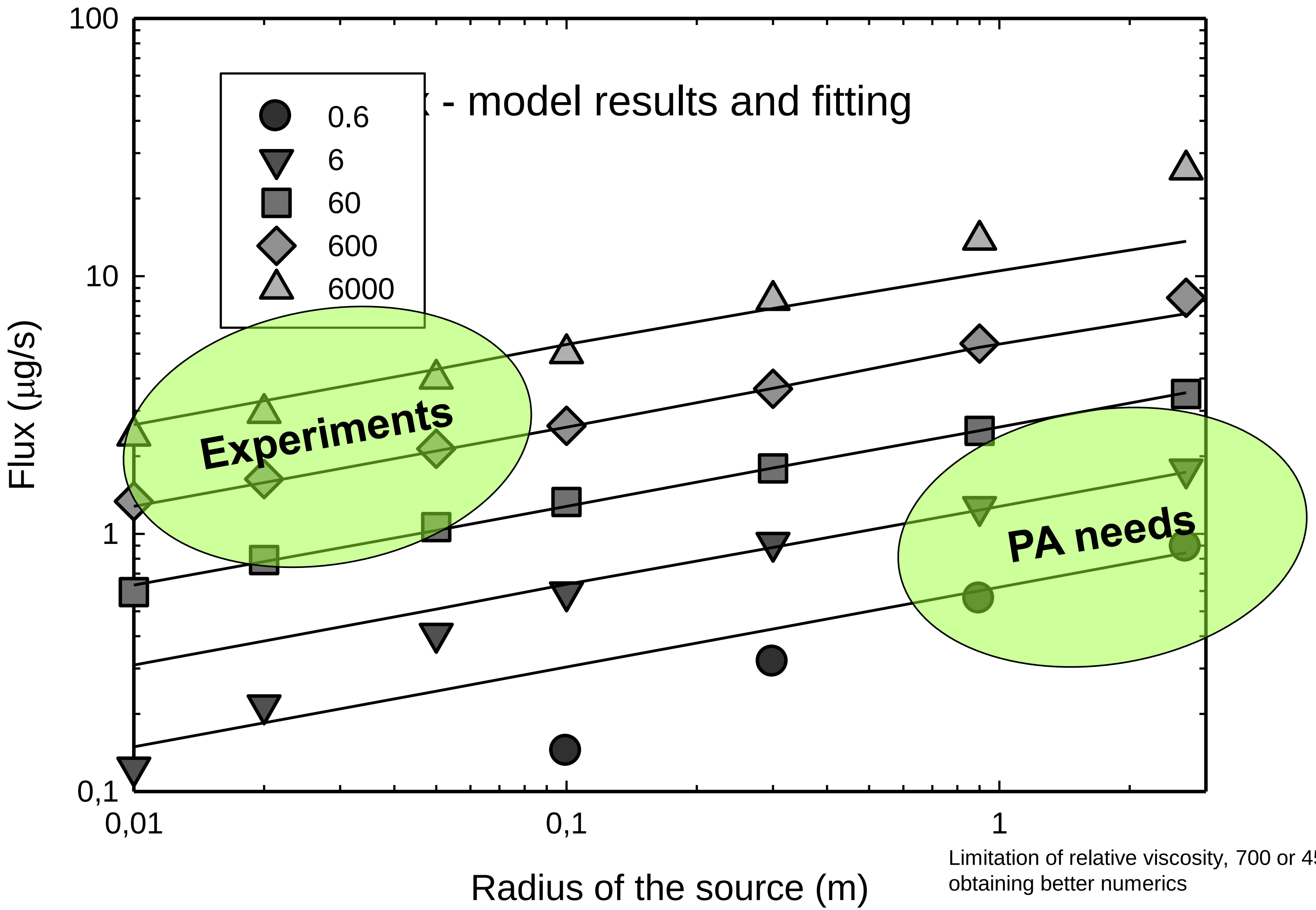


Figure 1. a) 10 mM; b) 1 mM; c) 0.1 mM and d) 0.01 mM

Q as a function of R and v: $Q=0.73\times(v\times R)^{0.31}$

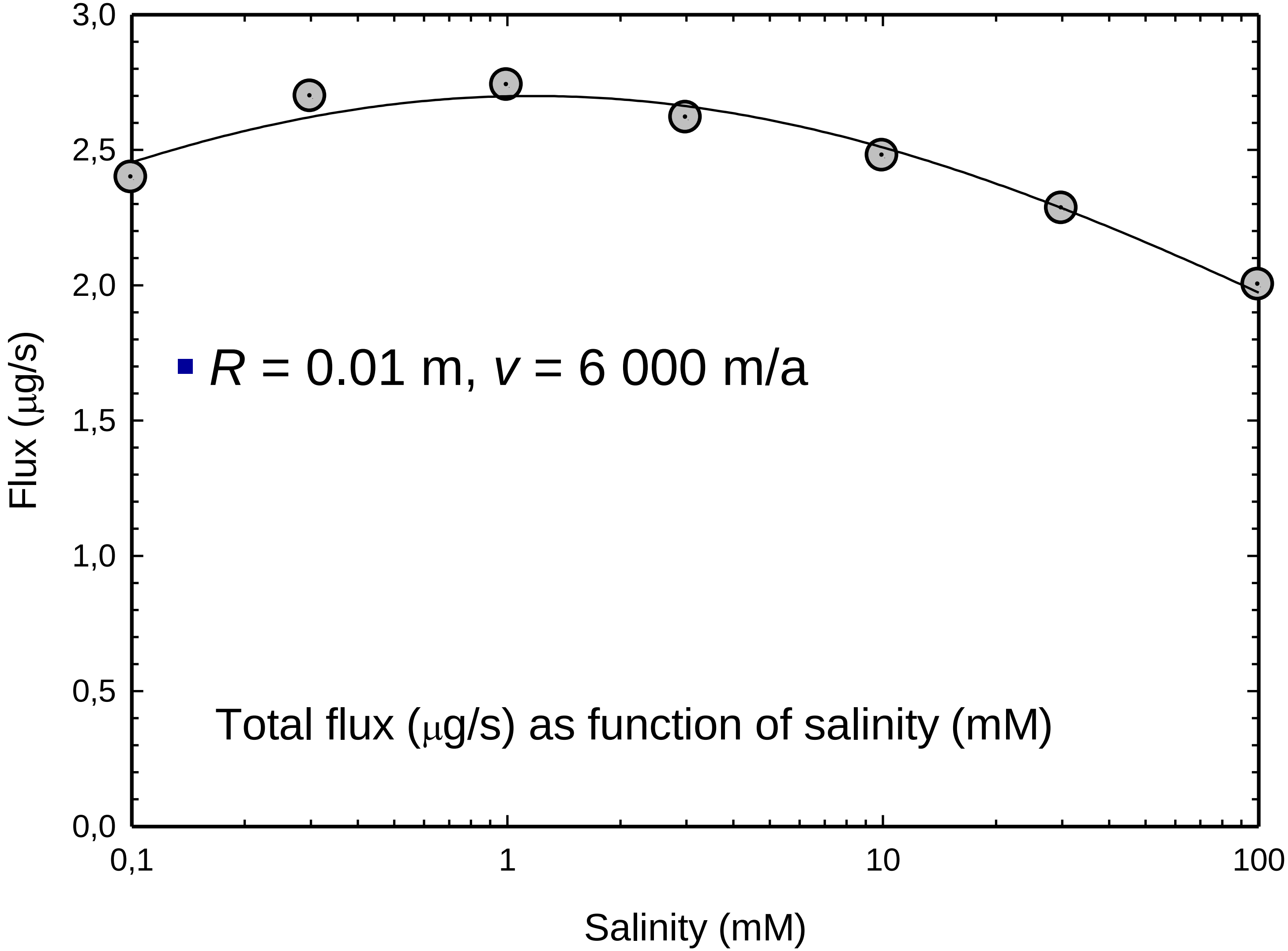
- Fitting deviates at high and low velocity



Limitation of relative viscosity, 700 or 45 000, for obtaining better numerics

Almost no salinity effects

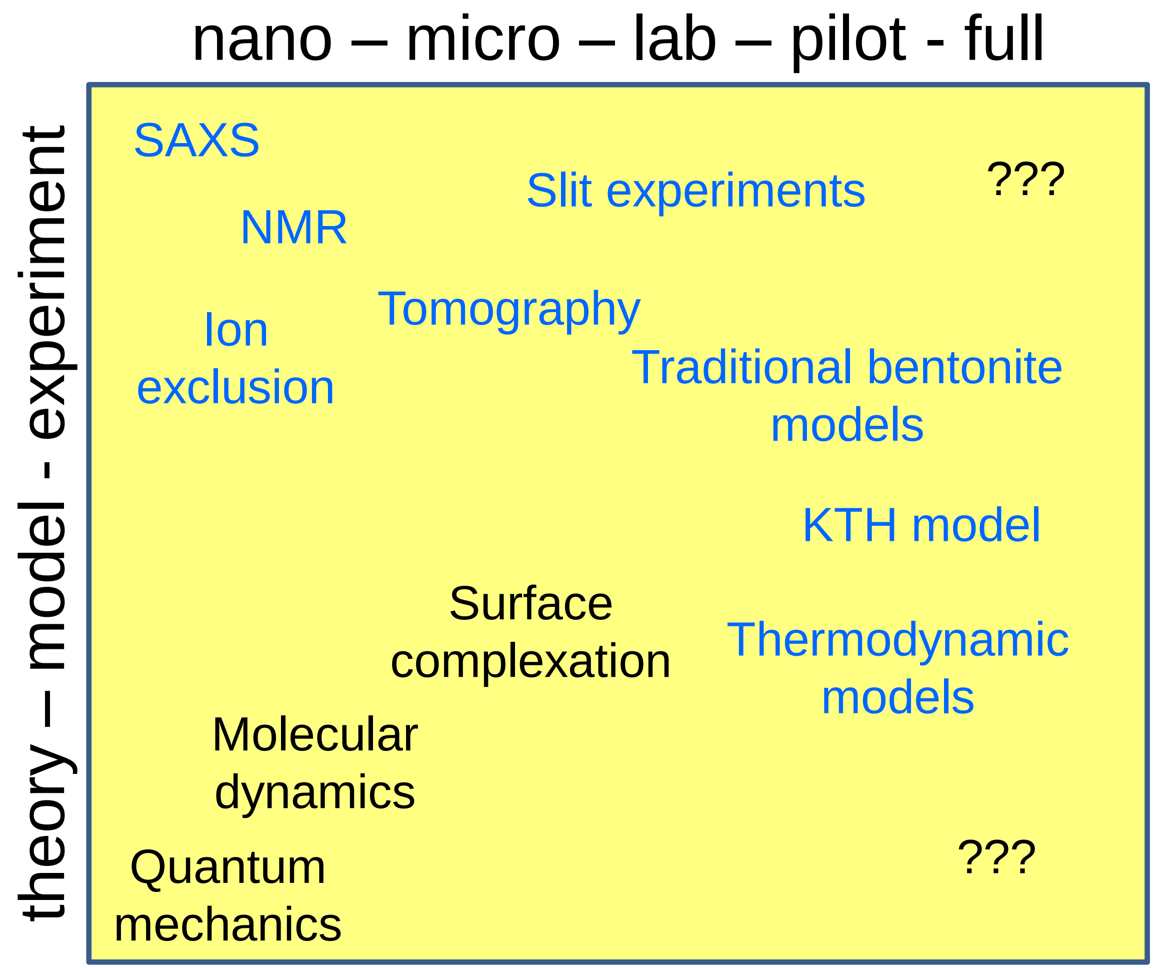
Numerical problems start to be harder at higher salinity!



Discussion and conclusions

Discussion I

- Many methods to study bentonite
  - experiments and modelling
  - nano to full scale
- Ideal macroscopic model should be
  - Consistent with almost all experimental and nano level modelling results
  - Not only model erosion but other topics too
- Full scale experiments are impossible for chemical erosion



Blue ones in BELBaR

Discussion II

- Models, experiments and real systems. Differences between
  - Models and experiments
    - Initial swelling in experiments even when the samples are totally wetted
    - Some model for swelling needed to take care of that
  - Models and real systems
    - Scaling possible, if the model describes reality, but how to obtain that good models
  - Experiments and real systems
    - In reality bentonite is very old, when erosion starts
    - Scaling difficulties both spatial and temporal

Conclusions I

- Much better understanding of chemical erosion achieved in BELBaR compared to the starting point
- Still problems in scaling the results to PA purposes
- Much good modelling and experimental results available
  - BELBaR
  - Many other projects
  - How to integrate these?

Conclusions II

- Formulate the issues important for long-term safety assessment
  - Scaling of experimental results to real conditions
- Identify main uncertainties related to colloids in safety assessment
  - Which processes are really happening in repository's future?
- Bentonite erosion and production of colloids (WP2)
  - Colloid formation on interface between bentonite and water – colloidal diffusion is pretty slow and therefore water flow may have very important role: detailed know-how of water flowing in just colloid formation state is still lacking
- Improvements to models (WP5)
  - Some advances have been done
  - New model approaches proposed
- Thanks for collaboration!


VTT
TECHNOLOGY FOR BUSINESS

BELBaR

Summary and evaluation by the End-User Review Board

Jarmo Lehikoinen (Finnish Radiation and Nuclear Safety Authority, STUK)

Jinsong Liu (Swedish Radiation Safety Authority, SSM)

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

BELBaR

Introduction

- ✓ The emphasis in the evaluation of the presentations in the abstract collection has been on the merits and usefulness of the project outcomes mainly from the end-user (here, regulatory) point of view.
- ✓ However, it would be safe to say that the expertise of the consortium and the set of state-of-the-art experimental techniques used in the BELBaR project were truly impressive.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

BELBaR

Summary of the project achievements

- ✓ The project outcomes have the potential to pave way for new investigations where the most critical uncertainties are mitigated and managed, and bits and pieces of information put together systematically to expand the knowledge base.
- ✓ Such improved knowledge would also enable the construction of refined conceptual models to more credibly bound the potential risk posed by clay colloid formation and phenomena associated with it.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Summary of the project achievements (cont'd)

BELBaR

- ✓ Thanks to the BELBaR project, the future performance assessments are in a better position to make more informed choices in a safety case to argue for the long-term performance of the bentonite-based barriers and the host rock and, ultimately, for the post-closure safety.
- ✓ The results and new insight gained from the project also enable both an implementor and a regulator to better identify, mitigate and manage the uncertainties anticipated to pose the greatest risk to the performance of a disposal system and to the post-closure safety.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Evaluation of the meeting's presentations

The presentations are grouped into four topics:

- Characterisation
- Process study and mechanism understanding
- Colloid mobility and radionuclide sorption (ir)reversibility
- Modelling

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Gratitute to the invited speakers

- We all really appreciate the speeches made by the invited speakers
- The presentations have brought the project to a wider perspective of the issues we are dealing with
- We will remember the video footage of clay avalanche and the cartoon picture of fertilising the lake.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Characterisation (I)

BELBaR

- The End-User Review Board considers it very positive that a variety of analytical techniques, which had not previous been widely used in this area, have now been used to characterise the properties of bentonite and the colloids it forms.
- A large amount of information has been obtained and the information is valuable for performance assessment of a final repository
    - cation exchange capacity,
    - external and total surface areas
    - microstructure of the layered clay, etc.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Characterisation (II)

- The aggregation and sedimentation behaviour of clay colloid particles have been much better understood, which can be of great importance for evaluation of the conservativeness of the different modelling approaches used in the performance assessment.
- The finding that the accessory minerals may lead to aggregation that otherwise does not occur is of great importance for the performance assessment and probably need to be further confirmed.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Characterisation (III)

- While characterising the rheological properties of clay suspensions the project reveals several interesting phenomena that may require further attention to be paid to when the results are incorporated in performance assessment.
  - to distinguish between gel and paste that is formed,
  - to consider the effect of edge-face interaction,
  - to unambiguously define a gel phase

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Process study and mechanism understanding (I)

- The End-User Review Board has the opinion that the understanding of the mechanisms involved in the erosion process has been greatly deepened through this project.
- The erosion tests using artificial fracture and other setups have confirmed some of the previously gained understanding of the mechanisms
  - bentonite erosion is influenced by water flow rate,
  - hydration/water-saturation is related to relative humidity,
  - colloid stability depends on ionic strength of the solution and on the cation exchange properties of the bentonite,
  - particles of the accessory minerals are left behind during the erosion process and are also capable of mitigating erosion.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Process study and mechanism understanding (II)

BELBaR

- It is of special interest that many new phenomena and processes related to the bentonite erosion have been discovered during the project.
  - the swelling of bentonite has different temperature dependences for swelling in monovalent and divalent counterion solutions,
  - the displacement along the axis of the sample is uneven during swelling, with largest displacement occurring at the end of the sample in direct contact with solution.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Process study and mechanism understanding (III)

- Regarding the colloid stability, several new findings possibly of great importance for performance assessment have been obtained.
  - the temperature dependence of the yielding of the gel has been shown to have an origin from edge-face interaction and enthalpy for such interaction has been obtained
  - the colloid stability depends not only on solution type and ionic strength, but also on pH. Could this be considered as evidence for edge-face interaction?

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Process study and mechanism understanding (IV)

- Some relative new observations concerning the erosion behaviour of bentonite are:
  - the erosion behaviour is more related to the smectite clay content than to the exchangeable counterion(s);
  - erosion in sloped fractures is substantially increased. (This phenomenon need to be considered in future performance assessments where Na-montmorillonite is assumed to form a conservative case, as it is known that Na-montmorillonite is more sensible to erosion. But Ca-montmorillonite has been observed to readily form stacks of platelets, making it more sensitive to sedimentation under gravitation.)

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

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Process study and mechanism understanding (V)

- Intercalation of CO_2 into the interlayer of nano-space of smectite clay may lead to swelling. Can this phenomenon have significance for performance assessment?

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Colloid mobility and radionuclide sorption (ir)reversibility (I)

- The results gained still beg the question of full reversibility of radionuclides in actual repository conditions.
  - Key role of experimental time to attain full sorption reversibility.
- The much slower desorption rate for tetravalent actinides also begs the question of a conservative assumption regarding the reversibility of their sorption; would full irreversibility be such an assumption?

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Colloid mobility and radionuclide sorption (ir)reversibility (II)

BELBaR

- Improved knowledge of the rates involved in the radionuclide desorption from bentonite colloids enables more credible assessments of the effect colloid-mediated radionuclide transport may have on the post-closure safety under varying flow conditions.
- Application of an average radionuclide distribution coefficient for all colloidal sizes was found acceptable in modelling.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

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Colloid mobility and radionuclide sorption (ir)reversibility (III)

- The lower affinity of radionuclides towards a dominantly divalent-cation form of bentonite than towards sodium form implies less colloid-mediated radionuclide transport.
- When bentonite colloids were found to have a non-negligible mobility, their potential to enhance radionuclide transport was evident. Clearly, this should have implications for whether or not colloid-mediated radionuclide transport should be considered in a safety case.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Colloid mobility and radionuclide sorption (ir)reversibility (IV)

- In hindsight, making normative assumptions, like "*Reversible, linear sorption of radionuclides onto colloids has been assumed*", for a project is considered questionable as it could tacitly guide a practitioner to select parameters that support these assumptions (and to result in "self-fulfilling prophecies") and may not serve to challenge the current understanding, although this likely has not taken place in the BELBaR project.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

BELBaR

Colloid mobility and radionuclide sorption (ir)reversibility (V)

- An aspect that was not touched upon by WP3 concerns the role of biocolloids (e.g. bacteria) to mediate the radionuclide transport.
- While the End-User Review Board tend to agree with one of the partners in that the main uncertainties still remain in the quantification of colloids in actual repository conditions and in the mobility of colloids, WP3 certainly has succeeded in mitigating these uncertainties to be managed in a safety case while arguing for the post-closure safety.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

EURATOM

Colloid mobility and radionuclide sorption (ir)reversibility (VI)

- It would also seem that the results from WP3 regarding radionuclide sorption (ir)reversibility and the role colloids may have in mediating radionuclide transport have implications for some of the issues in D1.2 that the project was planning to revisit.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Modelling (I)

- The End-User Review Board can give the comment that the modelling of bentonite erosion has made a large progress during the project, which has both increased the number of processes dealt with in the model, and enriched the tool-kit for performance assessment to select suitable models.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

Modelling (II)

- The classical "KTH-model" has been expanded and the numerical methods have been improved. The scaling approach has been developed based on the "KTH-model" by focusing on the system's Péclet number.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

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Modelling (III)

- An attempt has been made to model the ion-ion interaction, by using the weighted correlation approach in the framework of density function theory of statistic mechanics. The model may have significance in performance assessment for a better understanding and quantification of the erosion of Ca-montmorillonite.
- The novel density function approach to describe the selectivity of cation exchange process has paved the way for theoretical prediction of selectivity constants.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

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Modelling (IV)

- The electrophoretic mobility model has been introduced into the study of several processes related to erosion, such as surface conductivity effect.

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

BELBaR

Thank you for your attention

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement 295487.

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Build-up of Accessory Mineral Layers During Erosion of Buffer Material

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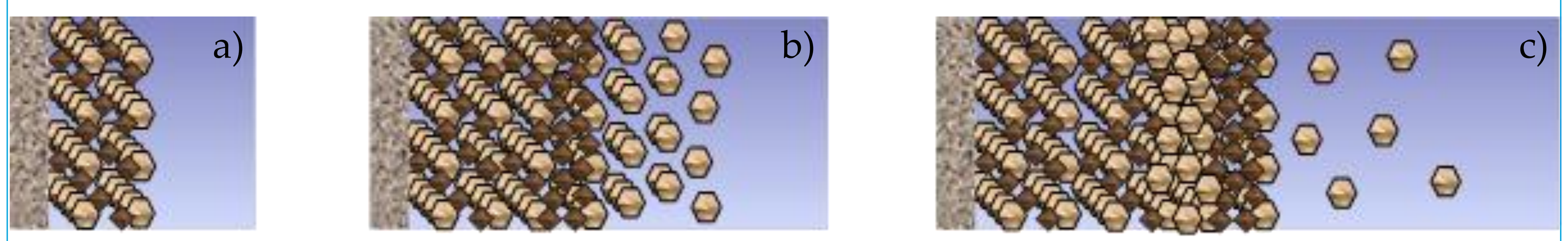
INTRODUCTION

Following erosive loss of colloidal montmorillonite through contact with dilute groundwater at a transmissive fracture interface, accessory phases within bentonite, such as quartz, feldspar, etc., might remain behind and form a filter bed or cake. As more and more montmorillonite is lost, the thickness of the accessory mineral bed may increase and the continued transport of montmorillonite slows and possibly stops if the porosity of the filter bed is sufficiently compressed. As the accessory mineral filter bed retains montmorillonite colloids, a filter cake composed of montmorillonite itself may also be formed. Ultimately, depending on their extent, properties, and durability, such processes may provide the bentonite buffer system with an inherent, self-filtration mechanism which serves to limit the effects of colloidal erosion.

