Öppen

Anteckningar

DokumentID	Version	Status	Reg nr	Sida
1225162	1.0	Godkänt		1 (53)

Författare Olle Olsson	Datum 2009-11-15
Granskad av	Granskad datum
Godkänd av Olle Olsson	Godkänd datum 2010-01-29

Expertmöte Bufferterosion 2009-11-06

Plats:	SKB Blekholmstorget, E4:115	
Tid:	2009-11-06 kl 9.00 - 14.00	
Deltagare:	Jinsong Liu	SSM
	Birgitta Kalinowski	SKB
	Björn Deverstorp	SSM
	Öivind Toverud	SSM
	Bo Strömberg	SSM
	Shulan Xu	SSM
	Mick Apted	Monitor Scientific (SSM)
	David Savage	Quintessa CTD, UK (SSM)
	Håkan Wennerström	Lund Universitet (SSM)
	Timo Saaario	VTT (SSM)
	Randy Arthur	Monitor Scientific (SSM)
	Göran Sällfors	Chalmers (SSM)
	David Bennett	Terra Salus (SSM)
	Allan Hedin	SKB
	Olle Olsson	SKB
	Patrik Sellin	SKB
	Marika Westman	SKB
	Ivars Neretnieks	KTH
	Magnus Hedström	Clay Technology AB

1 Inroduction and welcome

Olle Olsson welcomed the participants to the meeting.

The agenda for the meeting was approved.

2 Introduction, summary and treatment in SR-Site

Patrik Sellin presented the background to the buffer erosion issue and how it is intended to be treated in SR-Site. The presentation is included as Appendix 1 to these minutes.

He summarized the results of the Bentonite Erosion Project. The scientific results from this project were presented at a meeting in December 2008. The focus for this meeting is the application of the results in the safety assessment SR-Site.

SSM/BRITE asked what effects a large loss of buffer would have on the diffusivity. SKB responded that a considerable part of the buffer can be lost before advective conditions will occur. A loss of buffer will increase porosity but the effects on diffusivity are limited. The diffusivity data needed for calculations are available.

SKB informed that filtration has been studied and SKB concludes that there is currently not sufficient evidence to claim that a filter will form or that a filter can be engineered with sufficient long term performance. BRITE asked if it will be used as an argument in the assessment. SKB responded that it will be mentioned but not used in the quantitative assessments. SKB will consider continued research on this topic but no decisions have yet been made.

SSM/BRITE asked about the reasons for the change in allowable mass loss of buffer compared to SR-Can. SKB responded that estimates in SR-Can were based on calculations made for a situation where the internal friction in the bentonite is high. The current estimate which allows loss of a larger buffer mass before advective conditions will apply are a consequence of current knowledge on internal friction in the bentonite and homogenization. The limit is based on the buffer density that gives a swelling pressure of 100 kPa (see OH with diagram in Appendix 1). This value is applicable for salinities up to 1 M.

3 The transport model

Ivars Neretnieks presented the model used to estimate the release of bentonite colloids into fresh water. The presentation is included as Appendix 2 to these minutes.

SSM/BRITE asked to what extent gel formation is dependent on the CCC. Ivars responded that the value of the CCC only matters at the gel/water interface. *Clarifying note: The transition from sol to gel happens at the CCC. Abend and Lagaly /2000/ writes: "A stable colloidal dispersion coagulates when a certain amount of salt is added. The threshold salt concentration is called critical coagulation concentration". At high density montmorillonite is a repulsive gel, it expands or develops a swelling pressure even in contact with molar concentrations of salt. At lower densities, e.g., when a gel expands into a fracture it could turn into a sol if the electrolyte (salt) concentration of the water is below the CCC or forms an attractive gel if the concentration is above the CCC. Ivars did not make the distinction between attractive and repulsive gels but his modelling is always performed at concentrations below the CCC so he has always studied the repulsive gel/sol (water) interface. Erosion depends in his model on the viscosity of the repulsive gel and the water velocity.*

SSM/BRITE asked about the role of groundwater chemistry. Ivars answered that groundwater composition only becomes important when the gel becomes dilute. An attractive gel has a yield strength that presumably depends on the water to solid ratio and the salt concentration. Decreasing the amount of clay gives a weaker attractive gel and at some point one would reach the limit where it is no longer practical to measure any yield strength. It is not important for compact gels. It was asked if the formation of a gel will occur for all swelling clays. Yes, in principle but the issue is if colloids will be released.

The concepts of gel and sol were discussed. A sol will form when the concentration is below the CCC and when colloidal particles are formed. There will in practice be no release of particles above the CCC. No particles are found in the experiments when the concentration is above, neither with NMR nor with turbidity measurements. Any colloid release above CCC will be negligible with regards to buffer stability.

SSM/BRITE asked if pure clay without gypsum and other accessory minerals had been considered. Yes, they have been considered but many of these minerals can be dissolved and removed before a future intrusion of dilute glacial melt water. Hence, their presence cannot be taken credit for in this context. SKB pointed out that this is a sensitivity study and the conclusion is that it is difficult to show that engineering measures will resolve the issue. It helps to start with high Ca-contents but it is difficult to show that it is sufficient.