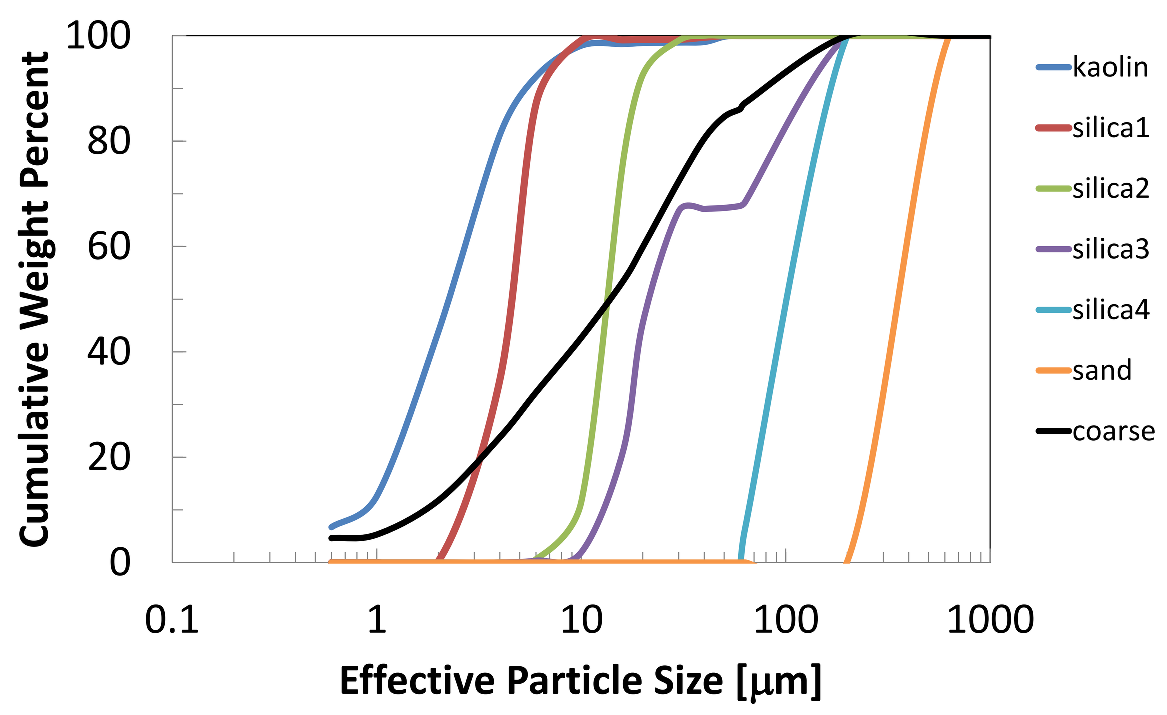
CONCEPTUAL VIEW



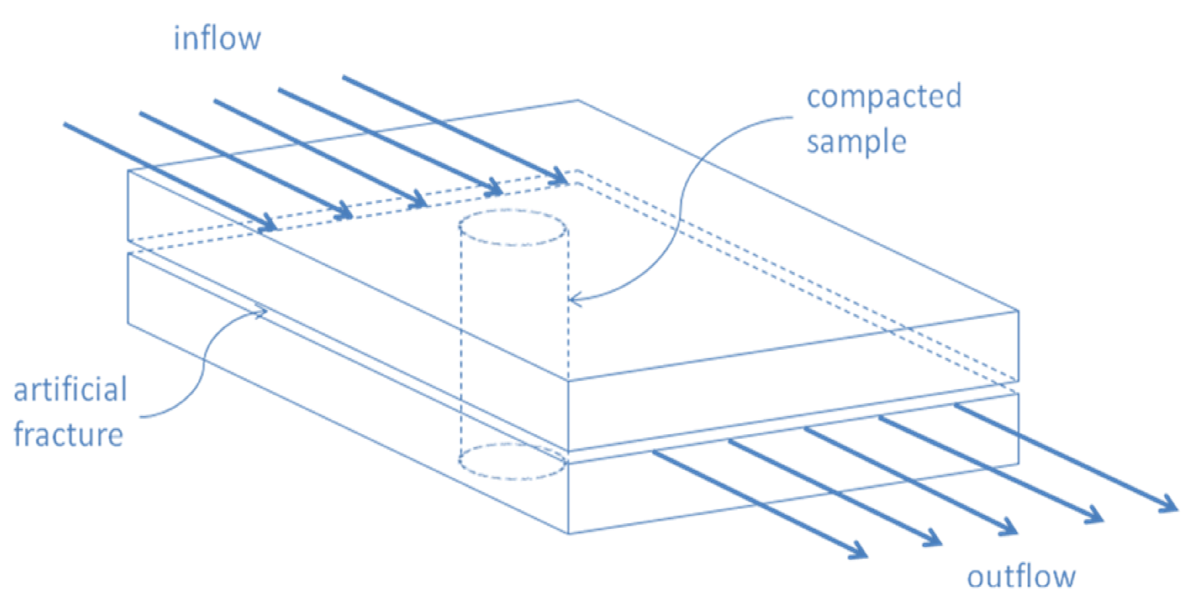
Conceptual view of a) extrusion of bentonite buffer material into an intersecting fracture, b) subsequent montmorilllonite erosion and accessory mineral filter bed formation, and c) montmorillonite filter cake formation. Montmorillonite colloids are represented as tan hexagons, accessory mineral particles as brown diamonds, and compacted bentonite buffer by the solid block on the left.

MATERIALS AND METHODS

In order to examine whether the erosion of bentonite material through contact with dilute groundwater at a transmissive fracture interface could intrinsically result in 1) the formation of an accessory mineral filter bed and cake and/or 2) filter caking of montmorillonite itself, a series of laboratory tests were performed in a flow-through, horizontal, 1 mm aperture, artificial fracture system. Bentonite buffer material was simulated by using mixtures (75/25 weight percent ratio) of purified sodium montmorillonite and various additives serving as accessory mineral proxies (kaolin, quartz sand, chromatographic silica). A test was also performed using MX-80 bentonite washed free of soluble material and thoroughly exchanged with sodium cations. The fracture erosion tests were performed using a Grimsel groundwater simulant (relative to Na^+ and Ca^{2+} concentration only) contact solution at an average flow rate of 0.09 ml/min through the system.



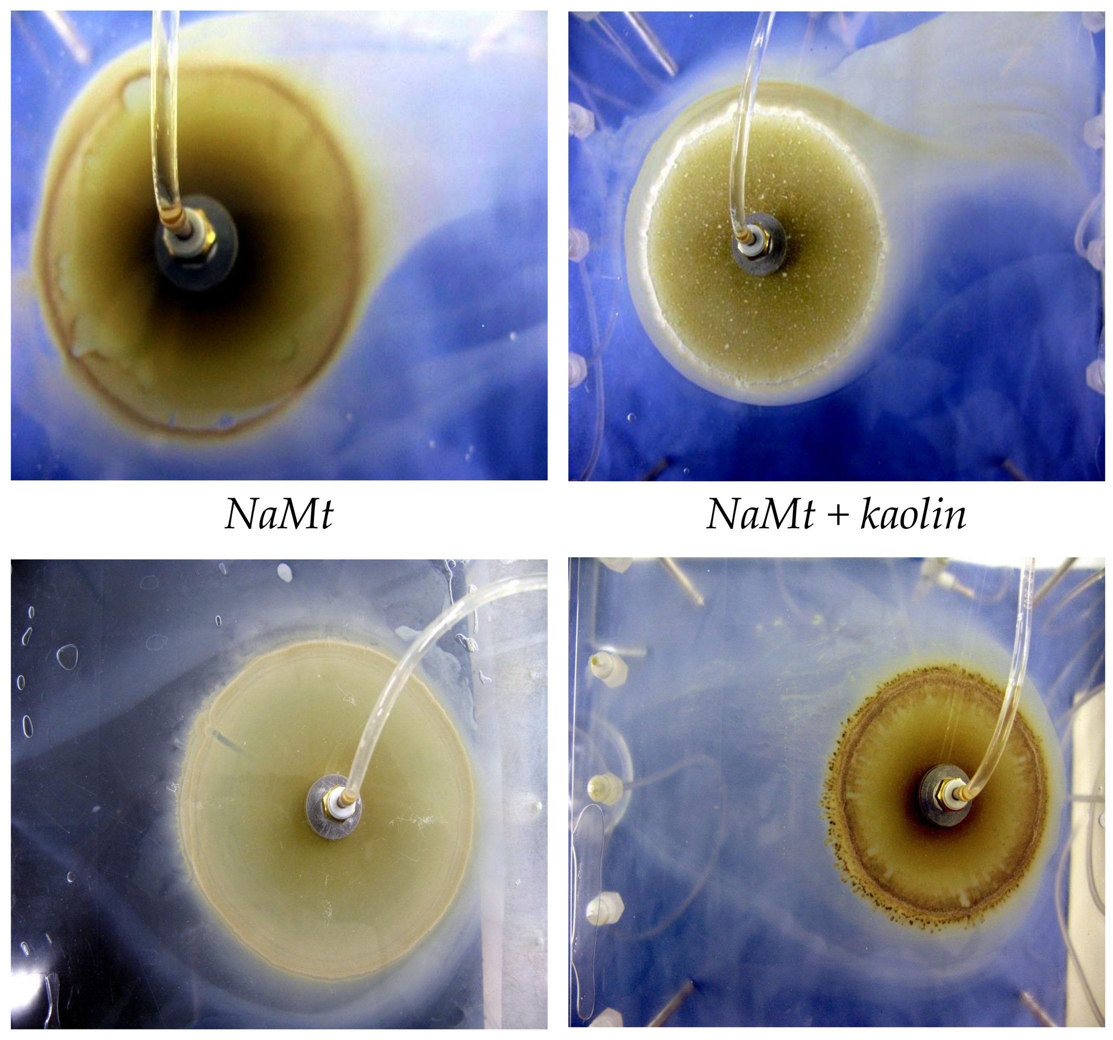
Effective particle size distribution of the added "accessory" minerals and bentonite coarse fraction from sedigraph analysis



Schematic representation of the flow-through, artificial fracture test system.

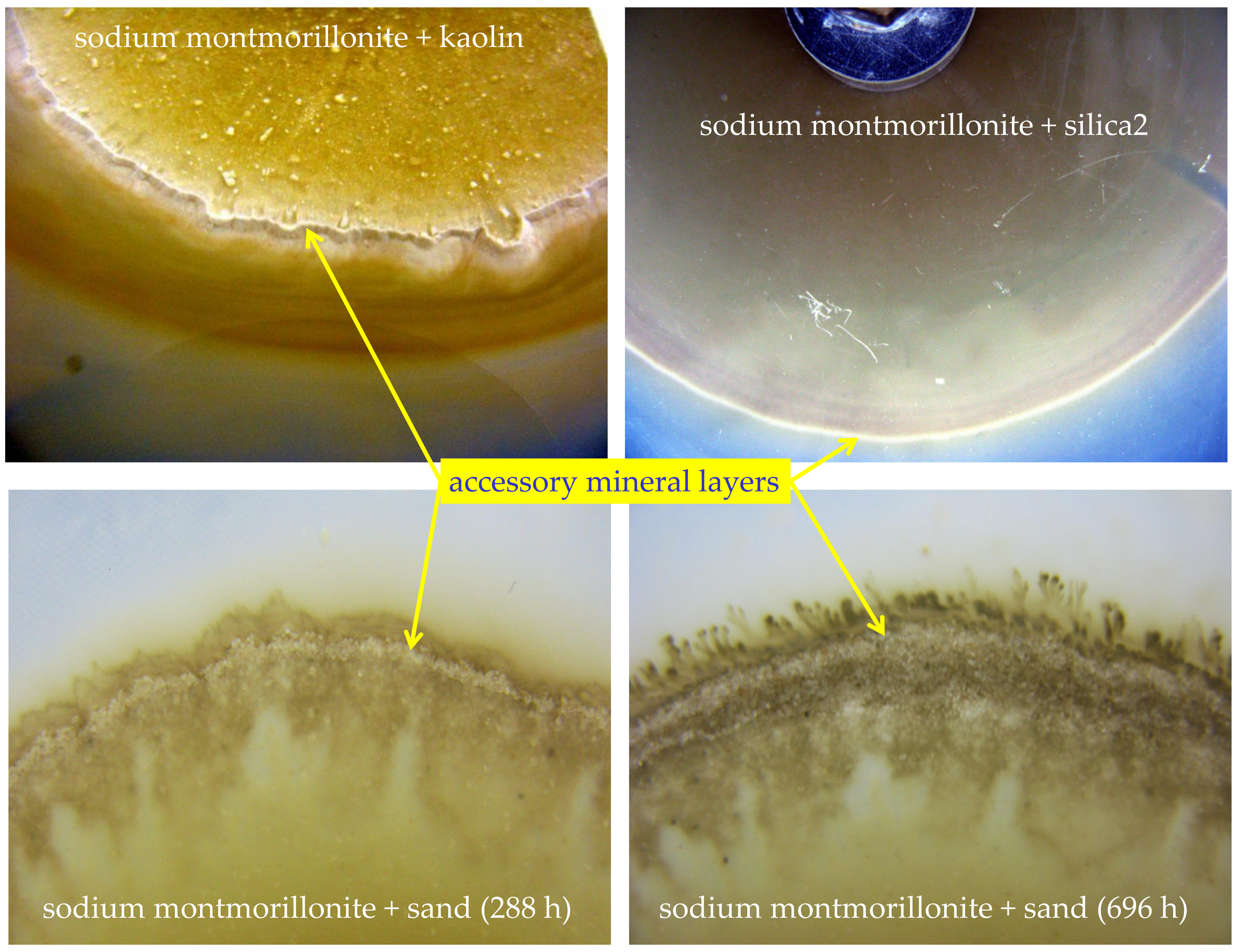
TEST CONDITIONS

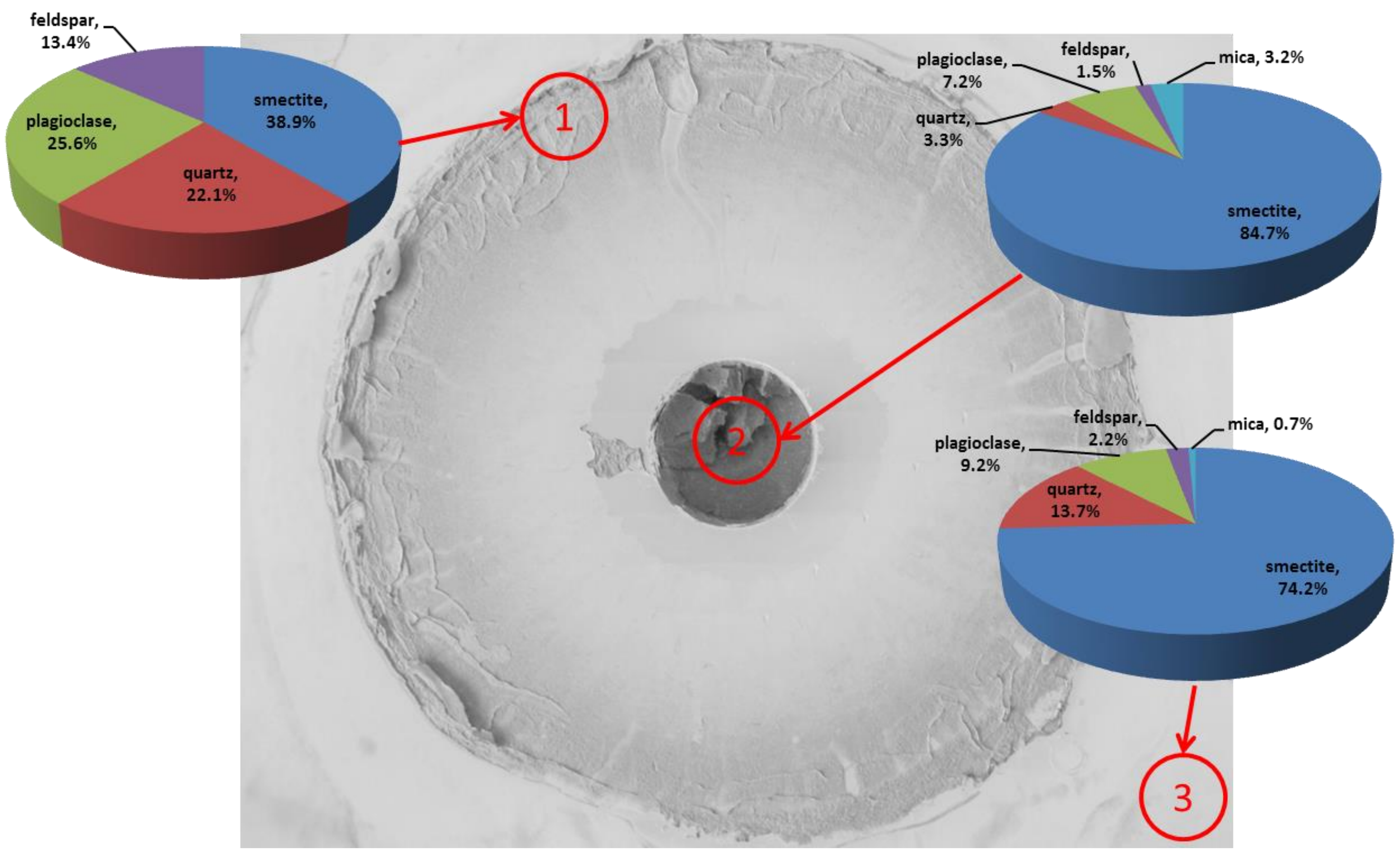
The tests are designed to lead to the development of eroding clay conditions, i.e., sodium montmorillonite (NaMt) against a dilute solution (Grimsel groundwater simulant).



NaMt *NaMt + kaolin*
NaMt + silica2 *NaMt + sand*

RESULTS





Flow-through test in artificial fracture with conditioned MX-80 after drying overlaid with mineralogical composition results from samples at the indicated positions. Sample material at erosion interface (1) contains a larger fraction of accessory minerals than starting material (2).

CONCLUSIONS

These results provide evidence that, following erosive loss of colloidal montmorillonite through contact with dilute groundwater at a transmissive fracture interface, accesory phases (from within bentonite) remain behind and form layers which increase in thickness with erosion time. Moreover, these bed layers were found to be stable over the course of the tests. However, no significant attentuation of the erosion of montmorillonite was observed in the tests with added accessory materials relative to montmorillonite alone in a 1 mm aperture fracture; the mineral layers may not fill the entire aperture.

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A Large Deformation Model with Strong Chemical-Mechanical Coupling for Bentonite to Assess the Bentonite Buffer Behaviour in Spent Nuclear Fuel Disposal Conditions

Veli-Matti Pulkkanen • Markus Olin
VTT Technical Research Centre of Finland

Introduction

Modelling the deformation of bentonite in a state where it has structure requires a continuum mechanical model. To include the contribution of water movement and salinity to this model requires the use of continuum thermodynamics leading to a so-called continuum thermomechanical model. The model has to be formulated in a large deformation mathematical setting, since bentonite can swell highly (the strain is higher than a few per cent in the most of the applications). In this work, the conceptual and mathematical basis for this type of model for bentonite is formulated and a few example simulations are presented to illustrate the capabilities of the model. The swelling by lowering salinity covered by the model corresponds to the starting of erosion in dilute water conditions.

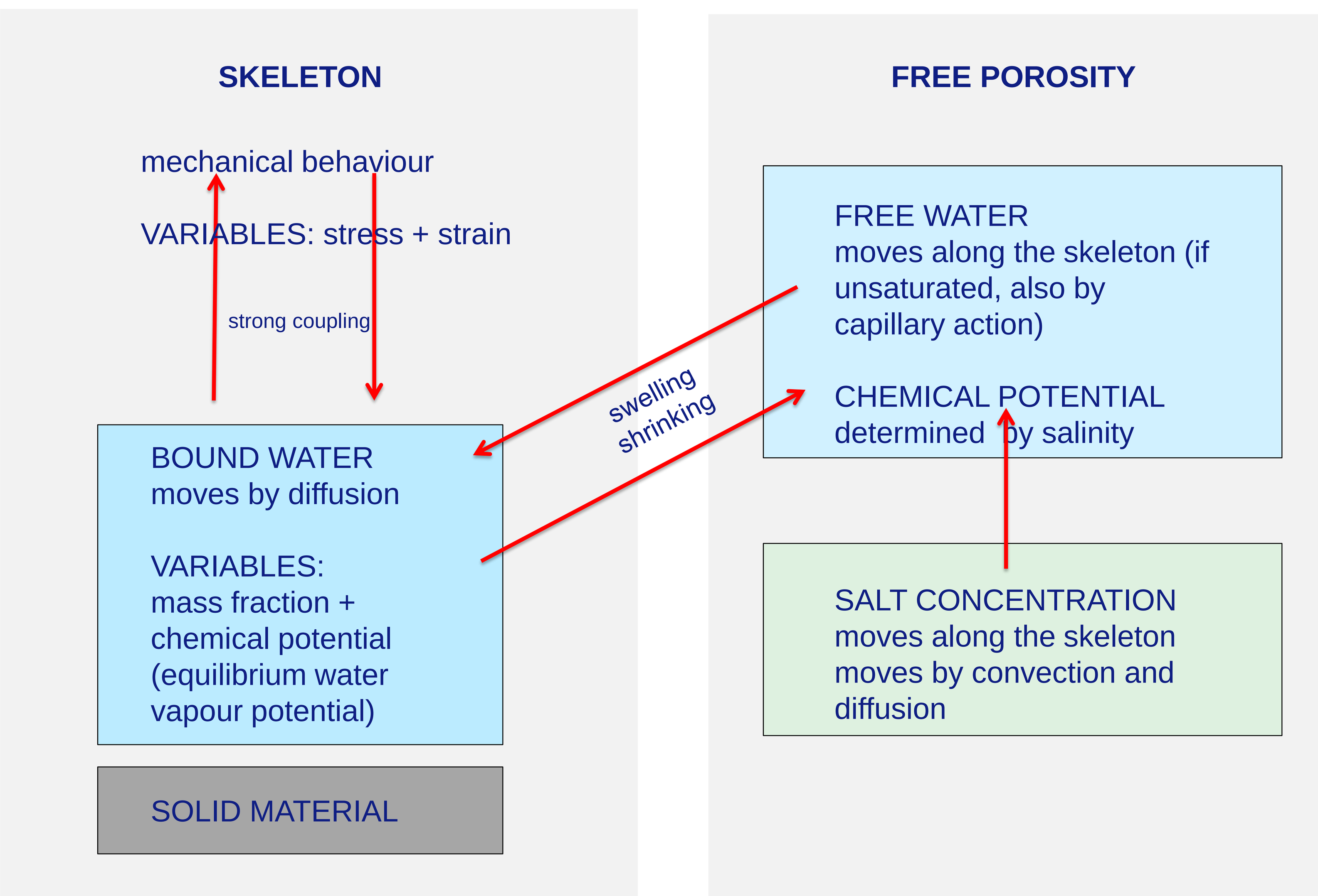

Figure 1. An illustration of the model concept and couplings.

Concept

The model concept and couplings are illustrated in Figure 1.

The work-conjugate variable pairs used in the model for the bentonite skeleton are

- stress (2^{nd} Piola stress) – strain (right Cauchy-Green deformation tensor) for the mechanical deformation
- water mass fraction – chemical potential for the bound water

between which a two directional strong coupling is formulated using the basic principles of thermomechanics.

In the free porosity

- free water moves along the skeleton (or by capillary action in unsaturated state)
- salt (NaCl) moves along the skeleton and by convection-diffusion

The exchange of water between the bound state and the free pore water causes the swelling. The exchange is determined by the potential energy difference of the waters. The stress-strain state contributing to the bound water potential, the swelling stops when the mechanical energy is in balance with the chemical potential difference of the waters.

An example simulation

The simulation demonstrates swelling of a fully saturated bentonite sample 1) when the outer boundary of confined bentonite body is freed and the bentonite let to swell into artificial fracture and 2) during two steps of salinity decrease on the outer edge. The parameters of this simulation are not for any particular bentonite type and the scales are not necessarily accurate.

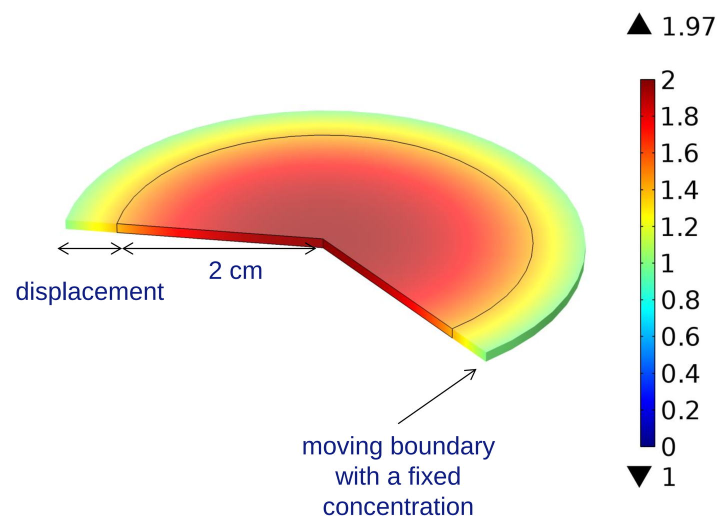

Figure 2. Model geometry and example of the concentration profile (mol/l) at t=190 d (time is not scaled).

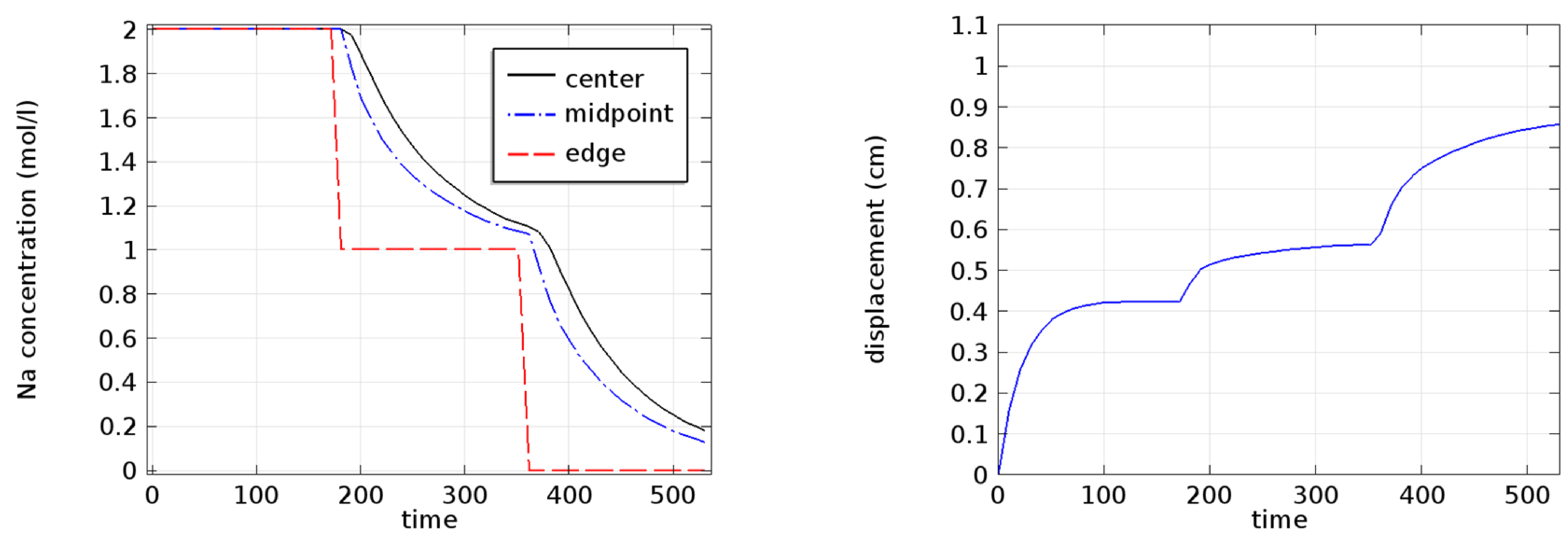

Figure 3. Results from the weakly coupled simulation. The sample swells when it is free from confinement (t<180 d) and when the salinity at the edges is lowered in two steps (from 2 to 1 mol/l during 180 d<t<360 d and from 1 to 0 mol/l during t>360 d).

Conclusions

A large deformation model needed to describe the swelling of bentonite has been developed. The emphasis has been on the rather complicated conceptual and mathematical formulation of the model. With the model, for example, the swelling of saturated bentonite can be simulated when the boundary conditions for a bentonite body are altered (opening of a confined space) and when the salinity of bentonite decreases.

Refernences

Pulkkanen, V.-M. (to be published in 2016) Doctoral Thesis.

Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement n°295487, the BELBaR project. Funding from YTERA (Doctoral Programme for Nuclear Engineering and Radiochemistry) is acknowledged.

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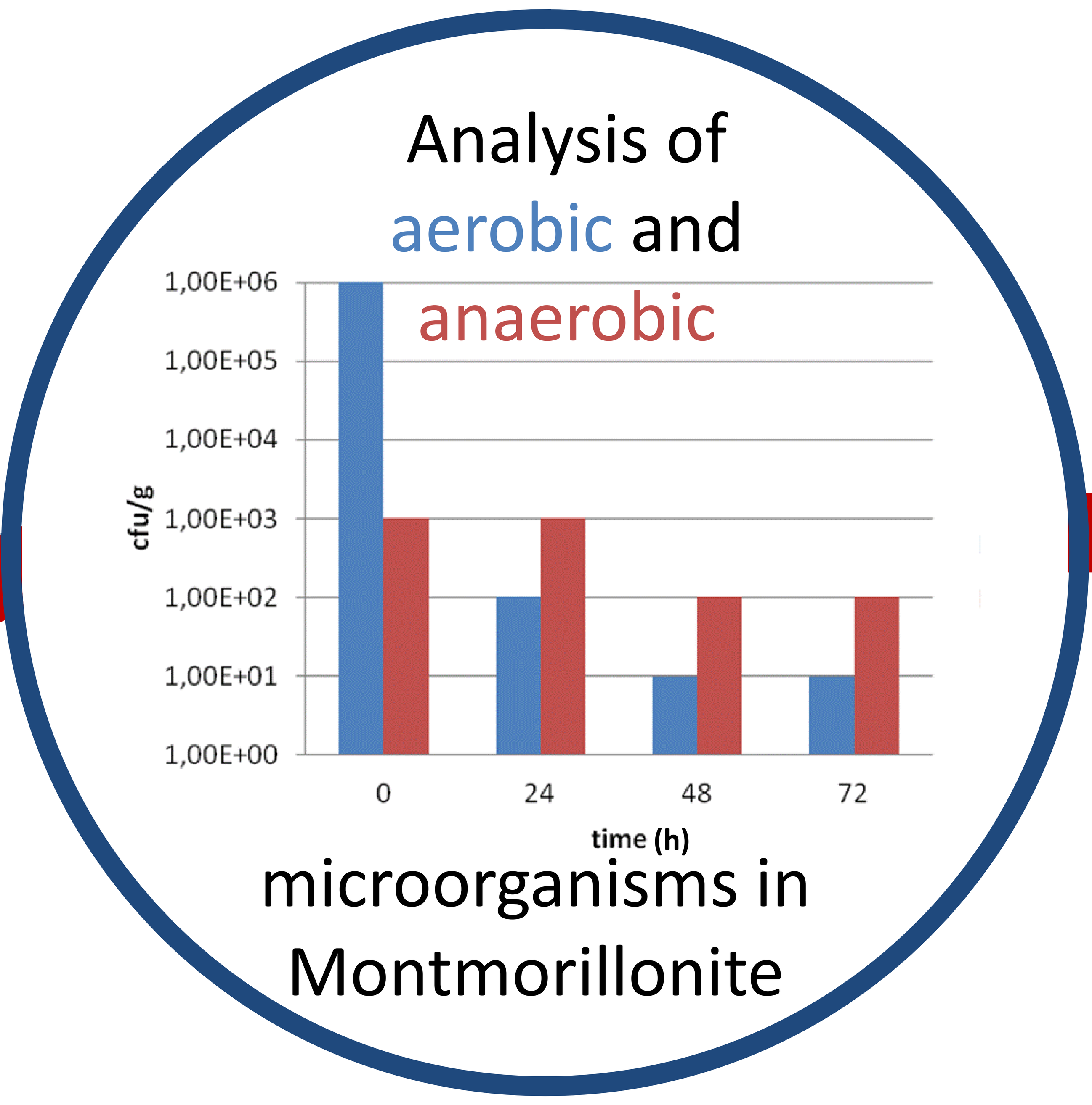


TASK 1

Description of microbial inhabitation in Montmorillonite

The most frequented strain isolated from the anaerobic consortium was very similar to *Desulfovibrio* in its cultivation patterns on SRB agar. It remained viable in Montmorillonite after 24 h of high temperature exposition (100°C).

TASK 2

More detailed characterisation of these microorganisms (physiology, metabolic features)

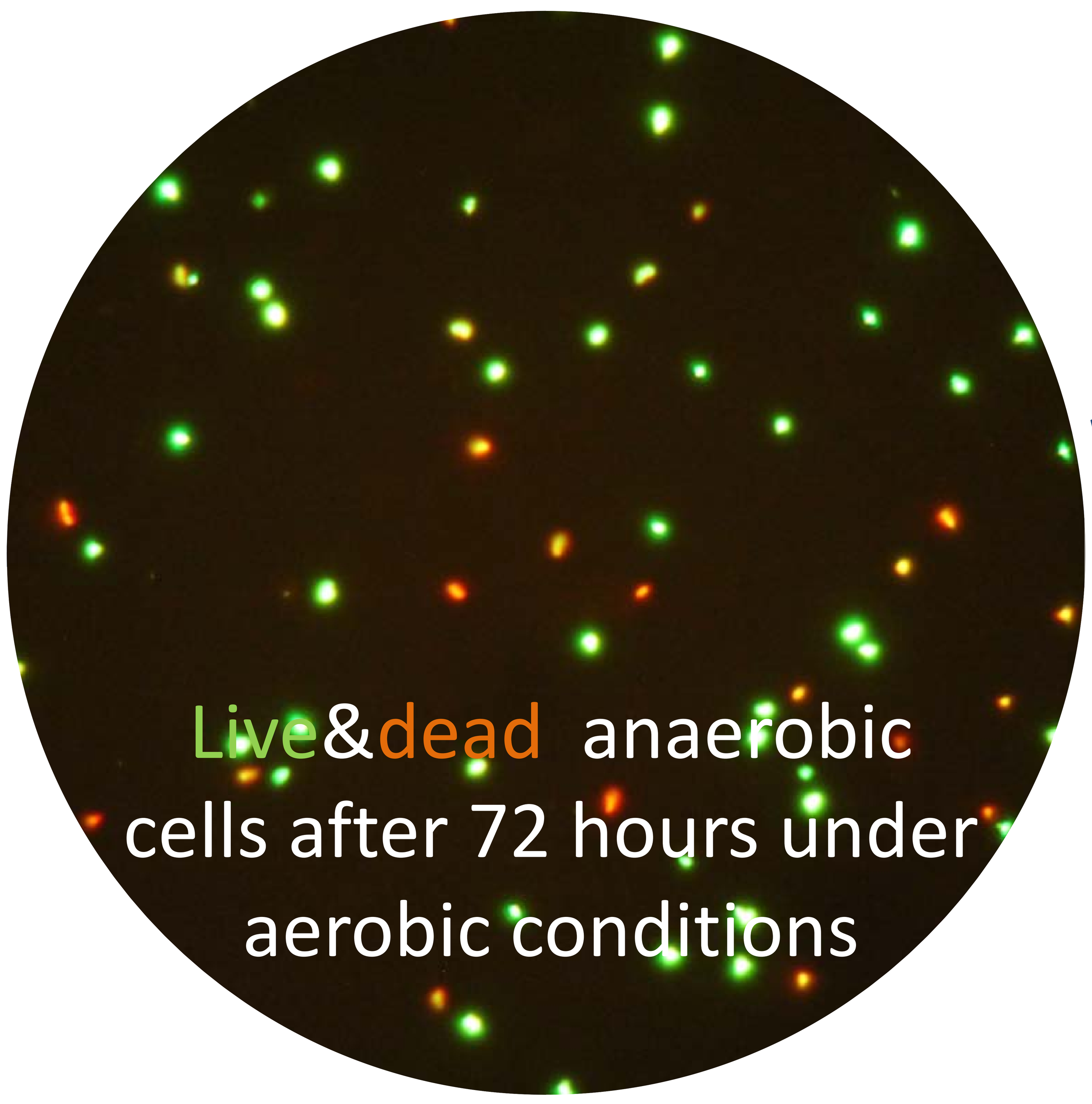
All biofilm growth form has been carefully released from the solid particle surface by ultrasound detachment. Prepared microbial suspension was processed by LIVE/DEAD protocols immediately.

GEOMICROBIOLOGICAL ASPECTS OF CLAY COLLOIDS – CULTURABLE MICROORGANISMS

TASK 3

Description of the changes which have been done by these microorganisms (extracellular compound production)

After 6 days of anaerobic cultivation, the content of exopolymeric compound (expressed as total saccharides) increased on clay particles from the origin 10 mg/g to 56 mg/g.



TASK 4

Simulation of SRB colonisation)

Capabilities of the microorganisms to attach the surface was found slightly lower (10^8 cfu/g of Montmorillonite) when compared to the reported biofilm count of 1.5×10^{10} cfu/g of bentonite clay.

TERAMED

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GENERATION AND STABILITY OF BENTONITE COLLOIDS

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INTRODUCTION

In Finland, the repository for spent nuclear fuel (SNF) will be excavated at a depth of about 500 meters in the fractured crystalline bedrock. The repository holes will be compacted with bentonite clay. The bentonite is assumed to be a potential source of colloids which could enhance the migration of radionuclides in the case of canister failure. The potential relevance of the colloids for radionuclide transport is highly dependent on their release and stability in different chemical environments and their interaction with radionuclides. [1] As the bentonite barriers are a critical part of SNF disposal concept, investigation of the processes that control bentonite erosion, clay colloid generation and stability under different chemical conditions is essential to ensure safety.

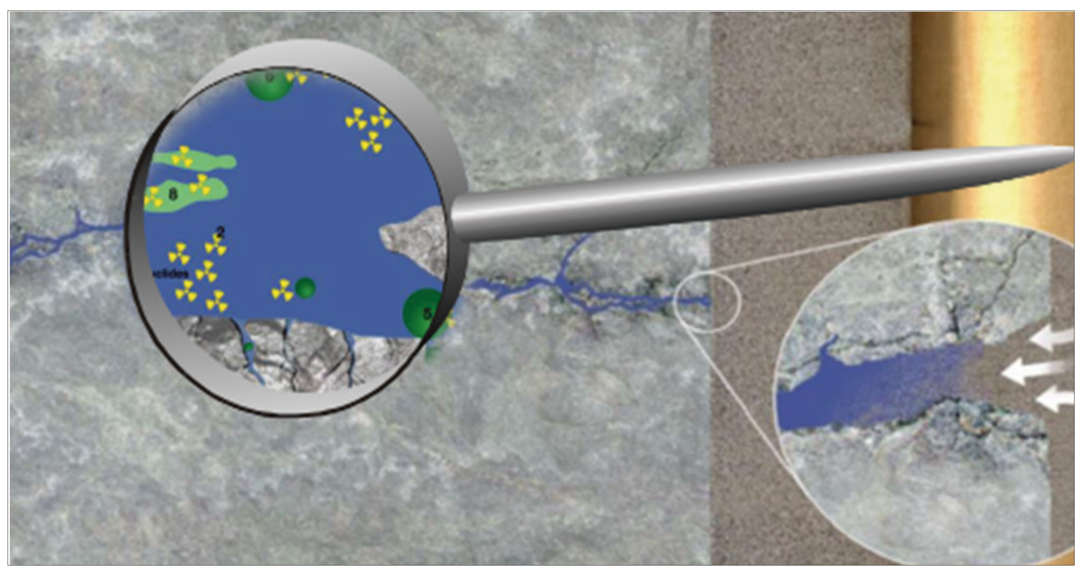

Fig. 1. Colloid/radionuclide and host rock interaction. (EU/BELBaR/T. Schäfer)

EXPERIMENTAL

- MX-80 Volclay bentonite (76 % montmorillonite) and Nanocor PGN Montmorillonite (98 %)
- OLSO (I = 0.517 M) and Allard (4.2 mM) reference groundwater
- NaCl, $CaCl_2$ and diluted OLSO (1 mM – 0,1 M)
- 2 g bentonite powder or 2 pellets and 45 mL solution
  → Samples stored with gentle agitation or without agitation
  → Centrifugation
- Particle size, concentration and zeta potential
- The solutions were changed and the samples were put back to the agitation
- The measurements were repeated at an interval of approximately 50 days
- Photon correlation spectroscopy (Malvern Zetasizer Nano ZS)
- The stability of bentonite colloids was also investigated in the long term experiment with a sampling interval of a year

RESULTS

The size of bentonite colloids increased as the ionic strength of the solution increased. Similarly, the zeta potential approached zero as the ionic strength increased.

The ZP's were under -20 mV in dilute solutions indicating the stable colloids. In more saline solutions, the particle size distribution was wide and varied from a few nanometers to thousand of nanometers. The ZP's were close to 0 mV.

The colloid formation was dramatically increased with the agitation. Although, the colloid formation was significantly decreased after the first sample measurement and changing of the solutions.

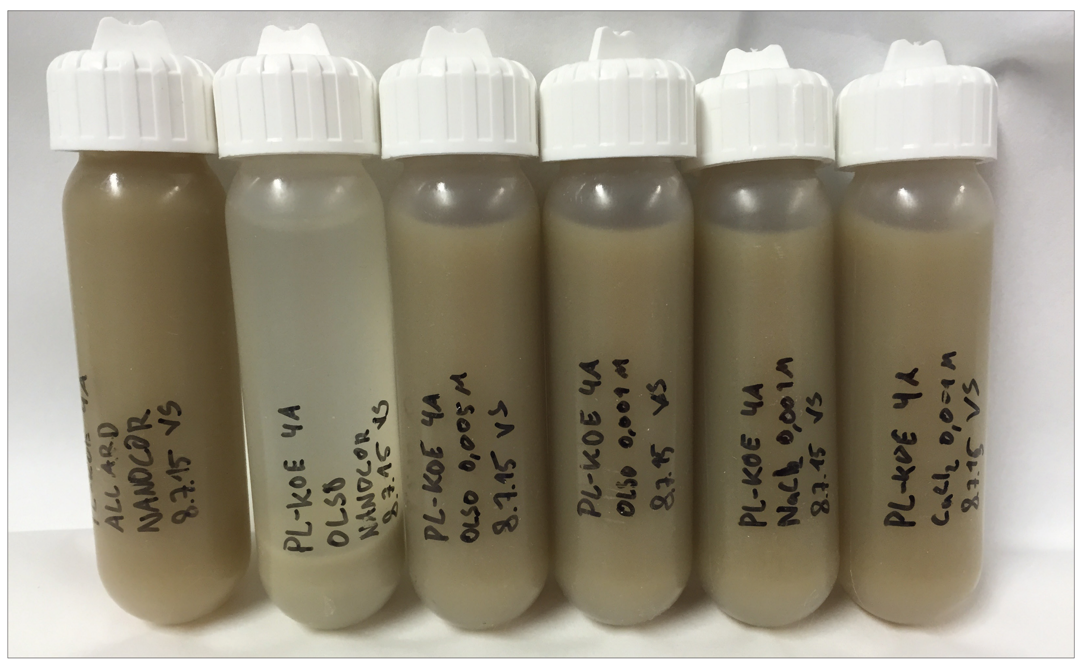

Fig. 2. Formation of bentonite colloids in different water solutions. Allard, OLSO, OLSO 5 mM, OLSO 1 mM, NaCl & CaCl2 1 mM, respectively.

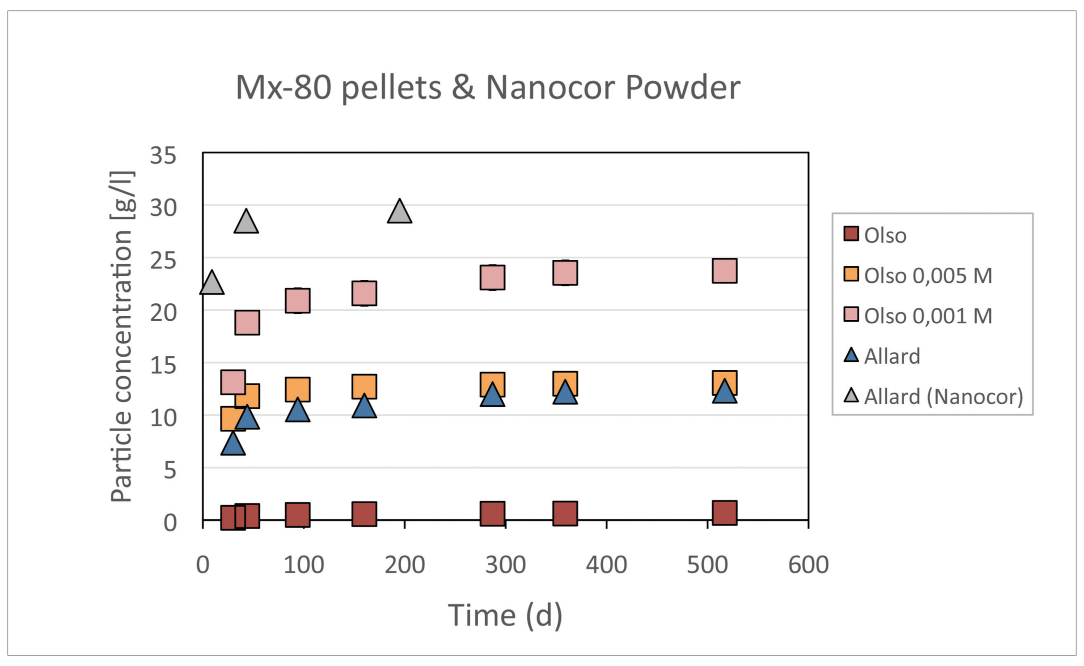

Fig. 3. Mean cumulative particle concentration of colloids formed from MX-80 bentonite pellets and Nanocor PGN powder in different water solutions.

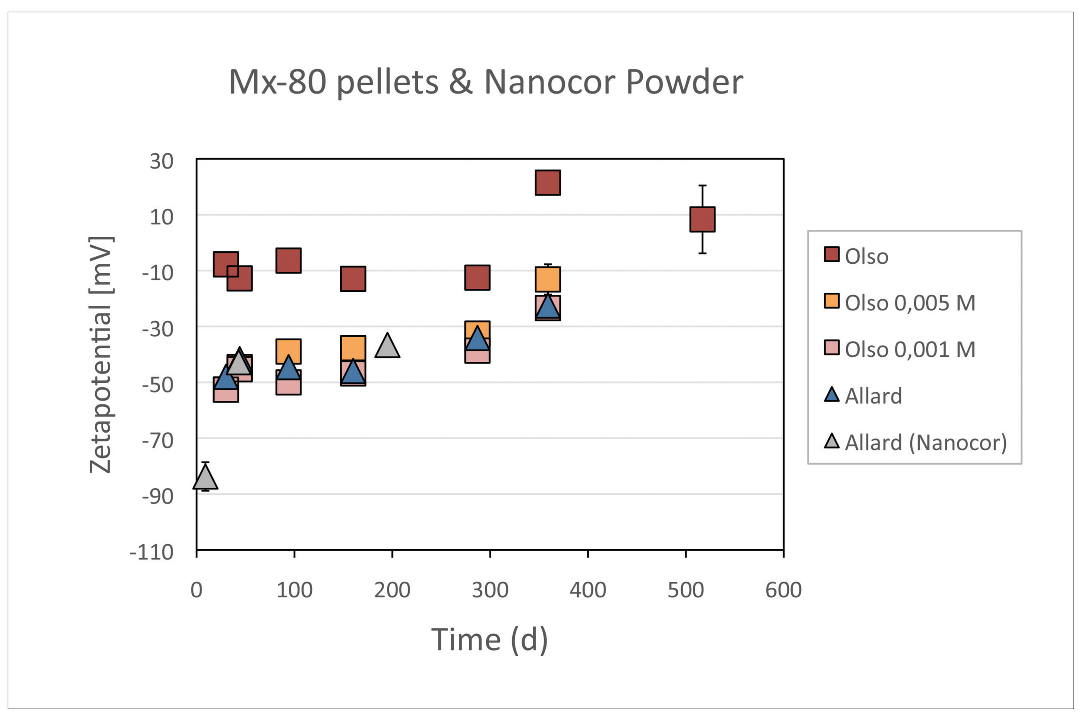

Fig. 4. Mean zeta potential of colloids formed from MX-80 bentonite pellets and Nanocor PGN powder.

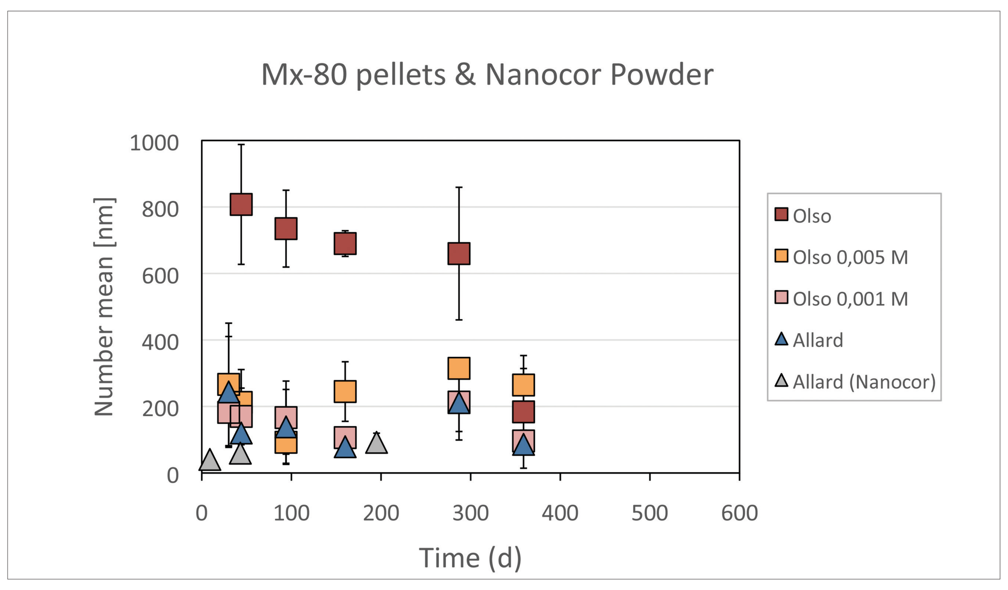

Fig. 5. Mean particle size of colloids formed from MX-80 bentonite pellets and Nanocor PGN powder.

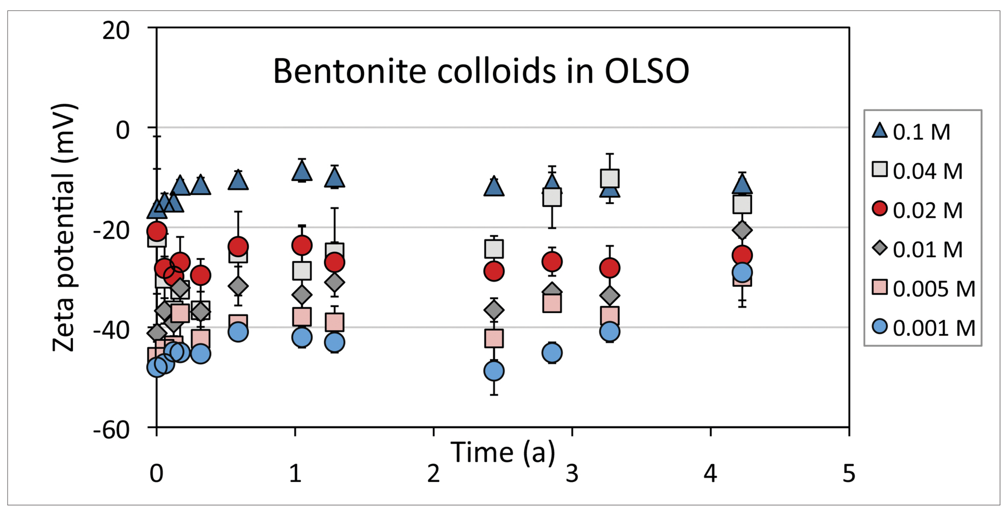

Fig. 6. Mean zeta potential of colloids formed from MX-80 bentonite powder in diluted Olso reference groundwater.

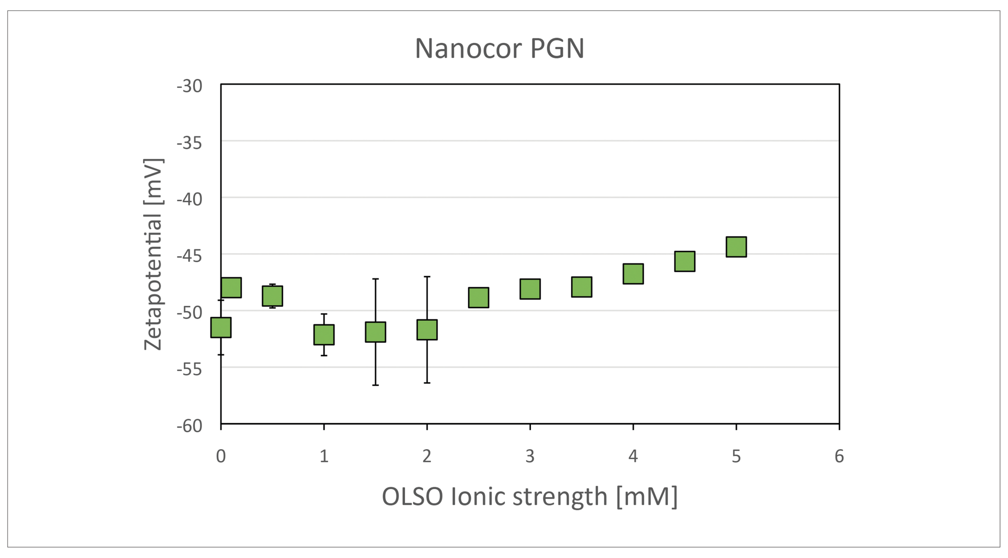

Fig. 7. Mean Zeta potentials of colloids formed from Nanocor powder in the different dilutions of OLSO.

CONCLUSIONS

There can be seen a clear difference between saline Olso and more diluted samples.

The colloid release was notable in the beginning of the contact in dilute solutions but decreased evidently.

The stability of bentonite colloids depends strongly on the ionic strength and the valence of the cations in the solution. The colloid dispersion has remained stable in low salinity solutions so far over four years.

At saline conditions in Olkiluoto, colloids are unstable → No effect on the radionuclide transport. The possible post-glacial dilute groundwater implies that the colloids may have to be taken into account.

REFERENCE

[1] Schäfer T. Huber F, Seher H, Missana T, Alonso U, Kumke M, Eidner S, Claret F and Enzmann F (2012). Nanoparticles and their influence on radionuclide mobility in deep geological formations. Appl. Geochem., 27(2), 390-403.

These results have received funding from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487, the BELBaR project.

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Monitoring free swelling of MX80 bentonite in a narrow channel using X-ray imaging

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ABSTRACT

Axial wetting and free swelling of compacted MX-80 bentonite samples in an aluminium tube of diameter 10 mm were studied using X-ray imaging (Fig. 1). The experimental setup is reminiscent of bentonite swelling into a fracture of rock surrounding the bentonite buffer in a planned nuclear waste repository. The method is based on comparison of X-ray images of the sample in the original unwetted state and in the wetted and deformed state. The method is similar to that introduced recently for full 3D reconstructions [1]. The measurement yields the time evolution of the axial distribution of the partial densities of the bentonite and water during the wetting process. To this end, the X-ray beam hardening and irregularities in the beam intensity were dynamically corrected (Fig. 2) in order to obey the linear relationship between the X-ray attenuation coefficient and the partial densities of bentonite and water (Fig. 3). The deformation of the samples was measured by tracking the metallic particles added in the bentonite powder (Fig. 4). The local dry density at each instant of time was obtained based on the initial dry density and the measured displacement field. The local water content in the sample was then found based on the calibrated correlation shown in Fig. 3. A typical duration of measurements with a sample of length 20 mm was four days. Three initial water contents (w_0) of the bentonite samples used were 12%, 17% and 24% while the initial dry density was fixed to 1.65 g/cm^3. The salinity of the water used in wetting was 0.1 M (NaCl). Figure 5 shows the final result for a bentonite sample (w_0 = 12%) at four different time steps.

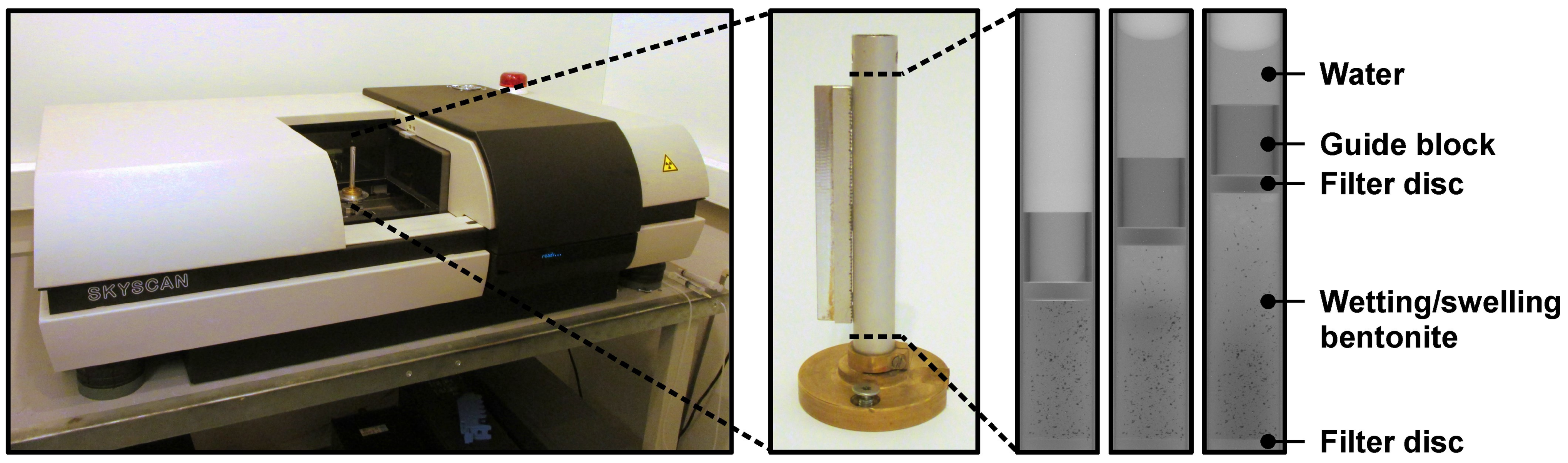

Figure 1: Skyscan 1172 microtomographic device used in X-ray imaging, an aluminium tube sample holder and X-ray images (I/I_0=exp($-\mu x$)) of the tube during swelling.

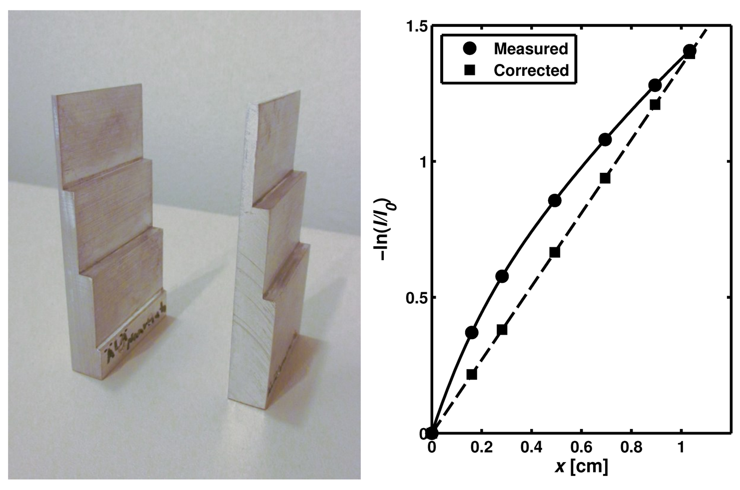

Figure 2: The dynamic flat field correction is used to alleviate artifacts arising from irregularities of beam intensity and from beam hardening effect. The correction is based on taking X-ray images of aluminium plates of varying thickness.

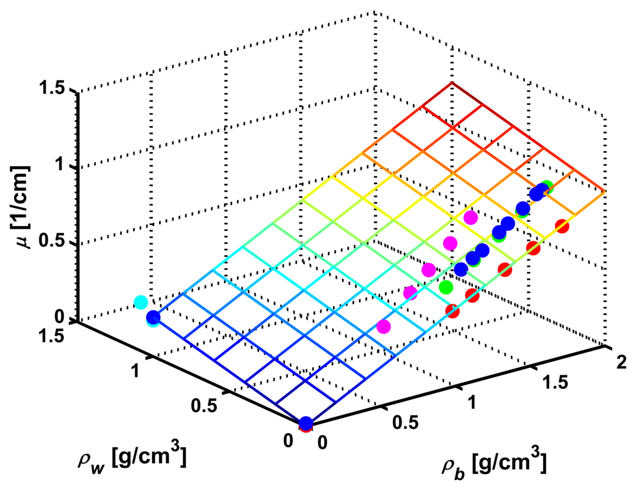

Figure 3: The measured X-ray attenuation coefficient (μ) of calibration samples (solid symbols) together with the linear fit (the plane μ=μ_0+c_b·ρ_b+c_w·ρ_w).

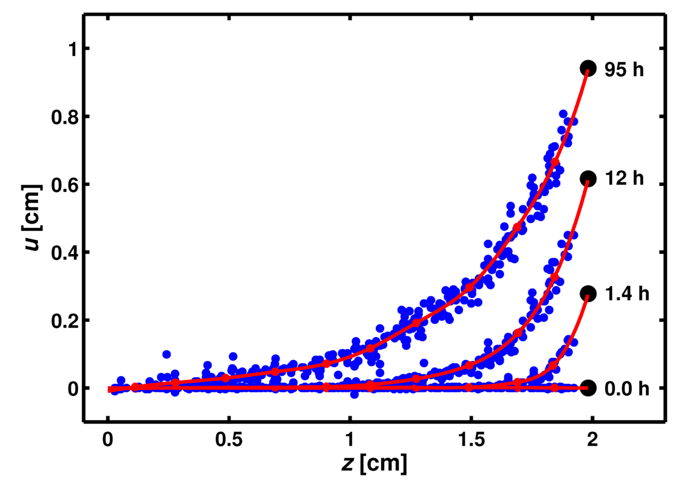

Figure 4: The axial displacement (u) of swelling bentonite at various times obtained by tracking added tracer particles visible in the X-ray images (see Fig. 1).

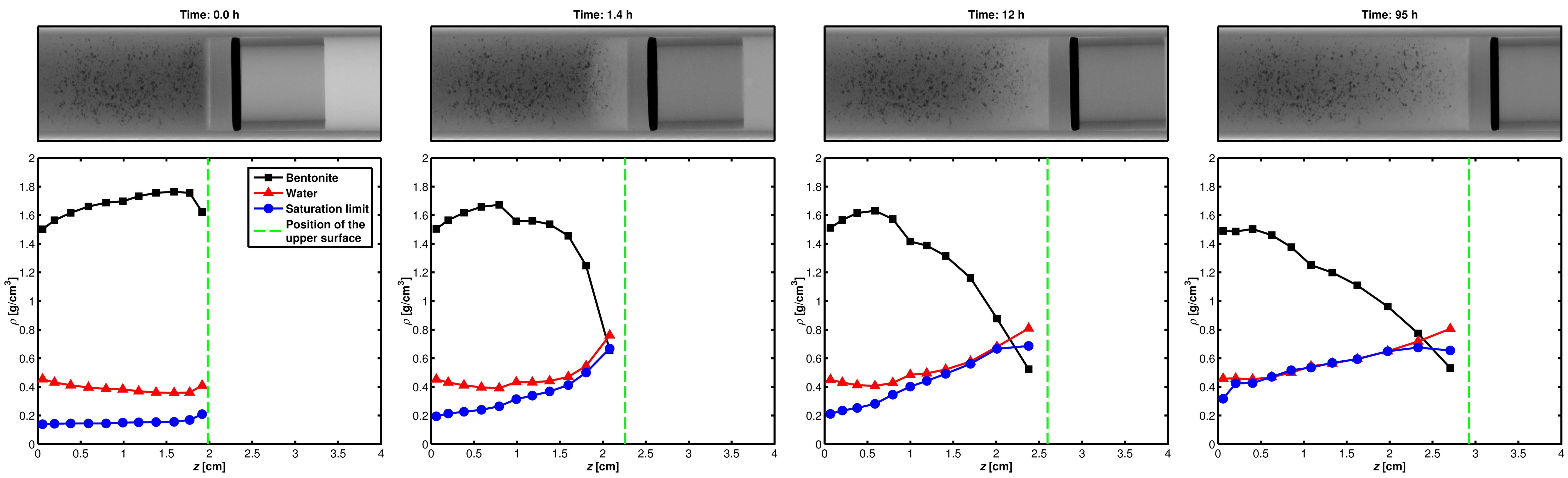

Figure 5: The measured axial distribution of dry density and water content in a freely swelling bentonite sample (w_0 = 12%) at four different times. Also shown are the corresponding X-ray images of the sample (horizontally above the graphs).

CONCLUSIONS

A non-destructive method based on X-ray imaging has been developed and used to study free swelling of MX-80 bentonite in a narrow channel. The results obtained seem qualitatively plausible. The accuracy of the method depends considerably on the X-ray beam stability and the success of the deformation measurement. The results are useful e.g. in validating models of bentonite swelling and eroding in rock fractures as well as of bentonite buffer behaviour, in general.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement n° 295487.

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UNIVERSITY OF JYVÄSKYLÄ

Institute for Nuclear Waste Disposal (INE)

Modelling the impact of fracture geometry on bentonite erosion

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Background

Natural fractures are characterized by complex geometries [1]. Numerous laboratory and numerical studies carried out in the last decades have shown the importance of fracture geometry and aperture distributions on the fracture flow field. One of the most pronounced features is flow channeling arising from heterogeneity in fracture hydraulic conductivities as function of fracture apertures and geometries. These flow gradients lead to complex patterns of hydrodynamic dispersion of e.g. solute and particle/colloids present in the seeping water.

Objectives

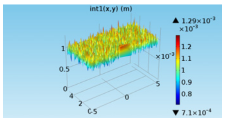
The "KTH" model [2] on bentonite erosion was used by Moreno et al. [3] to calculate bentonite erosion rates in a parallel plate fracture geometry (constant fracture aperture of 1mm). The aim of this study is to investigate the impact of fracture aperture on bentonite erosion behavior and bentonite erosion rates. For this, the KTH model was modified to incorporate normal distributions of fracture apertures to obtain more complex fracture flow fields. Simulations cover a range of standard deviations (STDs) (0.1mm, 0.3mm and 0.5mm) and mean fracture flow velocities (315 – 0.315m/yr).

Conceptual model

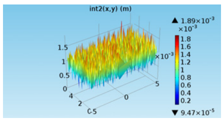
Fracture aperture distributions

Since detailed natural aperture (and/or hydraulic conductivity) distributions of field scale fractures are not available, synthetic random fracture aperture distributions were generated and used in the model. From µ-computed x-ray tomography (µCT) characterizations (resolution of 80µm and 32µm) of cm scale drill cores from Äspö, Sweden by e.g. [4] information on natural fracture aperture distributions are known. These measured aperture distributions follow normal/log-normal distributions with standard deviations in the range of ~30% of the mean aperture.

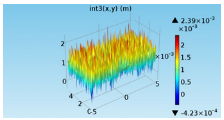
STD 0.1 mm



STD 0.3 mm



STD 0.5 mm



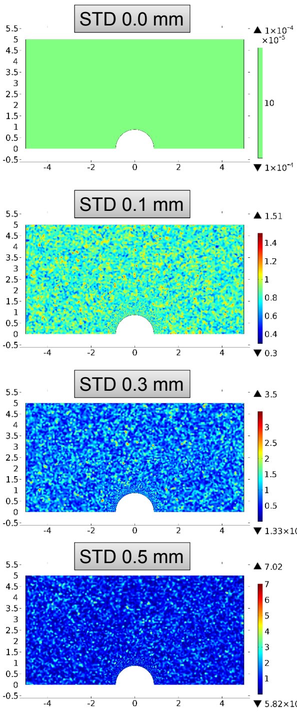
Hydraulic conductivities and Darcy flow fields

Based on the synthetic aperture distributions, hydraulic conductivity fields were calculated using the cubic law [5]:

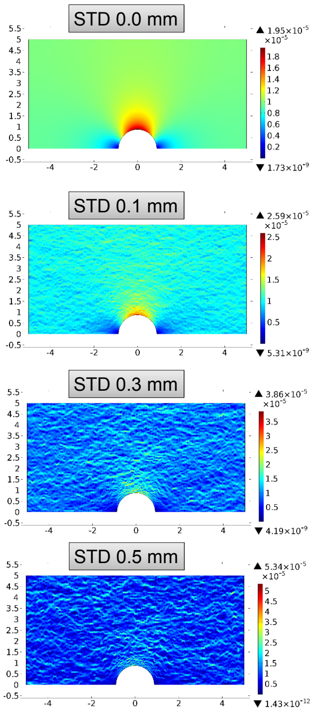
$$K_f = \frac{\rho g}{12\mu}\delta^2$$

where K_f is the hydraulic conductivity [m/s], ρ is the density of water [kg/m³], g is the gravitational constant [m/s²], μ is the dynamic viscosity [Pa ·s] and δ is the aperture [m].

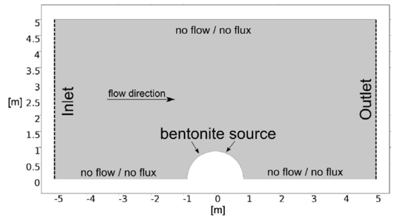
Hydr. conductivity fields



Darcy flow fields



Model setup

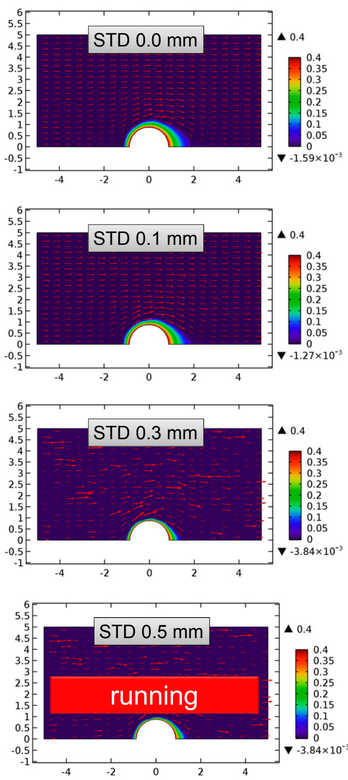


- COMSOL Multiphysics V5.1
- Model setup as in [3]
- Pressure inlet and outlet
- No flow and no flux boundaries at model bottom and top
- Flow field coupled to bentonite transport
- 10m x 5m model size and bentonite deposition hole of 1.75m

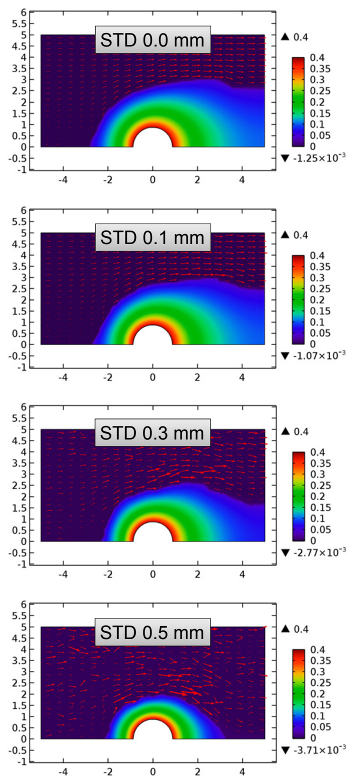
Preliminary qualitative model results

Bentonite erosion behavior

315 m/yr



31.5 m/yr



"Conclusions" and Outlook

- Use of random aperture fields introduce complex flow velocity distributions
- Complex flow fields impact bentonite extrusion behavior into fracture
  - "Distance to gel/water interface" decreases
  - Bentonite "tail" is reduced
- Simulations for 3.15m/yr and 0.315m/yr still running and calculation of rates pending

The work presented has received funding from EU FP7/2007 - 2011 under the grant agreements Nº 295487 (BELBaR, Bentonite Erosion: effects on the Long term performance of the engineered Barrier and Radionuclide Transport).

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A NOVEL DENSITY FUNCTIONAL THEORY MODELING on SWELLING BENTONITE: INTERACTION FORCES and ION EXCHANGE

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Background

Theoretical studies of the interaction forces and ion exchange play an important role in explaining the mechanisms governing the swelling of bentonite. To that end, a novel density functional theory (DFT) approach[1] of a planar electrical double layer with the primitive model is applied to calculate the interaction forces between smectite particles (montmorillonite) and the Gaines-Thomas selectivity coefficient[2,3] of the Ca\Na ion exchange equilibrium.

Theory

1. DFT Theory

$$\rho_i(\mathbf{r}) = \rho_i^b(\mathbf{r})\exp\left\{-\beta(z_i e\psi(\mathbf{r}) + \Delta u_i^{hs}(\mathbf{r}) + \Delta c_i^{(1),hs}(\mathbf{r}) + \Delta c_i^{(1),el}(\mathbf{r})\right\}$$

$$c_i^{(1),el}(\mathbf{r};\rho_i) = c_i^{(1),el}(\mathbf{r};\rho_i^{\mathrm{RFD}}) + \sum_j \int d\mathbf{s}\left(\rho_j(\mathbf{s}) - \rho_j^{\mathrm{RFD}}(\mathbf{s})\right)c_{ij}^{(2),el}(\mathbf{r},\mathbf{s};\rho_i^*)$$

$$c_{ij}^{(2),el}(\mathbf{r},\mathbf{s};\rho_i) = \int c_{ij}^{(2),el}\left(r;\rho_i(\mathbf{r}')\right)\omega_{ij}(\mathbf{r}')\mathrm{d}\mathbf{r}' \qquad \omega_{ij}(\mathbf{r}') = \frac{\kappa^2(\mathbf{r}')\Theta(|\mathbf{r}'-\mathbf{r}^m| - d_{ij})}{\int d\mathbf{r}'\kappa^2(\mathbf{r}')\Theta(|\mathbf{r}'-\mathbf{r}^m| - d_{ij})}$$

2. Applications of DFT modeling

Net osmotic pressure:[5] $P_{osm}^{net} = k_B T\sum_j \rho_j(d_j/2) - \dfrac{\sigma^2}{2\varepsilon_0\varepsilon_r} - P_{osm}^{bulk}$

Surface excess:

$$\Gamma_i = \int_0^\infty (\rho_i(x) - \rho_i^b)dx \qquad \sum_j e z_j \Gamma_j = -2\sigma$$

Ca\Na Ion Exchange reaction:

$$\frac{1}{2}Ca^{2+} + Na\text{-}X \leftrightarrow \frac{1}{2}Ca\text{-}X_2 + Na^+$$

Gaines-Thomas selectivity coefficient:

$$K_{GT} = \frac{[Na^+][Ca\text{-}X_2]^{0.5}}{[Ca^{2+}]^{0.5}[Na\text{-}X]} = \frac{[Na^+]\beta_{Ca}^{0.5}}{[Ca^{2+}]^{0.5}\beta_{Na}}$$

Results

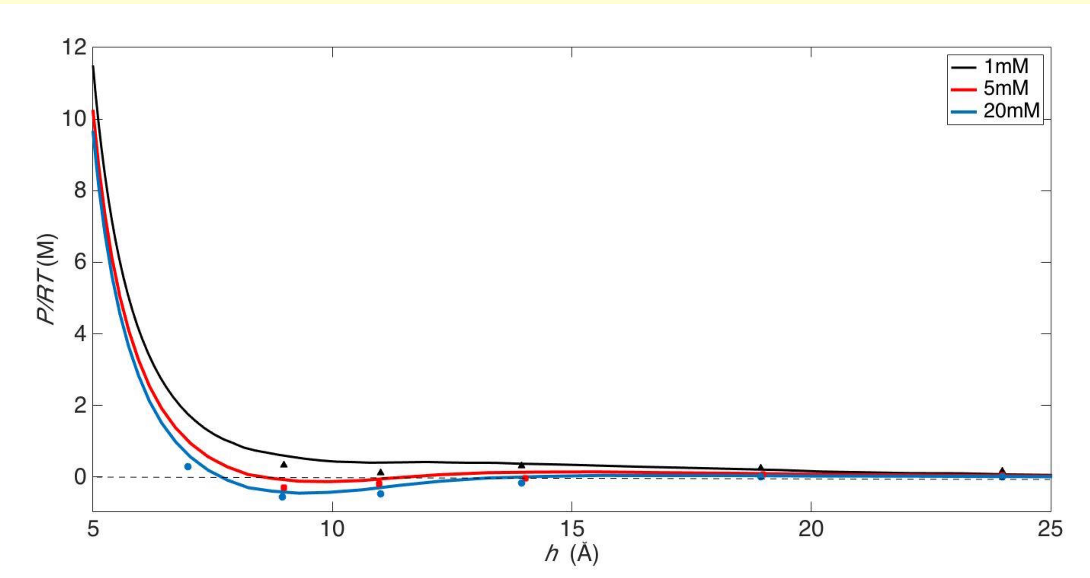

Figure 1. Net osmotic pressure as a function of separation. d = 0.4 nm, σ = -0.14 C/m^2, C_{Na} = 100 mM, C_{Ca} is varied as indicated in the graph. The symbols are Monte Carlo data[4]. The curves show the DFT calculations.

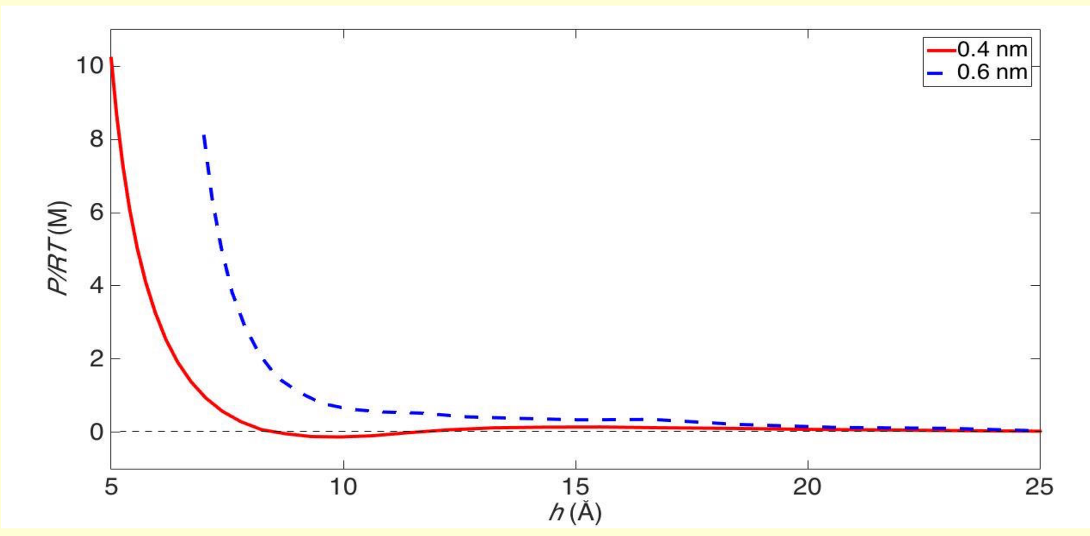

Figure 2. The DFT calculations of net osmotic pressure as a function of separation. σ = -0.14 C/m^2, C_{Na} = 100 mM, C_{Ca} = 5 mM. The monovalent ion size is kept constant at 0.4 nm, while the divalent ion size is varied as indicated in the plot. ε_r = 78, T = 298 K

Table 1. Comparison of the selectivity coefficient from DFT calculations and experimental results[6] for calcium-sodium exchange in Wyoming montmorillonite under confined conditions. σ = -0.11 C/m^2, ε_r = 78, T = 298 K. ISE and ICP/AES indicates the methods used to determine the ion concentrations.

$d_{mono} = d_{di}$ = 0.425 nm

Samples	C_{Na} (mM)	C_{Ca} (mM)	DFT K_{GT} ($\sqrt{M}$)			Experiments K_{GT} ($\sqrt{M}$)		Experiments
			h = 10 Å	h = 15 Å	h = 20 Å	ISE	ICP/AES	*Average interlayer separation h*
WyNa 01	29.3	2.0	5.7	3.8	3.3	2.1	2.0	18.7
WyNa 02	35.8	2.1	5.7	3.8	3.3	2.8	2.3	12.2
WyNa 03	47.9	4.5	5.6	3.9	3.4	2.8	2.0	8.1
WyCa 04	28.4	3.1	5.7	3.9	3.4	1.3	2.6	16.4
WyCa 05	41.6	5.3	5.7	3.9	3.4	2.1	2.8	11.5
WyCa 06	48.2	6.9	5.7	3.9	3.4	2.5	2.6	8.3

d_{mono} = 0.425 nm, d_{di} = 0.72 nm

Samples	C_{Na} (mM)	C_{Ca} (mM)	$C_{Na}/(C_{Na}+C_{Ca})$	DFT K_{GT} ($\sqrt{M}$)		Experiments K_{GT} ($\sqrt{M}$)		Experiments
				h = 15.0 Å	h = 20.0 Å	ICP/AES	ISE	*Average interlayer separation* (Å)
WyNa 01	29.3	2.0	93.6%	2.6	2.0	2.0	2.1	18.7
WyNa 02	35.8	2.1	94.5%	2.6	2.0	2.3	2.8	12.2
WyNa 03	47.9	4.5	91.4%	2.6	2.1	1.9	2.8	8.1
WyCa 04	28.4	3.1	90.2%	2.6	2.1	2.6	1.3	16.4
WyCa 05	41.6	5.3	88.7%	2.6	2.1	2.8	2.0	11.5
WyCa 06	48.2	6.9	87.5%	2.6	2.1	2.6	2.5	8.3

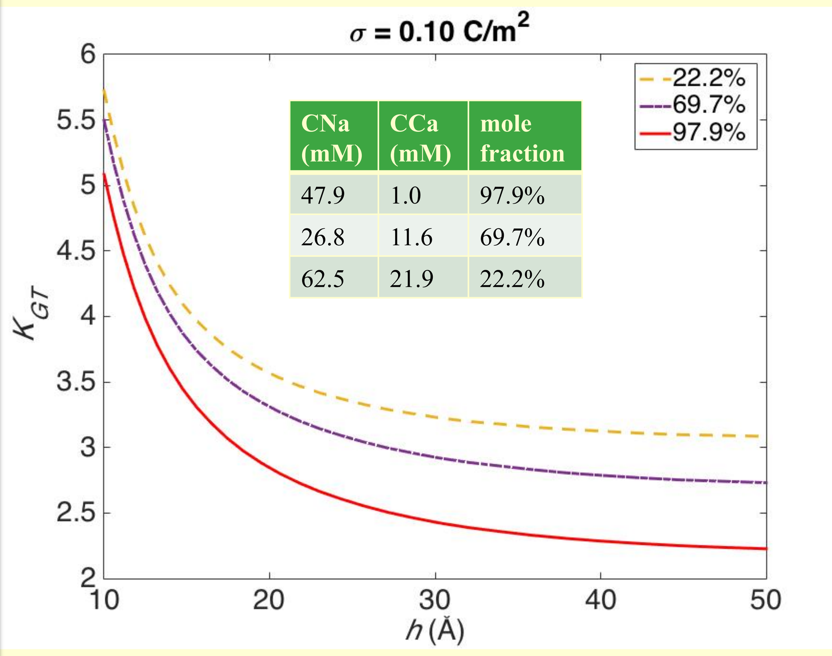

Figure 1. DFT Selectivity coefficient K_{GT} for WyCa as a function of the separations. The sodium mole fraction in the bulk is indicated in the plot. d = 0.425 nm, ε_r = 78, T = 298 K.

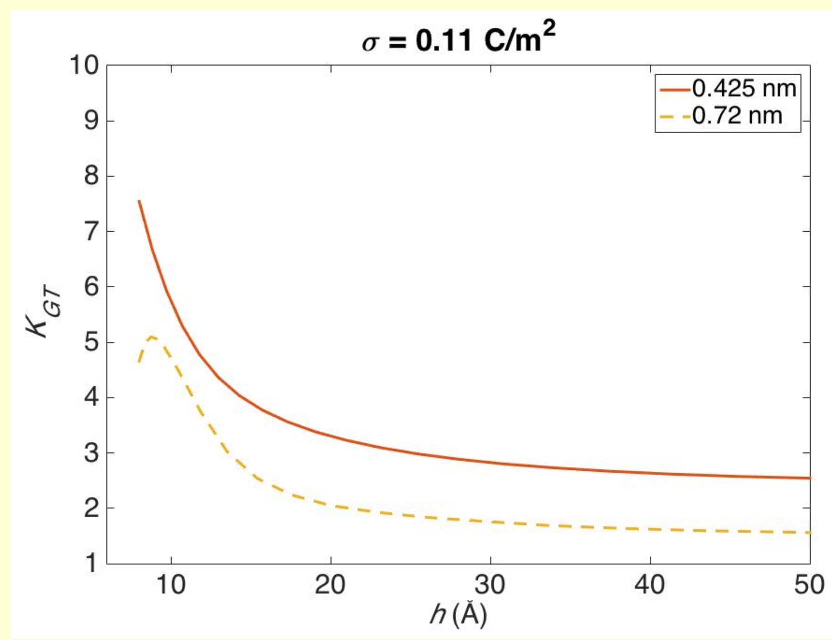

Figure 2. DFT Selectivity coefficient K_{GT} for WyNa as a function of the separations. The calcium ionic diameter d_{di} is indicated in the plot. d_{mono} = 0.425 nm, ε_r = 78, T = 298 K. C_{Na}=29.3 mM, C_{Ca}=2 mM.

Conclusions

- The novel DFT approach that is robust enough to be applied to model the swelling behaviour at atomic scale and ion exchange equilibrium of montmorillonite clay.
- The mole fraction in bulk, surface charge density, and ionic diameter play a significant role on swelling of bentonite when saturated with groundwater.

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Colloidal particle detachment of bentonites

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38 bentonites (incl. 2 ill/smt clays) with natural cation population from all over the world

Fotographs

CEC data

	Na^+ ICP [meq/100g]	Na^+ [%]	K^+ ICP [meq/100g]	Mg^{2+} ICP [meq/100g]	Ca^{2+} ICP [meq/100g]	sum of cations [meq/100g]	CEC ICP [meq/100g]	sum-CEC [meq/100g]	CEC VIS [meq/100g]	calcite	gypsum
B1	17	17	2	45	52	116	97	19	102	+	
B2	13	13	2	47	42	104	103	1	102		
B3	12	11	2	35	53	102	105	-3	104		
B4	19	17	2	46	38	105	108	-2	107		
B5	14	14	3	33	67	117	100	17	100	+	+
B6	17	16	2	36	52	107	107	1	110		
B7	66	67	5	5	33	109	98	11	99	+	
B8	69	100	0	1	16	86	69	17	72	+	+
B9	62	91	1	2	31	95	68	27	70	+	+
B10	28	29	2	22	54	105	96	9	96	+	
B11	63	65	1	17	34	115	97	18	99	+	
B12	56	51	1	26	41	124	108	16	110	+	
B13	1	1	2	38	75	116	84	32	87	+	
B14	1	1	3	41	48	93	84	9	86	+	
B15	1	2	2	31	54	87	66	21	68	+	
B16	0	0	2	22	53	77	67	10	69		+
B17	68	68	7	4	38	116	99	17	103	+	
B18	28	27	3	37	46	114	105	9	107	+	
B19	20	24	3	33	47	102	83	20	85	+	
B20	58	71	2	8	35	102	82	20	85	+	+
B21	42	47	3	29	30	104	91	13	93		
B22	66	71	1	3	27	97	93	4	98	+	
B23	68	68	1	2	33	105	101	4	104		
B24	46	47	2	27	36	112	98	14	101		
B25	0	0	2	15	41	57	63	-6	62		
B26	20	22	3	16	49	88	93	-5	88	+	
B27	62	68	2	5	31	101	92	9	89	+	
B28	1	1	2	3	70	75	82	-7	82		
B29	0	0	1	23	44	68	76	-8	77		
B30	27	72	3	3	8	41	38	4	36		
B31	51	62	1	12	31	95	82	13	81	+	
B32	1	1	2	6	73	82	87	-5	85		
B33	57	69	2	5	33	97	82	15	81		+
B34	5	6	1	29	55	90	85	5	85		
B35	0	0	3	10	32	45	40	4	38	+	
B36	0	1	2	17	36	54	56	-1	53		
B37	1	1	1	27	56	84	85	-1	80	+	
B38	14	21	3	21	46	84	67	17	65	+	

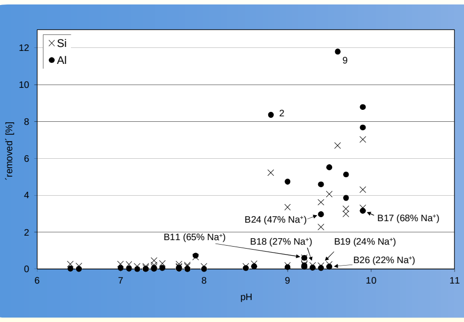
„pore water“ composition

	Conductivity [µS]	pH	K [mg/l]	Na [mg/l]	Cl [mg/l]	Mg [mg/l]	Ca [mg/l]	SO_4 [mg/l]	Al [mg/l]	SiO_2 [mg/l]	Fe [mg/l]	$Al_{removed}$ [% w/w]	$Si_{removed}$ [% w/w]	$Fe_{removed}$ [% w/w]
B1	161	8.5	2	41	14	2	2	4	1	16	0	0.1	0.1	0.1
B2	83	7.7	1	22	12	1	1	5	1	27	0	0.0	0.3	0.0
B3	34	7.5	1	10	2	1	2	1	1	32	0	0.1	0.3	0.1
B4	127	7.0	1	30	20	1	1	31	1	27	1	0.1	0.3	0.1
B5	306	7.3	9	54	3	7	17	141	0	15	0	0.0	0.2	0.0
B6	54	8.6	1	16	1	3	4	3	3	30	1	0.1	0.3	0.2
B7	365	9.9	10	106	5	48	14	33	158	771	31	8.8	7.0	7.0
B8	474	9.9	1	130	0	17	7	67	128	576	38	7.7	4.3	8.7
B9	467	9.6	1	135	0	25	13	105	184	799	52	11.8	6.7	12.3
B10	219	9.2	2	55	32	2	5	8	3	22	2	0.2	0.2	0.1
B11	370	9.2	1	93	52	4	6	29	9	57	8	0.6	0.6	0.4
B12	424	9.2	1	106	47	3	5	77	2	25	1	0.1	0.3	0.1
B13	86	8.0	4	3	1	5	10	3	0	13	0	0.0	0.1	0.0
B14	95	7.8	5	3	1	5	10	3	0	20	0	0.0	0.2	0.0
B15	92	7.8	3	4	1	5	10	5	0	12	0	0.0	0.2	0.0
B16	170	7.2	6	1	0	7	21	77	0	15	0	0.0	0.1	0.0
B17	370	9.9	8	98	5	21	11	36	58	361	17	3.2	3.3	3.9
B18	207	9.3	2	53	12	2	2	18	1	22	0	0.1	0.2	0.1
B19	174	9.4	2	43	8	2	2	8	1	19	0	0.1	0.2	0.1
B20	320	9.5	3	90	1	18	6	89	111	494	26	5.5	4.1	5.2
B21	266	7.9	3	63	59	4	3	26	16	70	2	0.7	0.6	0.7
B22	145	8.8	1	52	20	38	7	22	133	652	12	8.4	5.2	8.3
B23	95	9.0	1	39	10	21	7	8	88	393	9	4.7	3.3	5.4
B24	369	9.4	3	85	64	9	5	31	67	242	8	3.0	2.3	3.0
B25	17	7.4	2	1	3	0	1	1	0	12	0	0.0	0.1	0.0
B26	158	9.5	3	41	2	2	4	4	2	31	0	0.1	0.2	0.2
B27	382	9.7	2	96	3	13	4	69	79	355	18	3.9	3.0	3.5
B28	17	7.4	0	2	0	0	3	3	1	26	0	0.1	0.2	0.1
B29	15	6.4	1	1	0	0	0	0	1	27	0	0.0	0.3	0.0
B30	346	7.3	5	73	20	0	1	121	0	8	0	0.0	0.1	0.0
B31	367	9.7	3	92	25	23	8	29	75	390	33	5.1	3.3	5.0
B32	30	7.4	4	4	3	1	4	8	0	47	0	0.0	0.5	0.0
B33	342	9.4	3	86	1	15	5	87	95	425	23	4.6	3.6	4.5
B34	124	7.7	2	18	4	2	5	26	1	16	0	0.1	0.1	0.0
B35	74	7.7	6	1	1	1	5	2	1	10	0	0.0	0.1	0.0
B36	35	7.1	2	2	0	0	1	1	0	31	0	0.0	0.3	0.0
B37	34	6.5	2	2	0	1	2	6	0	20	0	0.0	0.2	0.0
B38	197	9.0	5	39	4	2	3	18	2	22	1	0.1	0.2	0.1

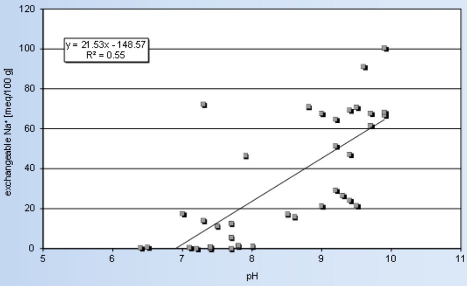
Dispersion in deionized water (1 g / 50 mL) - 48 h end-over-end - ultracentrifugation at 46,000 g

The supernatant was collected and investigated by ICP, turbid supernatants were evaporated for XRD + IR analysis

Details published by Kaufhold & Dohrmann (2008)



The amount of Al/Si measured by ICP represents the sum of dissolved cations and colloidal particles which survived centrifugation. The Al/Si concentration depends on pH and Na_+ content – both parameters are closely related (Kaufhold et al. 2008).

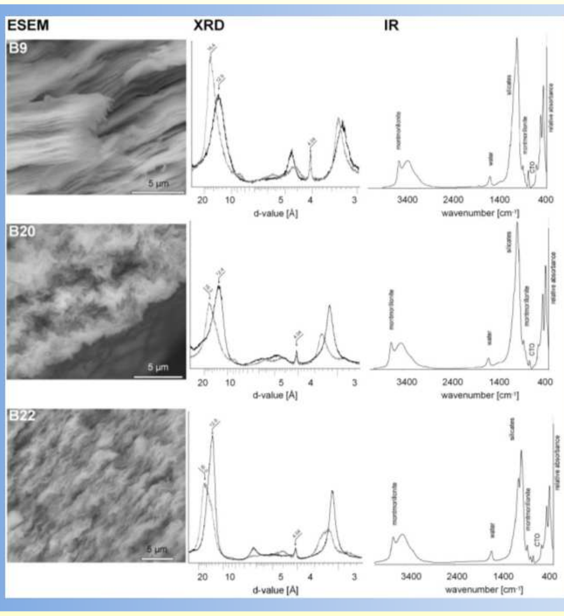


The dispersed solids in each of the centrifugation turned out to still be parts of either the tetrahedral or play a role. However, the solids are still smectites.

XRD confirmed the expandability observed after EG treatment.

In the IR spectrum all typical

Both, XRD and IR show evidence as opal-CT or cristobalite. This the tetrahedral layer may have detachment of very fine smectites.



samples showing turbidity after smectite. The detachment of octhedral layer were thought to which could not be centrifuged

because full swelling to 17 A was

smectite bands were observed.

for the presence of silica, either indicates that some destruction of occured along with the

Conclusions

The amount of released colloidal particles strongly depended on the amount of exchangeable Na^+/pH. The actual amount of colloidal particles which will be released from a geotechnical barrier is known to depend on the ionic strength and high ionic strength will reduce the amount of colloidal particles which can be released from the barrier. However, the probability of detachment of colloidal particles will still be larger in case of Na^+ as dominating exchangeable cation. A fast reequilibration of the exchange population as observed in the ABMI and ABMII are supposed to affect the tendency towards detachment of colloidal particles in a way that the initial cation population becomes less relevant.

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Kaufhold, S., Dohrmann, R., Koch, D., Houben, G. (2008) The pH of aqueous bentonite suspensions. - Clays and Clay Minerals, 56, 338–343.

Bundesanstalt für Geowissenschaften und Rohstoffe
Landesamt für Bergbau, Energie und Geologie

Microstructure of Bentonite and Dilute Water Erosion

Michał Matusewicz • Veli-Matti Pulkkanen • Markus Olin
VTT Technical Research Centre of Finland

Why to study microstucture?

MX-80 bentonite is considered as a possible material for a clay buffer in high-level nuclear waste repositories.
The evaluation of bentonite applicability is based on macroscopic experiments and modelling. As all macroscopic properties stem from the microscopic properties it is essential to know how the microstructure relate to properties observed in experiments.

Materials and methods

The microstructure of bentonite is studied using a set of complimentary methods. Small-angle X-ray scattering (SAXS), nuclear magnetic resonance (NMR), ion exclusion (IE) and transmission electron microscopy imaging (TEM) are used to characterize the samples' structure. Our approach included state of the art preparation of the frozen and embedded samples for TEM using high pressure freezing (HPF) method and novel NMR measurements in low temperatures.

The materials studied were purified Ca-[1] and Na-montmorillonites and MX-80 bentonite. The influence of different procedures of preparation of water-saturated, compacted bentonite samples was tested[2]. The information on microstructure has been collected from the range of different compaction levels and different salinity conditions.

Results

It has been demonstrated that the different ways of sample preparation have influence on the sample microstructure[2]. An example is shown in Figure 1, where SAXS patterns of compacted MX-80 bentonite prepared according to various procedures show clear differences.

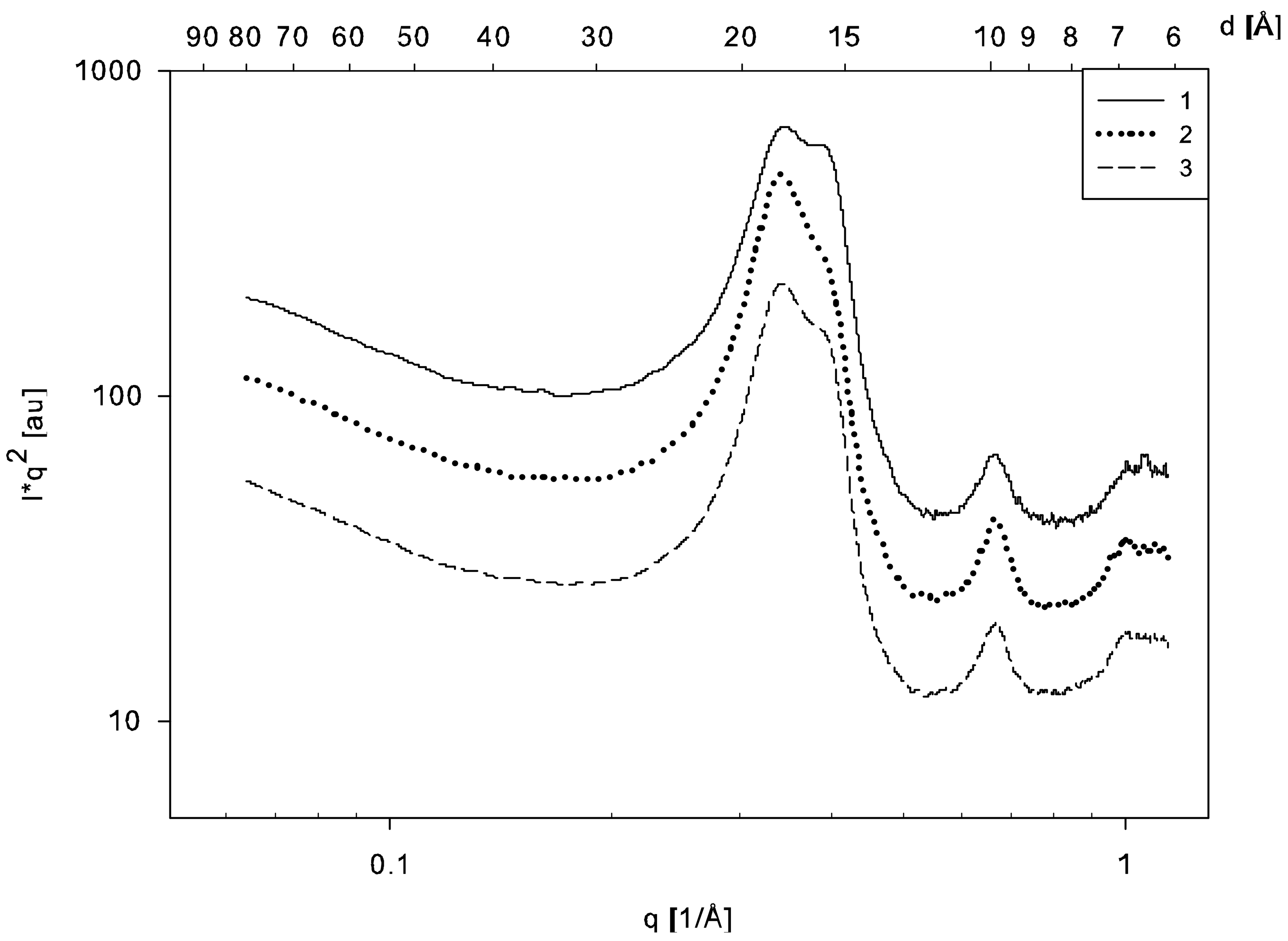

Figure 1. X-ray scattering curves of the MX-80 samples at 1.5 g/cm³ dry bulk density. Equilibration time 53 days. Numbers in the legend correspond to different ways of sample preparation: 1 – compacted to final density; 2, 3 – compacted to 1.8 g/cm³ and swelling to final density; 1, 2 – saturated with MilliQ water; 3 – saturated with 0.1M NaCl[2]

Combining the information from SAXS, NMR and IE quantification of the volume of the slit-like pores between the clay layers (interlamellar (IL) pores)) has been made and compared with the total pore volume. Figure 2 shows the plot of the volume of IL pores in Ca-montmorillonite and in MX-80 bentonite based on the SAXS calculation as a function of dry density of the clay. A clear tendency of forming larger stacked structures is visible for the calcium montmorillonite than for the predominantly sodium MX-80 bentonite.

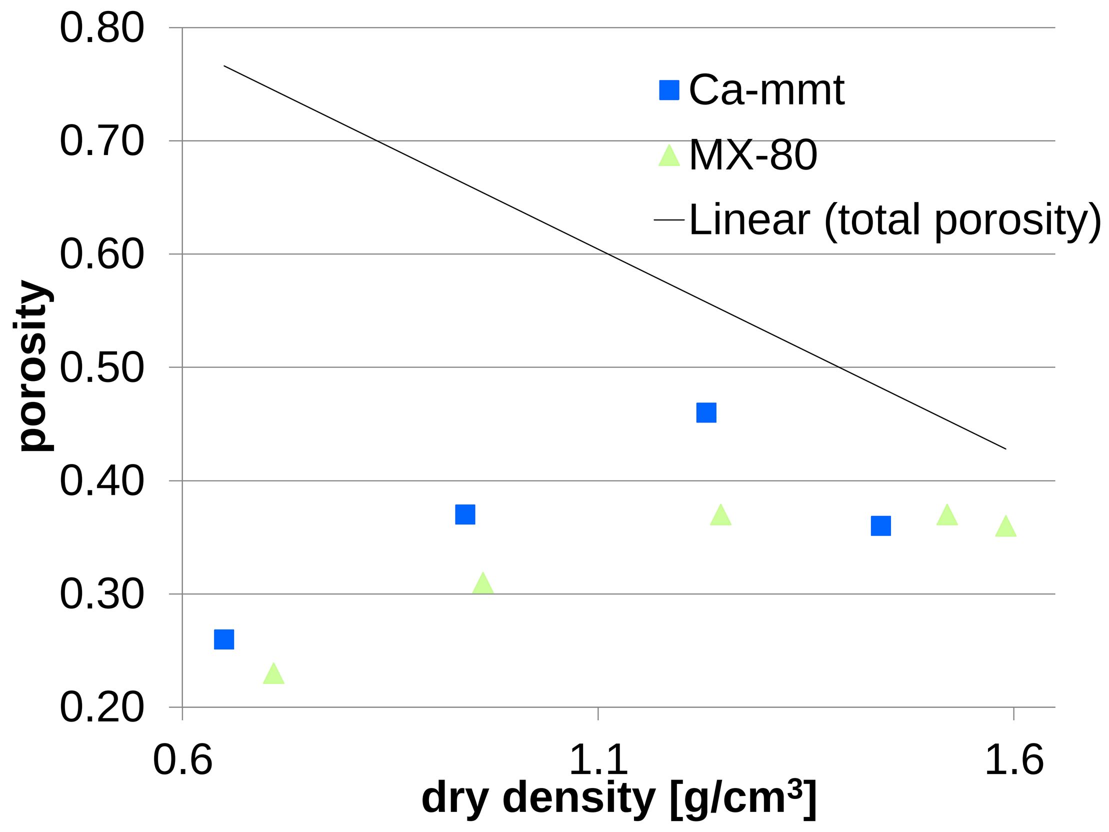

Figure 2. Estimation of the interlamellar porosity calculated basing on SAXS patterns of the Ca-montmorillonite and MX-80 samples saturated with MilliQ water. The solid line corresponds to the total porosity of the sample.

The TEM studies showed a clear difference in the microstructure of the MX-80 bentonite and the montmorillonite obtained by the purification of MX-80. Apart from removing the accessory minerals, aggregates of clay layers have been destroyed and montmorillonite layers organized differently. As can be seen in the Figure 3 the platelets seem to be more oriented in the purified clay, whereas in the MX-80 their orientation appears more random. This effect could be caused by the sedimentation after the purification process or the uniaxial compression method used to prepare the sample[3].

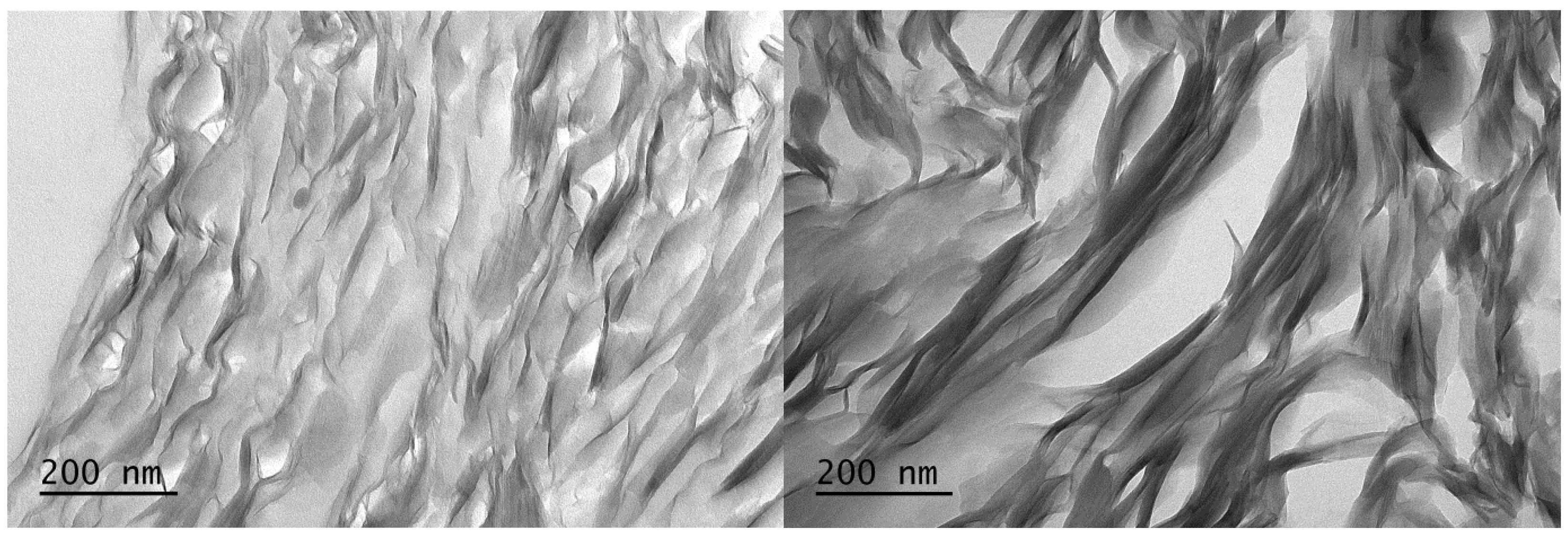

Figure 3. TEM micrograph of Na-montmorillonite (left) and MX-80 bentonite (right) magnified 23 000 times. Both samples have the bulk dry density of 0.7 g/cm³ and have been saturated with 0.1 M $NaClO_4$ solution.

Main applications

The knowledge acquired by the investigation of the microstructure is used to increase the basic understanding of the material and for bentonite model development. Especially, this knowledge is needed to understand the evolution of bentonite structure to a state where bentonite can erode. Consequently, it is an important contribution to ensure the safety of a deep geological disposal of high-level nuclear waste.

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Acknowledgements

TEM images were taken at EM Unit of the Institute of Biotechnology at Helsinki University. The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement n°295487, the BELBaR project. Funding from VTT Graduate School is acknowledged.

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RHEOLOGY MEASUREMENTS ON SMECTITE CLAY GELS

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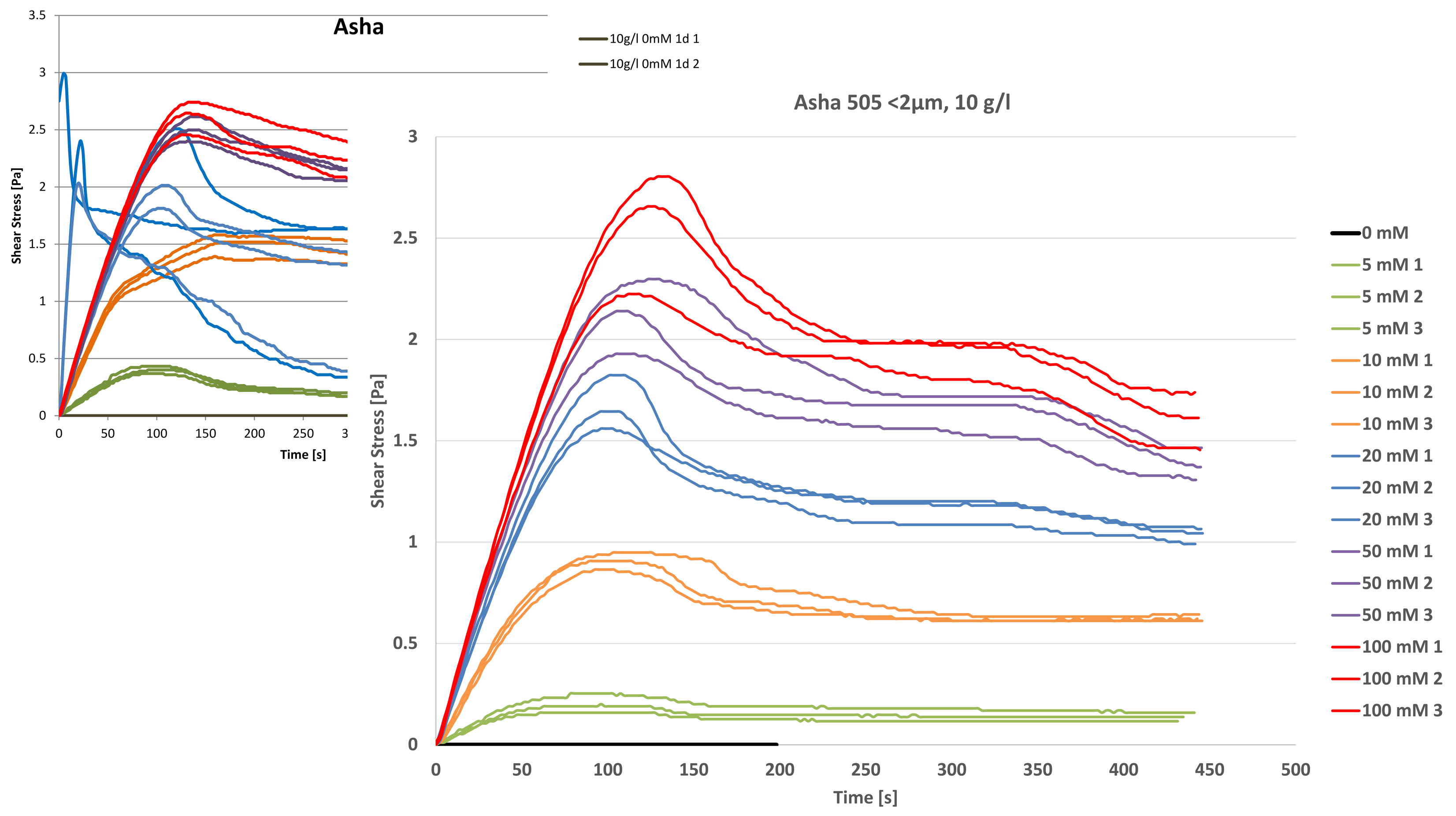
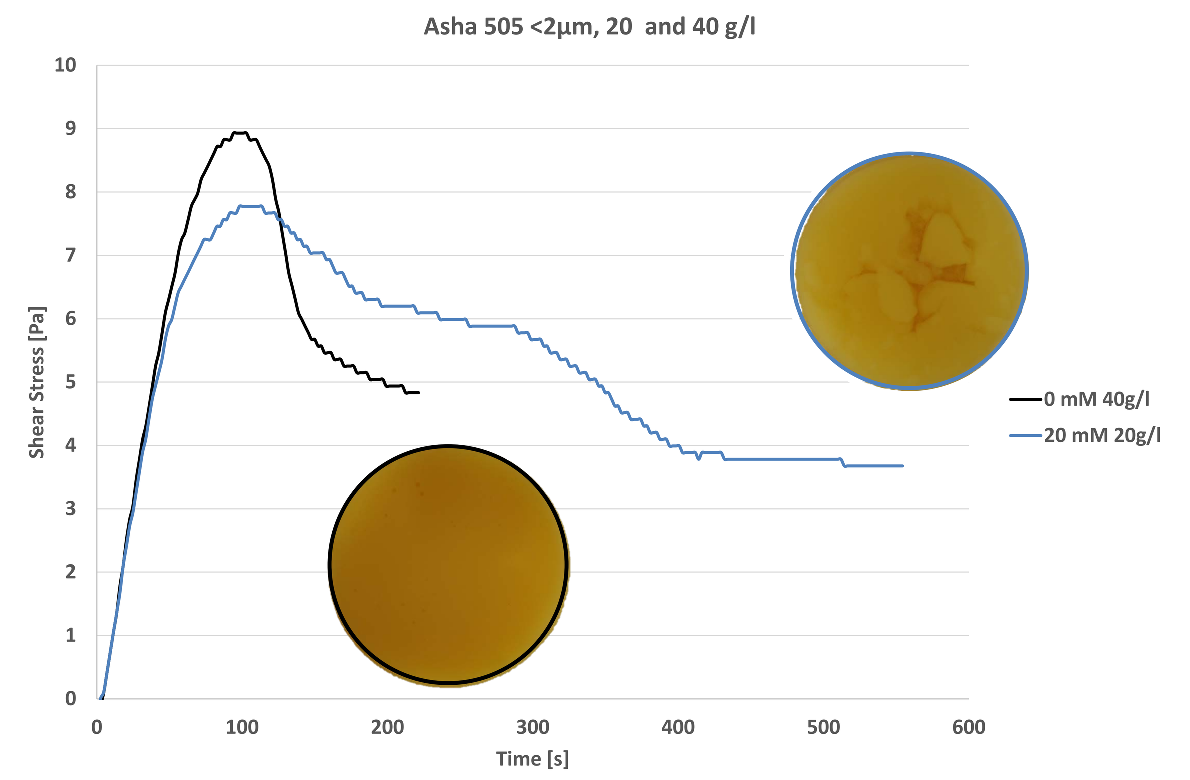
Clay Technology AB

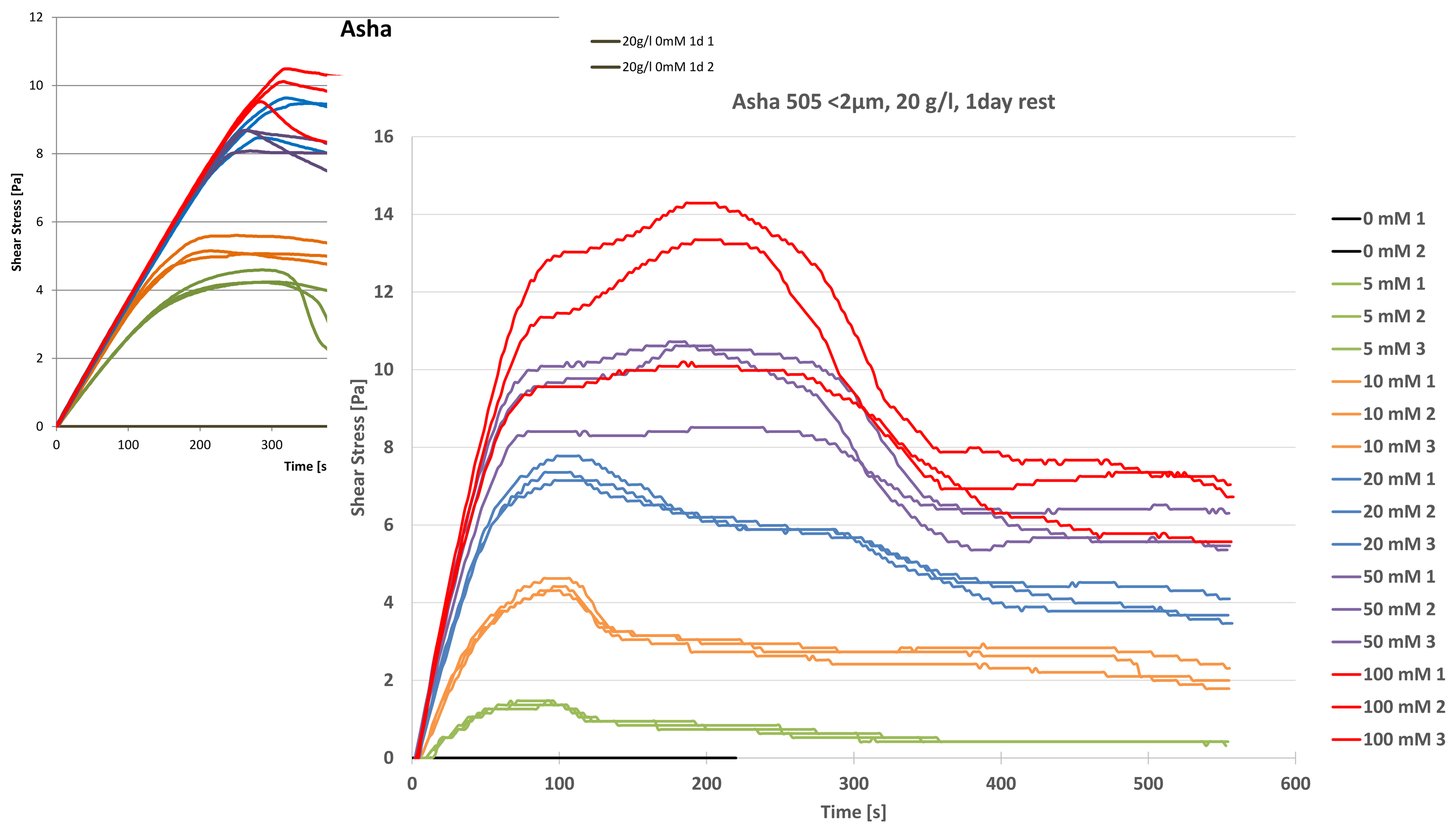
Setup
The clay fraction of the Ashapura (505) bentonite was extracted by centrifugation, oven dried at 60°C, milled and then mixed with deionized water to correct concentration. The test samples were prepared by adding equal volumes of adequate concentration of sodium chloride solution and clay suspension. They were mixed through shaking and then rested for 1 day and 1 week, respectively, until testing. Longer periods will be tested. Testing was made in a Brookfield Viscometer with V-73 and V-74 vanes. Testing speed 0.05 rpm.



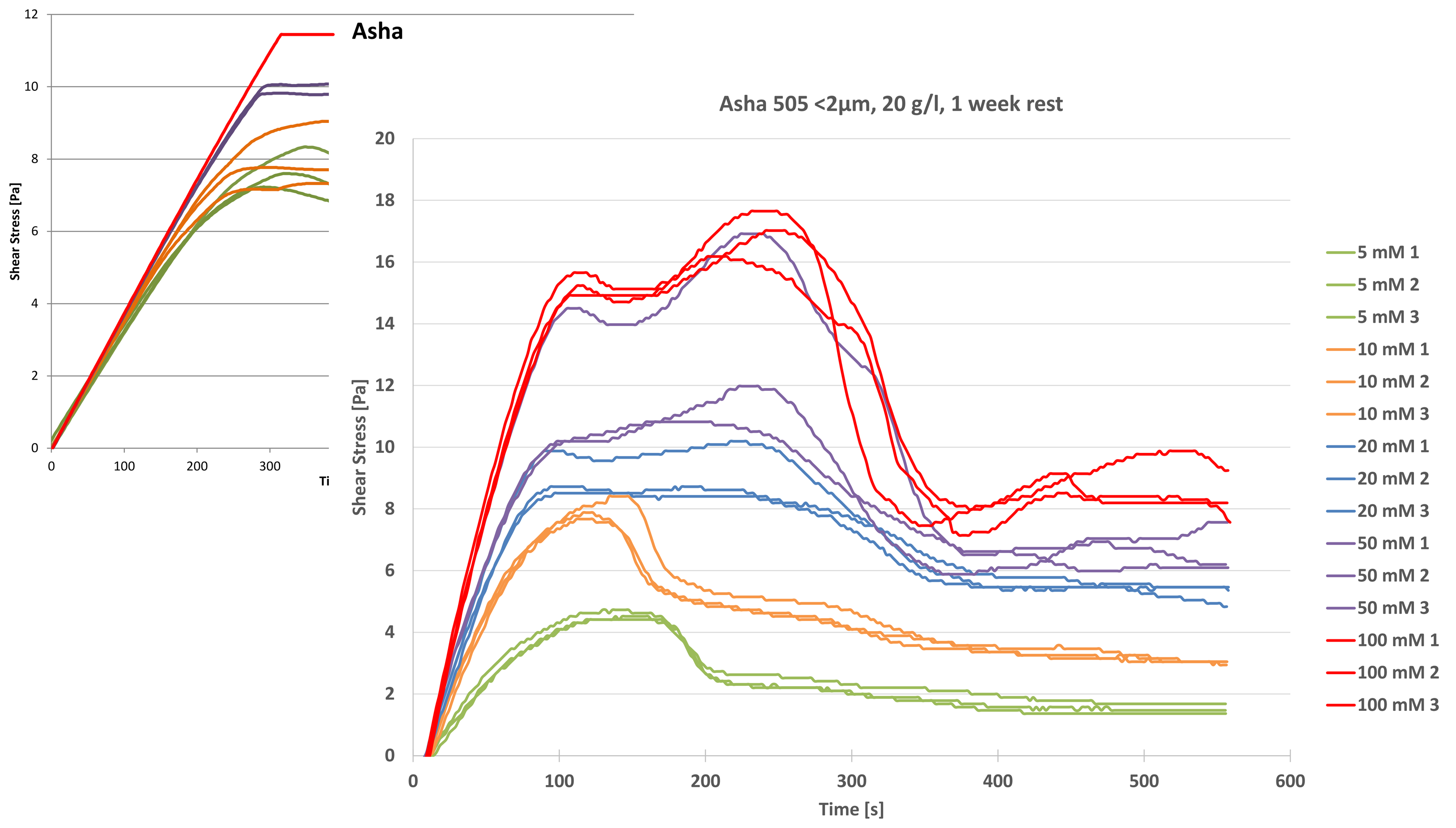
Preparation of 10 g clay/litre, rest time 1 day, three samples per concentration. Earlier result in background.



Two samples with similar maximum yield stress but corresponds to different phases. Blue (gel) retains the impression of the vane. Black (paste) instantly selfheals due to repulsion forces.



Preparation of 20 g clay/litre, rest time 1 day, three samples per concentration. Earlier result in background.



Preparation of 20 g clay/litre, rest time 1 week, three samples per concentration. Earlier tests in the background.

Results

The increase of maximum shear stress (yield stress) with salinity is nonlinear. The effect of increasing salinity is largest between 5 and 20 mM. Further increase in NaCl concentration gives a relatively limited effect.

Longer resting times increases the shear strength. This is also expected for clay particles where there are both positive rim charges and negative layer (face) charges. The build-up of a network through edge-face interaction is a slow process and the tests show that the first formed network is not necessarily the strongest. The effect of ageing is strongest for the 5 and 10 mM concentration.

Tests with different stock solutions are repeatable: giving both similar characteristic behaviour and quantitative values.

Comments
Gel formation is the only bentonite-specific mechanism that can prevent erosion of clay at a transmissive fracture. The present tests show strong sensitivity to the salinity of the external water. For Ashapura(505) a NaCl concentration of ~5 mM is needed to form a gel. However, at that rather low concentration the present tests show that the yield stress is significant.

Care at preparation and the testing is necessary. According to manual a vane inserted to half depth can be used to measure samples if full depth is above the range. This have been tested and this is not applicable to these samples. This is probably due to sedimentation during the gelling process. Consolidation of the gel may also contribute.

Reference:
Nilsson U, Hedström M., 2016. Rheology of dilute montmorillonite gels. Applied Clay Science. *To be submitted*

Acknowledgements
European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no 295487, the BELBaR project.
and
SKB Svensk Kärnbränslehantering AB.

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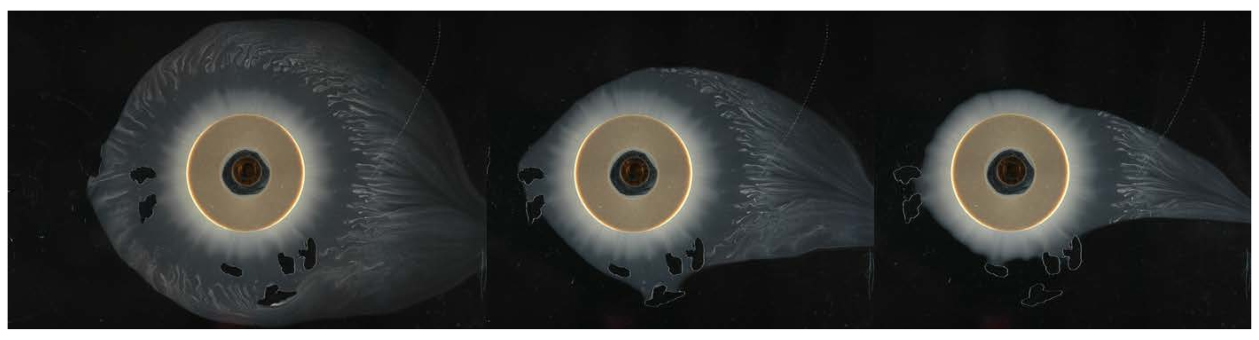
SMECTITE FREE SWELLING AND EROSION IN ARTIFICIAL FRACTURES

Emelie Ekvy Hansen, Ulf Nilsson, *Magnus Hedström*

Clay Technology AB Ideon Science Park, Lund, Sweden

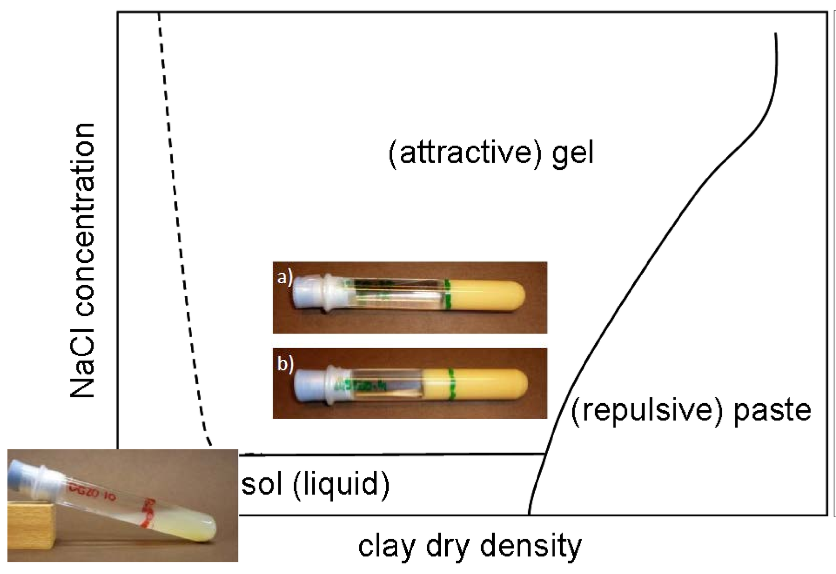
Introduction

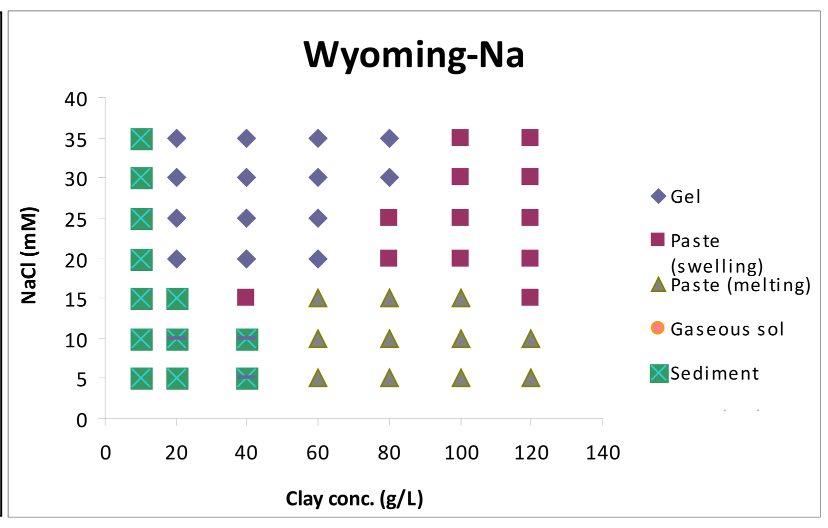
One scenario of interest for the long-term safety assessment of a spent nuclear fuel repository involves the loss of bentonite buffer material through contact with dilute groundwater at a transmissive fracture interface (SKB 2011, Posiva 2012). In dilute water, sodium dominated montmorillonite is known to form a colloidal sol which would easily be transported away with flow.



Top view of Na-montmorillonite in 0.12 mm artificial fracture, clearly showing erosion of the sol phase after 30 days of swelling in stagnant DI water. The sol is liquid, while the repulsive paste has solid character and a yield strength that can withstand the mechanical forces from the flowing solution (Eriksson & Schatz 2015). The flow does not mechanically erode the repulsive paste, rather it is mass transfer from paste to sol that determines erosion.

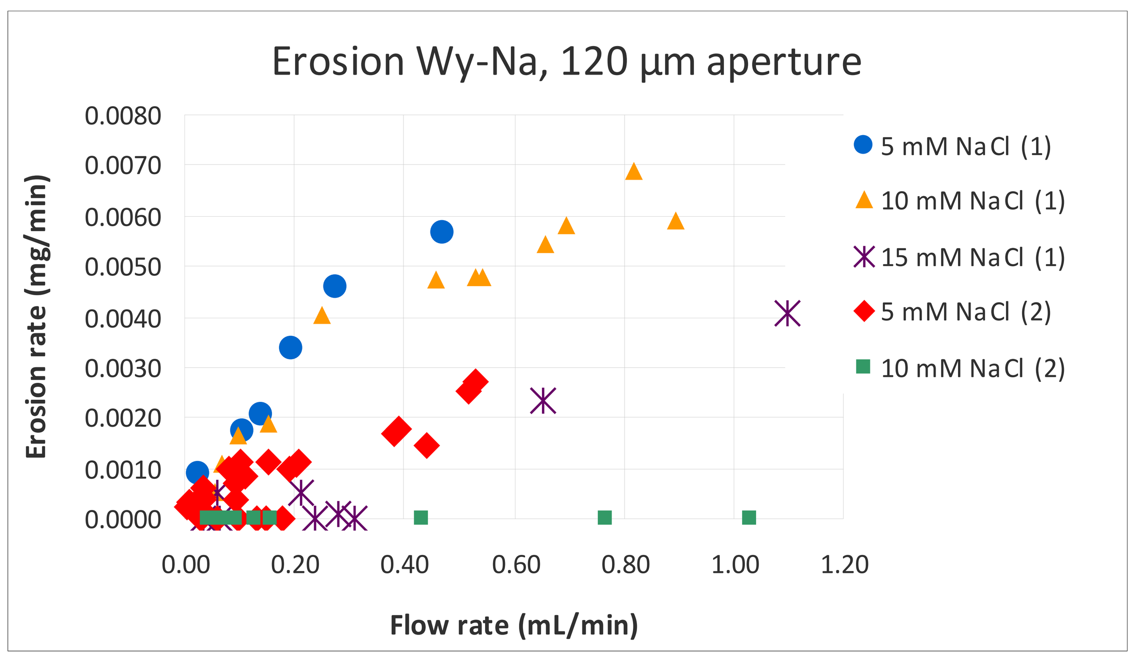
Montmorillonite phase diagram





Schematic (left) and actual (right) state/phase diagrams of Na-montmorillonite.
Rotating vane rheometry shows that the gels have yield strength that will withstand the shear forces from the flowing solution (Nilsson & Hedström 2016). Erosion stops in artificial fracture tests (Wy-Na) when the NaCl concentration is increased to 20 mM.

Hysteresis



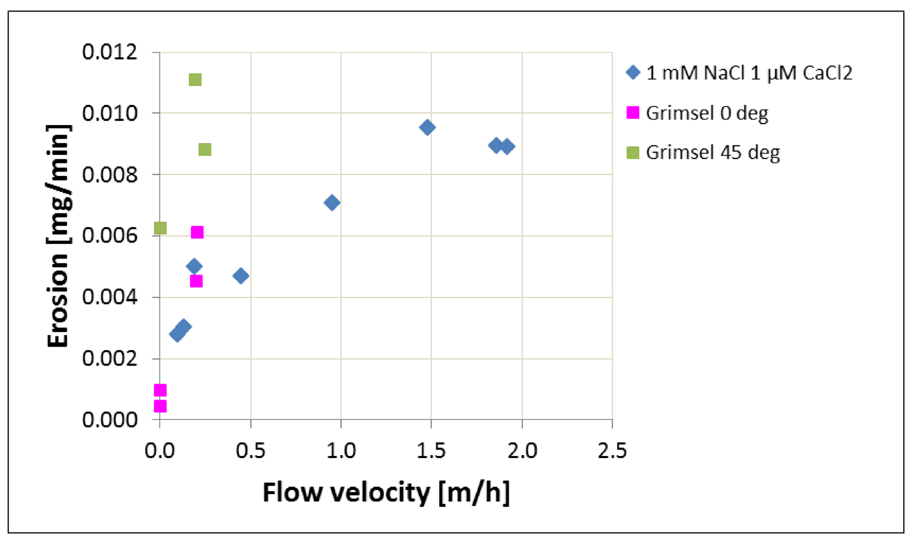
Erosion rates vs. flow rate.

(1) Increasing [NaCl]

(2) After reaching 20 mM NaCl concentration was decreased

Evidently there is a strong hysteresis related to the ionic strength changes. Note that at 10 mM (2) no erosion is detected as opposed to 10 mM (1).

Erosion in 45° sloped fractures



Grimsel: 0.7 mM NaCl, 0.14 mM $CaCl_2$

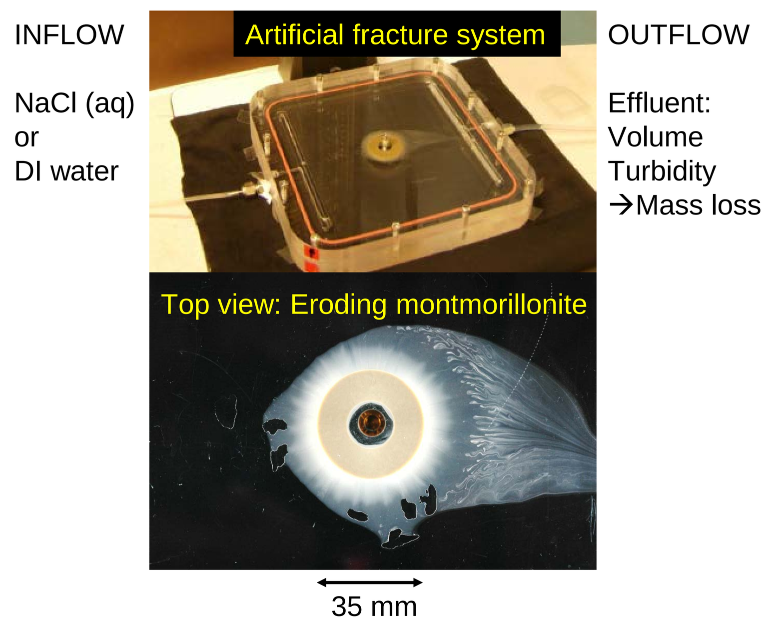
At no flow the erosion rate in a sloped fracture corresponds to a unit erosion rate of 170 kg/(m^2·year).

Experimental details: Artificial fracture system

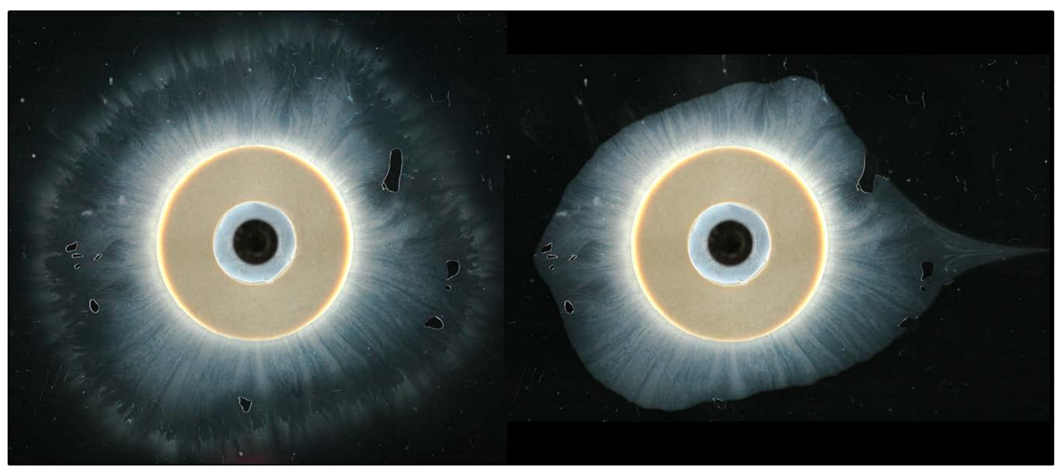
Extrusion/erosion behaviour of montmorillonite under dilute water conditions was studied using small-scale flow-through artificial fractures. The lateral dimensions of the fracture are 20 cm × 20 cm and the aperture is 0.12 or 0.24 mm. The compacted sample dimensions were 1 cm (height) × 3.5 cm (diameter) The montmorillonite dry density in the compacted sample was initially ~1260kg/m^3.

Homoionic Wy-Na or mixed 50/50 Ca/Na-montmorillonite extracted from MX-80 was investigated.

Clay mass loss was determined from turbidity of effluent.



Concentration of erodible clay phase (Wy-Ca/Na 50/50)



Free swelling 6.75 days After flushing DI water during 14 min

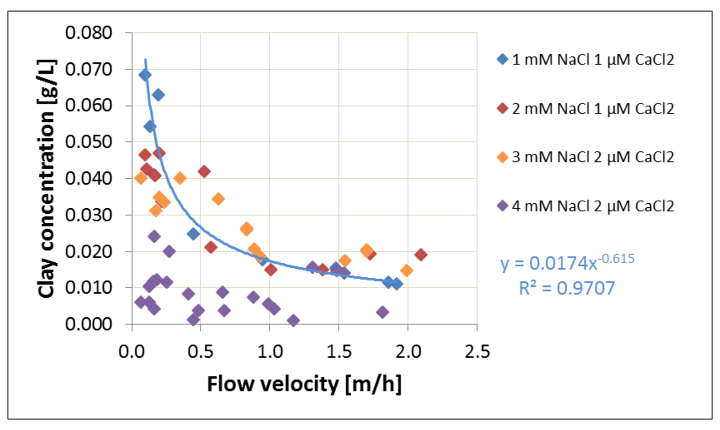
Area difference *aperture →volume change

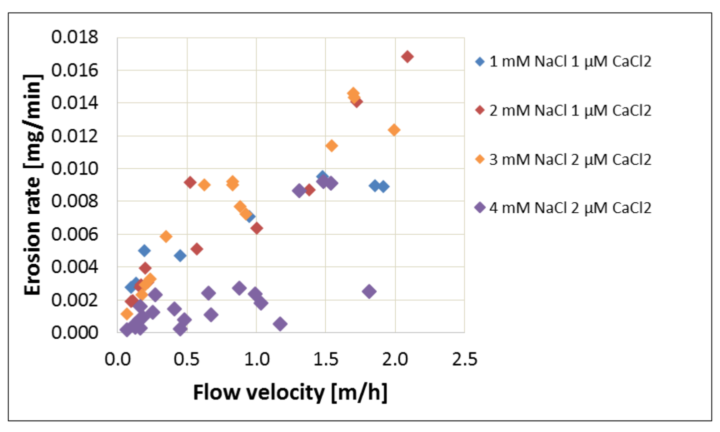
Turbidity of effluent → clay mass

Concentration of erodible phase ~30g/l (31, 32 and 34 g/l)

28g/l: yield stress 14 mPa (Eriksson & Schatz 2015)

Erosion of Wy-Ca/Na 50/50 at ionic strengths 1 to 4 mM





Erosion rates at 4 mM are substantially lower than the rates at 1 mM in agreement with earlier findings in Birgersson et al. 2009 and Schatz et al. 2013. Unit erosion rate for 1 mM case at lowest flow velocity is 65 kg/(m^2·year) while at 4 mM the erosion rate is almost an order of magnitude smaller.

The clay concentration in the effluent is several order of magnitude lower than the estimated concentration of the erodible phase (30g/l). This is a dilution effect: most of the flow is not in contact with the clay.

Summary

Erosion does not occur when salinity is high enough to cause gel formation.
Erosion rates at salinity below 4 mM may cause large loss of bentonite buffer.
In a sloped fracture the unit erosion rate of 170 kg/(m^2·year) translates to 500 kg over a 10 000 year period assuming an aperture of 50 µm and a 2 m deposition hole diameter.

References

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Acknowledgements

The research leading to these results has received funding from the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under Grant Agreement no 295487, the BELBaR project and Svensk Kärnbränslehantering AB SKB.

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Do Montmorillonite Particles form Gels in Aqueous Suspensions?

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Introduction

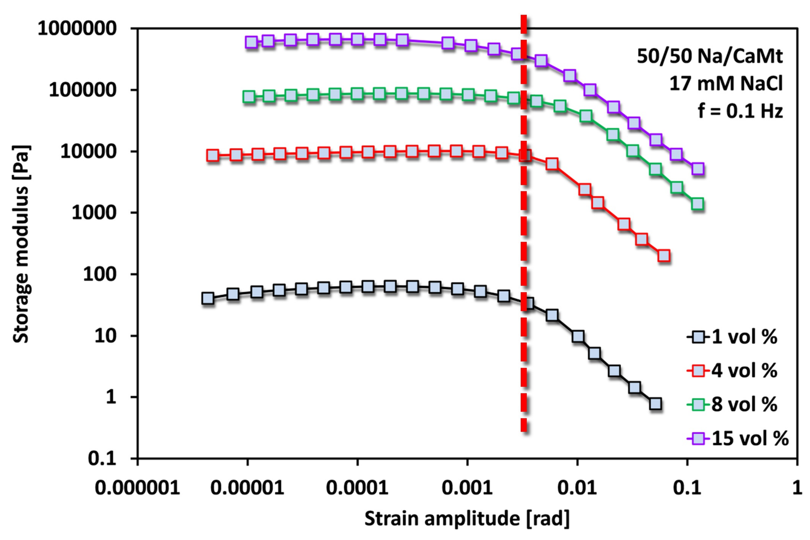
Clay mineral particles are considered to form gels at very low solids content in aqueous suspensions.[1] New evidence suggests that the solid-like consistency of clay suspensions may be due to steric or frictional forces between particle clusters rather than volume-filling bonded networks. This finding would suggest that clay mineral suspensions can be characterized as viscoelastic liquids instead of gels, as is commonly accepted.

Experimental

Rheological measurements were performed on purified (from Volclay MX-80 bentonite) and ion exchanged (Na, Ca) montmorillonite.[2] A TA Instruments DHR-2 rheometer equipped with plate-plate geomtery was used in all measurements. Optical Coherence Tomography[3] (OCT) was used for in situ imaging of clay samples emplaced within the measurement geometry.

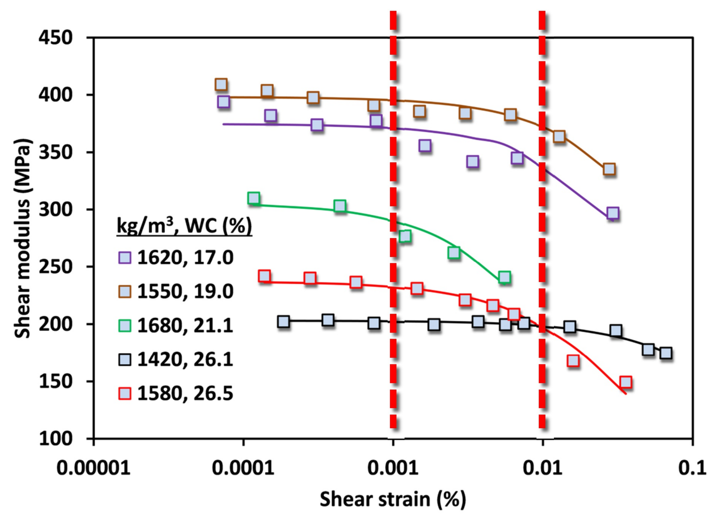
Length-scale: *strain sweep measurements and optical imaging*

~30 ← **Effective strain (µm)** → ~20 ~220

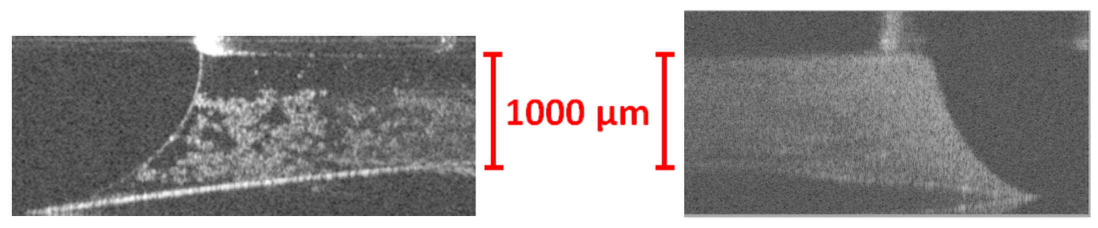


Dilute samples

The critical strain is on the same order of magnitude for dilute and compacted samples, thus indicating similarity in long-range structure.



Compacted samples[4]



0.1 vol % 5 vol %

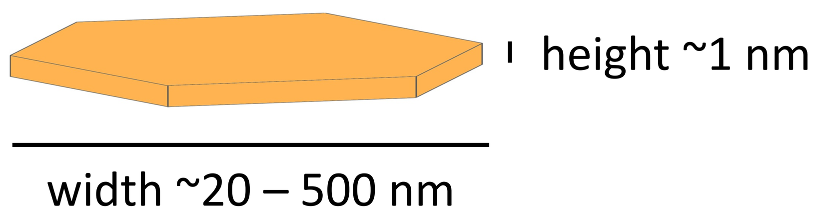
OCT images yield information about aggregate size and the macroscopic structure of montmorillonite suspensions. The structural length-scale perceived from OCT imaging corresponds very well to the critical strain.

material

Montmorillonite

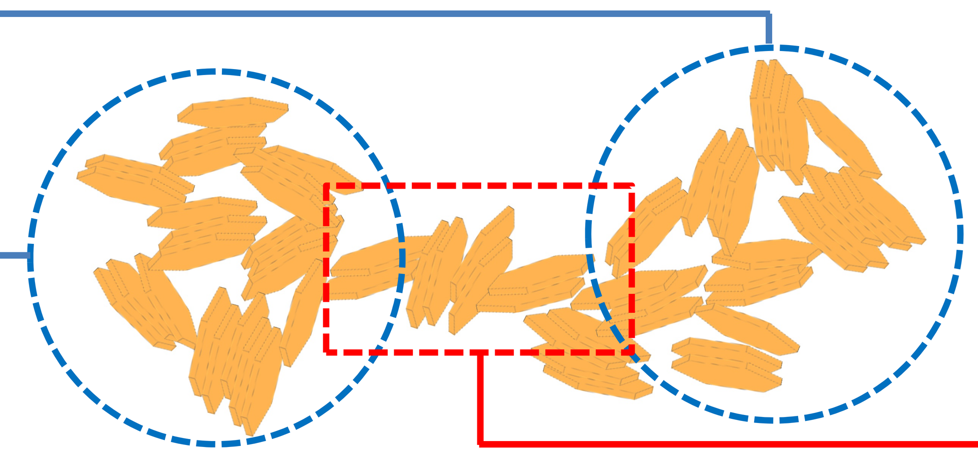
Generic formula: $(Na, Ca)_{0.6}(Al, Mg)_4Si_8O_{20}(OH)_4$

Single montmorillonite platelet:



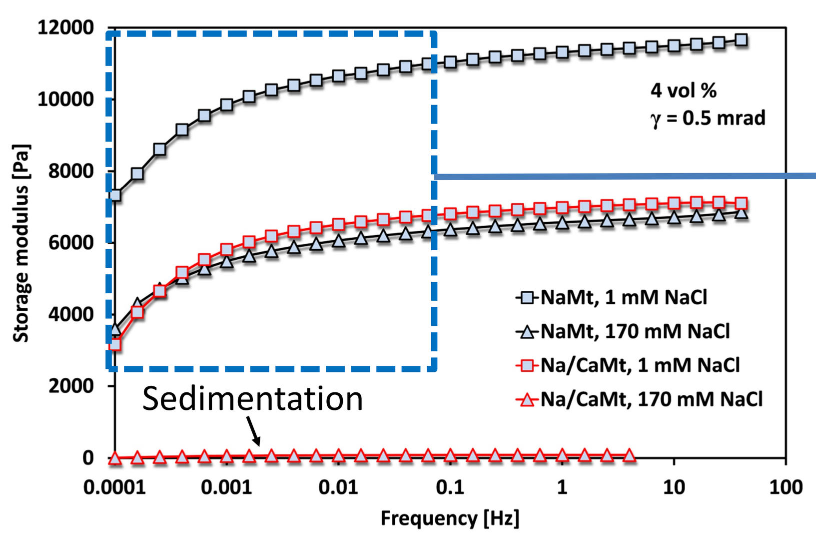
hypothesized structure and response to strain

Flocs / domains of higher density.
These deform under strain but do not break even above the critical strain.

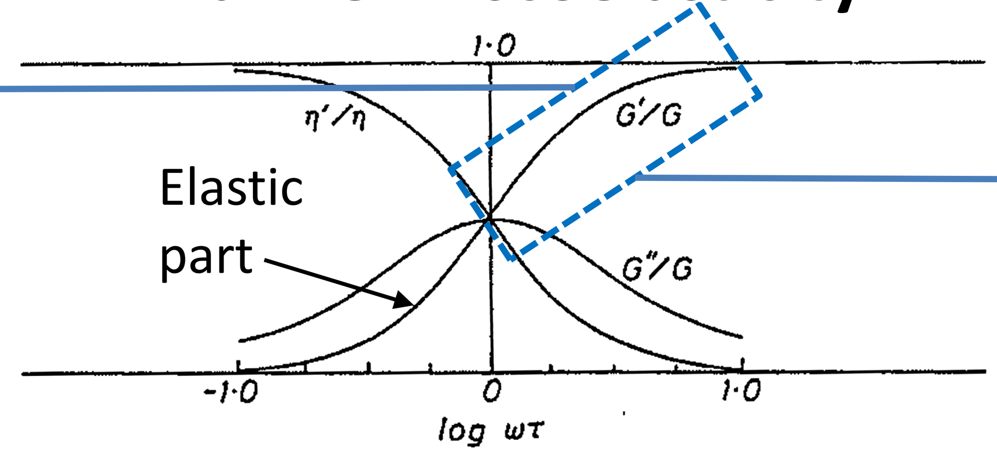


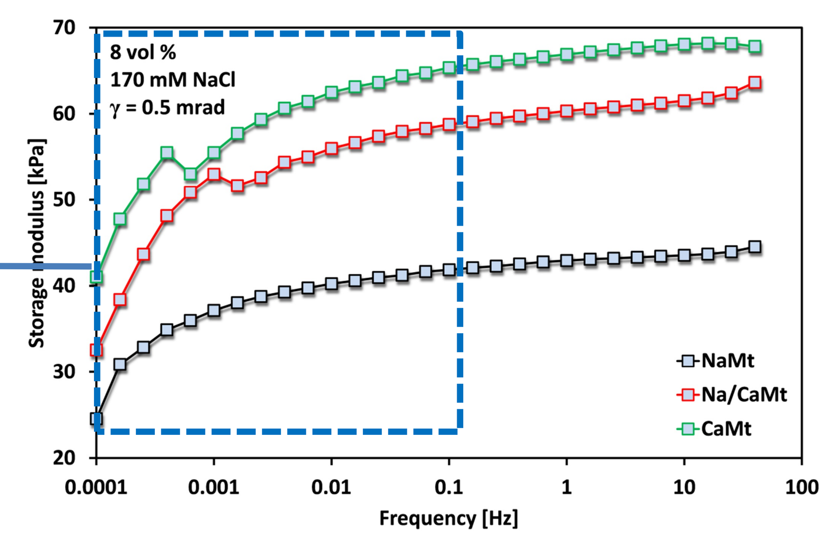
Bridges / domains of lower density
These deform under strain and normally break at the critical strain.

Time-scale: *frequency sweep measurements*



Maxwell viscoelasticity





Substantial relaxation at low frequencies indicate structural rearrangements, which is contrary to typical gel-like behavior.

Conclusion

The mechanical response of montmorillonite suspensions that have been allowed to swell freely seems to be governed by frictional forces between aggregates rather than inter-particle chemical bonds. This indicates that montmorillonite suspensions behave like highly viscous liquids instead of gels. Based on rheological data and OCT images the solid material (montmorillonite) is organized into domains of higher density (flocs) on the order of a few tens of microns which are interspaced by domains of lower density. Surprisingly, similar length-scales are found for highly compacted bentonite. It is worth noting that true gel-like behavior can be achieved for montmorillonite suspensions in controlled lab-environments, but it is highly unlikely to occur for free swelling montmorillonites (or bentonites) in natural environments. There are no stirrers in a nuclear waste repository.

Acknowledgements

This work has been funded by the European Atomic Energy Community's Seventh Framework Programme (FP7/2007-2011) under grant agreement no. 295487 (BELBaR Project) and Posiva Oy. Rheological measurements and Optical Coherence Tomography imaging has been carried out at VTT Technical Research Centre of Finland. Resonant column tests were performed on compacted samples at Universitat Politècnica de Catalunya, Barcelona.

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BENTONITE EROSION EXPERIMENTS UNDER DYNAMIC CONDITIONS

M. Bouby*, S. Heck, F. Geyer, S. Hilpp, T. Schäfer

Compacted bentonite is envisaged as a suitable hostrock / backfill material in most designs of high level radioactive waste repositories

?

What will happen if glacial melt water flows down to the repository and enters in contact with the compacted bentonite? Buffer mass loss and less diffusion control?

Erosion processes under realistic conditions have to be identified and understood, i.e. from:

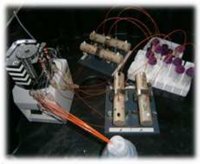
- *Compacted and confined bentonite,*
- *Under dynamic conditions to simulate the effect of a water conducting fracture*

MATERIAL

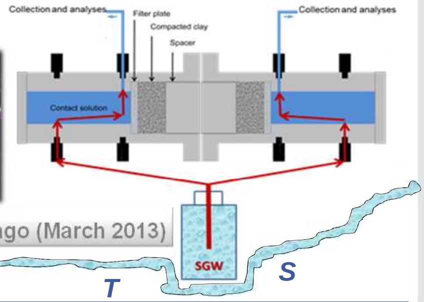
- MX80 (Volclay)
- Sieved fraction < 63 µm used
- Raw or homo-ionic : Na or Ca form
- Compacted into pellets (1.6 g.cm^{-3})
- Simulated glacial melt water type (SGW)

EXPERIMENTAL SETUP

- 4 Double-side reactors
- 2 identical clay pellets
- V_{dead} = 11.6 mL
- Erosion flow rate: (3.0 ± 0.1) µL.min^{-1}
- pH = (8.3 ± 0.3)

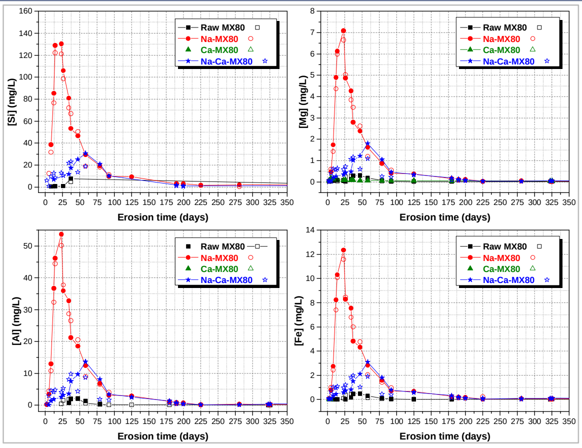


Started ~ 3 years ago (March 2013)



R E S U L T S

In agreement with literature



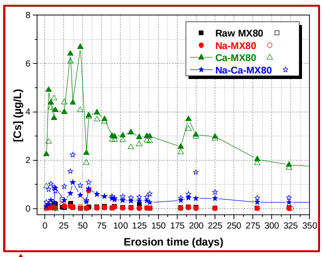
✓ *Typical main elemental clay components Breakthrough Curves (BCs) measured over 9 months (325 days)*

✓ *Clay colloid detachment clearly evidenced except from the compacted Ca-MX80 pellets*

✓ *Mineral dissolution: instantaneous release of Na^+, SO_4^{2-}, Cl^- from the Raw-MX80 pellets*

✓ *Ca^{2+} release from the Ca-MX80 clay pellets*

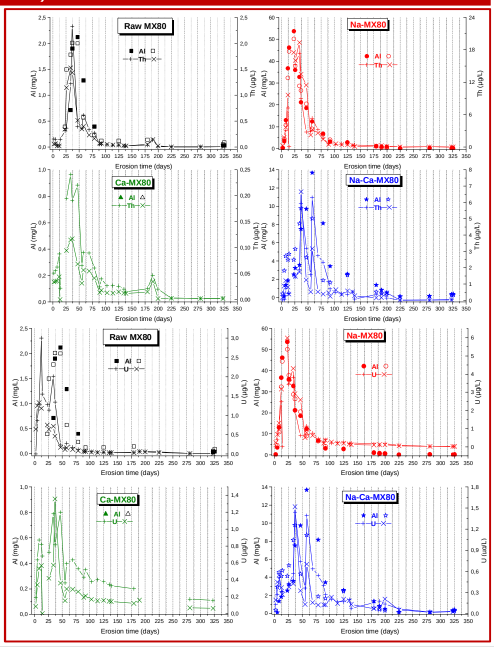
NEW: Cs, Th and U BCs !



↑ *Slow but significant relase of Cs, especially from the Ca-MX80 compacted pellets, Na/Cs exchange ?*

Release of naturally present RNs (Th, U) from the backfill material itself: the activity rate release can be determined; Erosion markers ? →

CCLs: unseful data for PA provided!



Main Characteristics & Results					
		Raw MX80	Na-MX80	Ca-MX80	Na-Ca-MX80
Dry Density		1.6 g/cm^3			
Dimensions		ø:19 mm; h: 10 mm			
Composition		100 % of raw material	100 % Na-MX80	100 % Ca-MX80	50:50 % Na- : Ca-MX80
	EROSION CONDITIONS				
SGW Composition	pH = 8.4 ± 0.1 and $E_{h(SHE)}$ = +0.35 ± 0.05 V $[Na^+]$ = 1.2 mM, $[Ca^{2+}]$ = 0.05 mM, $[F^-]$ = 0.1 mM, $[Cl^-]$ = 0.074 mM, $[SO_4^{2-}]$ = 0.04 mM, $[HCO_3^-]$ = 1 mM, Si traces				
Ionic Strenght		1.3 mM			
Test duration		2.5 years / 907 days / 21768 hours			
Flow		(3.0 ±0.1) µL / min or 2.3 10^{-4} m/s			
Sloped		yes			
Free Swelling		no			
Confined		yes			
Fracture dimensions	cm²	Stainless Steel Porous filter: 20 µm; Surface area: 2.86 cm²; porosity 29.4%. frit volume 134.7 µL. real surface contact area: 0.842 cm²			
Extrusion Distance		0.16 cm (Filter Thickness)			
	RESULTS				
pH		8.3 ± 0.3	8.3 ± 0.3	8.3 ± 0.3	8.3 ± 0.3
Mass Eluted (colloids)	mg	5.5 ± 0.1	77.8 ± 2.1	none	31.2 ± 6.3
Eluted mass loss/initial mass	%	0.11 ± 0.01	1.8 ± 0.1	none	0.6 ± 0.1
Eluted mass loss	kg/m²	0.065 ± 0.001	0.92 ± 0.2	none	0.37 ± 0.07
Average eluted mass loss rate (AMLR)	kg/(y·m²)	0.026 ± 0.005	0.37 ± 0.01	None	0.15 ± 0.03
Activity rate Th	Bq/(y.m²)	5.4 ± 0.3	44.7 ± 0.1	1.2 ± 0.4	20 ± 5
U	Bq/(y.m²)	19 ± 5	39.8 ± 0.1	*(25 ± 15)*	21 ± 4
Time used for AMLR calculations 21768 hours / 907 days					
Eluted mass loss rate (MLR)	kg/(y·m²)	0.051 ± 0.007	1.01 ± 0.02	none	0.37 ± 0.08
Time used for MLR calculations 7800 hours / 325 days					
Size: hydro. Ø		Raw MX80	Na-MX80	Ca-MX80	Na-Ca-MX80
PCS. f(I)	nm	162 ± 32	131 ± 3	-	132± 7
PCS. f(V)	nm	131 ± 98	93 ± 52	-	83± 40
Mole ratios (325 days)	Theo.				
Si/Al	2.49	-	2.54 ± 0.04	-	2.8 ± 0.6
Al/Mg	6.62	5.6 ± 1.2	6.75 ± 0.02	-	6.66 ± 0.01
Al/Fe	7.57	10.2± 2.5	8.93 ± 0.13	-	9.0 ± 0.1

KIT – University of the State of Baden-Wuerttemberg and National Research Center of the Helmholtz Association

These results have received funding from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487, the BELBaR project.

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WP3

MONTMORILLONITE COLLOID SIZE HETEROGENEITY EFFECTS ON: I. STABILITY, II. RADIONUCLIDES SORPTION III. SORPTION REVERSIBILITY

ROYAL INSTITUTE OF TECHNOLOGY

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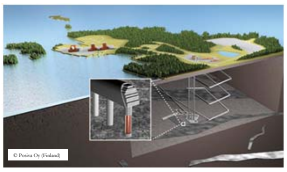
Deep nuclear waste disposal

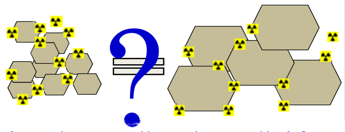


+

Glaciation cycles

=

Potential release of clay colloids, acting as radionuclide carriers under favorable physico-chemical conditions ➤ Colloidal mobility depends on their stability and size ➤



Are the smaller clay colloids miniatures of the bigger ones?

EXPERIMENTAL

- **Material**

Unpurified MX80 bentonite (Volclay Ltd.), purified fulvic acids (FA) from Gorleben site, Lower Saxony, Germany

- **Contact solution**

Synthetic carbonated ground water (SGW, glacial melt water type) containing Na^+ (28.4 mg/L), Ca^{2+} (1.5 mg/L), F^- (2.8 mg/L), Cl^- (2.6 mg/L), SO_4^{2-} (4.1 mg/L) ; HCO_3^-: 10^{-3} M. Initial pH: 8.4. IS: 1.3 10^{-3} M.

- **Characterization**

Photon Correlation Spectroscopy (PCS), Flow Field-Flow Fractionation (AsFlFFF), XRD, SEM-EDX, ICP-OES/MS.

COLLOID FRACTIONATION, SIZE AND STABILITY [2]

Suspension (i^{th} supernatant)	Separation by sedimentation (S) or centrifugation (C)	Mean size from 1:PCS[c] 2: AsFlFFF[d] in nm	Edge sites (mmol/kg)
S0	S (3 days)	1: ~ 692 2: ~229 (35%)	11.2
S1	C: 30' at 313 x g	1: ~610 2: ~198 (62%)	17.8
S2	C: 1h at 700 x g	1: ~337 2: ~189 (77 %)	33.5
S3	C: 4h at 1.200 x g	1: ~ 186 2: ~151 (88%)	67.0
S3.5	C: 30' at 26.000 x g	1: ~ 172 2: ~84 (>90%)	64.7
S3.5[UC]	C: 30'at 26.000 x g[a]	1: ~ 167 2: ~95 (>95%)	67.9
S3.5[UC, FA]	C: 30' at 26.000 x g[b]	1: ~ 143 2: ~124 (87 %)	89.5

Table 1: Sequential clay fractionation protocol, mean clay colloidal sizes obtained and total amount of edges sites (Al-OH+Si-OH groups) calculated acc. to [1]. S0 is the initial suspension: 10 g/L raw MX80 in SGW. **a:** one step centrifugation of S0; **b:** one step centrifugation of S0 containing in addition 11.8 $mg.L^{-1}$ FA; **c:** suspensions diluted to 10 $mg.L^{-1}$, measured 10 times during 5 sec, 5 times, mean values reported; **d:** peak maximum position and colloidal recovery.

- The fractionated clay suspensions present broad clay aggregate (nano-)size distributions (see AsFlFFF and ICP-MS results in [2]),
- Larger colloidal mean sizes than expected are obtained, nevertheless,
- The mean size of the clay aggregates decreases with the number of centrifugation steps (Table 1), so
- The fractionation protocol is successful.

→The total amount of edge sites is found to increase by a factor 6 from the largest to the smallest colloidal fractions.

→Presence of FA during the fractionation protocol increases the amount of collected clay colloids.

→No difference in stability in 0.01 M up to 3 M ionic strength (IS) is evidenced between the different clay suspensions.

[1] Tournassat, C. et al. (2003), Am. Min. 88: 1989–1995

[2] Norrfors et al., Applied Clay Science, 114(2015)179-189

RADIONUCLIDE (RN) BATCH SORPTION AND SORPTION REVERSIBILITY

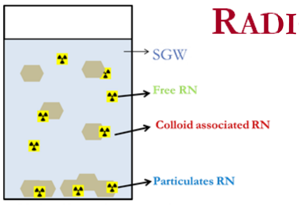


Fig.1: Schematic figure for distribution of RNs in sorption expt.

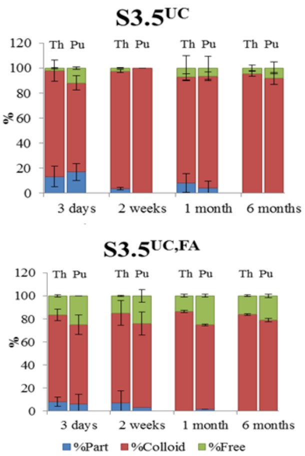


Fig. 2: Distribution of Th(IV) and Pu(IV) at varying sorption times.
%Part: RNs associated to (clay) particulates (bigger clay size fraction, RN precipitates), %Colloid: RNs associated to clay colloids, %Free: RNs fraction remaining free (and/or complexed by FA if present)

- [MontM] = 20 mg/L
- [RN]: 10^{-8}M ^{232}Th(IV); 5·10^{-9}M ^{99}Tc(VII); 10^{-8}M ^{233}U(VI); 10^{-8}M ^{237}Np(V); 2·10^{-9}M ^{242}Pu(IV)
- Sorption contact time: 3 days, 2 weeks, 1 and 6 months
- pH: 8.4 to 9.3
- $Eh_{(after\ 1\ y\ CT)}$: - 191 to -216 mV

- U(VI), Np(V) and Tc(VII) do not sorb onto the clay colloids under the present chemical conditions, whichever suspension tested
- Th(IV) and Pu(IV) sorb strongly (95% and 90% respectively) onto the montmorillonite colloids. They remain sorbed to larger colloids which sediment with time
- If FA are present initially, the amount of Pu and Th associated with clay aggregates is significantly decreased
- The mean colloid size does not affect the uptake of RNs significantly

→Conclusion: Smaller clay colloids seem to be miniatures of bigger ones

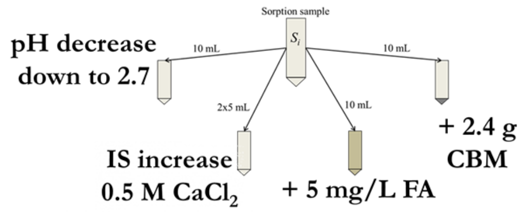


Fig.3: Schematic figure of the reversibility expt.
Desorption time: 1 week and 1 year

- Sorption of $U(VI)_{pH7.5}$ and Th(IV) is partly reversible at lower pH in all suspensions; Pu(IV) sorption does not appear reversible even at pH 2.7
- All clay colloids agglomerate at 0.5 M $CaCl_2$ IS. Th and Pu remain sorbed onto the sedimented clay particles
- FA added after a certain sorption contact time results in a reversible uptake of Th and Pu up to 10% and 20%, respectively
- Np(V), U(VI) and Tc(VII) are reduced and sorbed onto the crushed bedrock material (CBM)

IMPLICATION:

An "average K_D" can be used in reactive transport modeling for all colloidal sizes

[3] Norrfors et al., Applied Clay Science, 2016, In Press

IMPLICATION:

RN sorption reversibility is not guaranteed and is dependent of geochemical parameters (i.e. pH, IS, competing ligands, ...)

[4] Norrfors et al., Applied Clay Science, 2016, in prep.

ACKNOWLEDGMENTS TO:
The Swedish nuclear fuel and waste management Co. (SKB) for financial support and ÅF AB for travelling costs.
These results have received fundings from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487: the BELBaR project, from the European FP7 TALISMAN and the BMWi Project Kollorado-e.

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INNOVATION BY EXPERIENCE

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WP4

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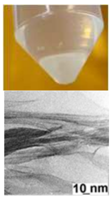
Influence of organic matter (fulvic acids, FA) on the (long term) stability of clay colloids prepared under different chemical conditions

M. Bouby*, Y. Heyrich, S. Heck, S. Hilpp, T. Schäfer

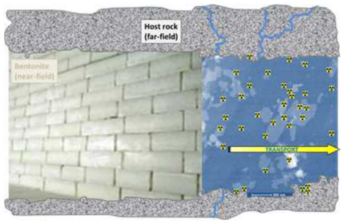
Introduction

• *Bentonite is envisaged as a suitable hostrock / backfill material in most designs of high level radioactive waste repositories*

•In contact with water, a GEL will form which can take a SOL character under specific conditions (ex: fresh age ice waters) resulting in the bentonite barrier erosion and thus a loss of its integrity



• The clay colloidal release may impact the radionuclide (RNs) dissemination in the geosphere, IF . . . . . .



…. The clay colloids are proved to be STABLE ?!

Aim of this work

✓ *The colloid stability depends on chemical parameters like the pH, the ionic strength (IS), the ionic composition and the presence of natural (in)organic complexing agents (like humic (HA) or fulvic (FA) acids)*

✓ *Agglomeration of bentonite clay colloids was already reported even under conditions (i.e. high pH, low IS) initially thought to be ideal for a clay colloid stabilisation [Bouby et al., GCA, 2011, 75(13), 3866]*

These additional experiments performed in the frame of the BelBar project (WP4) aim to examine in more details the effects on the long-term stability of clay colloids of :
1) the presence of specific ions (CO_3^{2-}, Ca^{2+}, Na^+,…)
2) the FA addition, as a potential source of dissolved organic carbon (DOC)

Preparation of clay colloidal stock suspensions

- *MX80 (Volclay)*
- *Sieving (Fraction < 63 µm used)*
- *10 g in 1L LiCl 1 M*
- *Contac time : 1 week under slow stirring + 4 days*

- *Repartition in tubes followed by*
- *4 extraction cycles consisting on*
  - *a centrifugation at 35' at 3500 rpm*
  - *a removal of the supernatant*
  - *the re-suspension of the clay solid/ gel-like residues in 6 different aqueous media at low IS*

Ultra pure water pH 5.7 (1)
NaCl $1.3\ 10^{-3}$ M pH ~5.7 (2)
$CaCl_2$ 0.433 10^{-3} M pH ~ 5.7 (3)
$NaHCO_3$ pH 5.7 (4)
SGW* pH 8.5 (5)
SGW** pH 5~6 (6)

**:SGW: Synthetic Ground Water, glacial melt water type, containing Na^+, Ca^{2+}, SO_4^{2-}, Cl^-, F^-, HCO_3^-, trace of Si*
***: like SGW, without HCO_3^-*

✓ The 6 supernatants collected at the end of the 4th cycles constitute the 6 clay colloidal stock suspensions

First characterizations: IC, ICP/OES, pH, PCS

Aqueous medium	[Colloids] g.L^{-1}	pH	Size range nm (PCS)
Ultra pure water	1.95	9.9	270-300
NaCl $1.3\ 10^{-3}$ M	1.38	9.9	240-300
$CaCl_2$ 0.433 10^{-3} M	1.56	9.9	240-350
$NaHCO_3$ 10^{-3} M	1.59	9.6	270-310
SGW pH ~ 8.5	0.92	9.3	290-350
SGW ~ pH 5-6	0.87	9.7	270-320

Table 1: First characterization of the 6 clay colloidal stock suspensions, i.e. the 4th supernatants

✓ [Si]/[Al] and [Al]/[Mg] ratios suggest the release of clay colloids

✓ Their size is in the range expected, further investigations are necessary to check the presence of smaller-sized clay particles

✓ The composition of the SGW strongly decreases the clay colloid production

Fast coagulation experiments

- *Dilution of the 6 clay colloidal stock suspensions in the corresponding aqueous media: [Colloids] = 10 mg.L^{-1}*
- *With or without FA (2.5 mg.L^{-1})*
- *IS: 0.1 M, 1 M, 3 M with NaCl, $CaCl_2$, $MgCl_2$*
- *PCS studies: evolution of the mean hydrodynamic diameter*

✓ **Whatever the initial aqueous media in which the clay colloids are suspended, they present the same coagulation behavior at moderate to high (0.1 M, 1 M, 3 M) IS in NaCl, $CaCl_2$ or $MgCl_2$ electrolyte**

✓ **In 0.1 M NaCl IS, the coagulation rate slows down**

✓ **The presence of FA only prevents or slows down the clay coagulation in 0.1 M NaCl but in none of the other conditions tested.**

In view of the literature, the results seem independent of the origin of the clay or the organic matter and can be generalized

Long term stability study

- *Dilution of the 6 clay colloidal stock suspensions in the corresponding aqueous media …*
- *… Containing or not additional FA [2.5 mg.L^{-1}]*
  - ✓ *[Colloids]: 1, 5, 10, 100 mg.L^{-1}*
- *12 samples available for each set of conditions, stored at room temperature (~21-22°C), preserved from light*
- *Samples are now 33 months old*

First analysis of **2.5 years old** samples from aqueous media (6) with FA: promising!

✓ pH constant: 6.4 ± 0.1
✓ Size (Ø, PCS$_I$): 205 ± 16 nm, after shaking: > 310 nm
✓ Colloid concentration gradient

Under the present experimental conditions, i. e. glacial melt water at quasi-neutral pH, the clay colloids undergo a slow agglomeration process even in presence of organic matter

These results have received funding from the European Atomic Energy Community's (EURATOM) 7th Framework Programme (FP7/2007-2011) under the grant agreement No. 295487, the BELBaR project.