SSM/BRITE commented that SKB needs to consider groundwater evolution also during temperate time. SKB responded that the chemical evolution of the groundwater is modelled in SR-Site (as it was in SR-Can). The conclusion is that we will never get below $X_{Ca}<20\%$. From a practical point of view a montmorillonite with $X_{Ca}<90\%$ behaves similar to a Na-bentonite when the concentration is below 2-4 meq/L. It is pessimistic to treat the system as pure Na-montmorillonite. Any amount of Ca would reduce swelling capability.

4 The experimental determination of CCC

Magnus Hedström presented the experimental evidence in support of the value for the CCC. The presentation is included as Appendix 3 to these minutes.

Magnus concluded that with Ca in the bentonite system erosion occurs below 2-4 meq/L if Cl is the anion. The same behaviour is expected for other “typical groundwater anions”: SO_4^{2-}, NO_3^- and HCO_3^-. Erosion is primarily associated with sol formation. From an attractive gel there will be no active release of colloids. Mechanical erosion from high shear forces could of course occur. Present day groundwater at both Forsmark and Laxemar are above this value. SSM/BRITE asked what SKB’s conclusion is about the pH effects. Magnus said that the effect of pH on erosion is small and this is tested and for a pure Wy-Na CCC is about 25 mM up to pH 9.1. See also figure 7-33 in the CT report..

5 Preliminary calculations for SR-Site

Allan Hedin presented the preliminary calculations made for SR-Site. The presentation is included as Appendix 4 to these minutes.

The calculations presented were based on the model presented by Ivars and site data on groundwater flow at Forsmark based on the results from the hydrogeological modeling that will be used in SR-Site. The “groundwater flow” is different compared to SR-Can. .

SSM/BRITE asked if variable aperture and channeling were considered in these calculations. SKB said that it was not included in results presented here but it will be included in the transport calculation in SR-Site. The values of fracture aperture used in these calculations are those used in the groundwater flow calculations for the fractures intersecting the ensemble of deposition holes.

SSM/BRITE asked if excavation will induce changes in fracture properties. SKB responded that such changes are not important as erosion will only occur where the flow is high, i.e. for extensive and connected fractures intersecting deposition holes. The effects of spalling have not been included so far but Ivars is working on this.

SKB said that the calculations presented show considerably fewer damaged canisters compared to results presented in SR-Can. A sensitivity study with the SR-Can model could be included in SR-Site.

The orientation of fractures is considered not important by SKB. However, Ivars stated that he did not consider gravity effects sufficiently well understood. Gravity effects on colloidal particles are included in the dynamic model. However, there are experimental observations of sedimentation that cannot be directly explained by the model. These effects are discussed in the project documentation.

SSM/BRITE asked if other safety functions are affected by buffer loss. SKB said that microbial activity cannot be excluded when swelling pressure is lost to a value below 2 MPa, ie long before advective conditions are reached.. Transport will still be diffusive though. Canister sinking has to be considered at approximately the same swelling pressure as when advective conditions will start to occur. Eventually, after a sufficient amount of buffer loss, all buffer functions will of course be affected.

SSM/BRITE asked if advective conditions could occur locally due to insufficient homogenization. SKB said it will not occur for this type of erosion process.

SSM/BRITE asked if the model is for a general or a specific bentonite. SKB said the model is for a general bentonite and only small differences have been observed between the bentonites tested.

6 Questions – discussion

SKB informed that there will be 4 top level reports that present the final results of the Buffer Erosion project. Of these, Ivars report is the summary report. There will be no single final report from the project. SKB’s conclusions will be presented in SR-Site.

SSM/BRITE asked how SKB handles situations where there are groups of with different views. SKB’s aim is to have a defensible and pessimistic model that can be defended under all circumstances.

The difference between the Clay Technology model and Ivars model is that the Clay Technology model predicts there will be no erosion of bentonite if there is no flow, which is contrary to predictions by Ivars.

SKB plans to continue work on buffer erosion but plans are not yet finalized.

SSM/BRITE noted that the model is made for a simple Na-system. Will a model be developed for a more realistic system? SKB: Yes, we are looking into the effects of divalent ions. Fracture aperture variations will also have to be looked into.

SSM/BRITE: Have you considered additives to improve performance? SKB: Yes, we have tried to look at filter cakes but adding material into the bentonite may not improve the filter effect. An engineered solution could be possible, but there are not enough evidence claim any effect.

What about gypsum? SKB: Gypsum will be dissolved and leave the bentonite after a comparatively short time in this context.

SSM/BRITE: There has been a change in criteria for advective conditions and buffer loss between SR-Can and SR-Site. What is the basis for this change? SKB: The approach suggested here would be consistent with how the bentonite is treated in the transport model. *However, after this meeting SKB has decided to revert to the SR-Can mass-loss criteria for the advective case. Based on discussions with our experts, SKB concludes that more investigations should be undertaken before complete homogenization can be claimed.*

SSM/BRITE: What is the experimental evidence on homogenization? SKB: We have some experimental data but will put more effort on this in the future.

SSM/BRITE: What is the impact of bentonite erosion on the backfill in the tunnels? SKB: We don’t see this as a problem as there is so much bentonite in the tunnels. The effect of bentonite loss in tunnels is also small compared to the deposition holes (e.g. no corrosion).

SSM/BRITE: Do you have rheological data for water ratios of 25 or more? SKB: Yes, Clay Technology have produced such data and there are data in the literature.

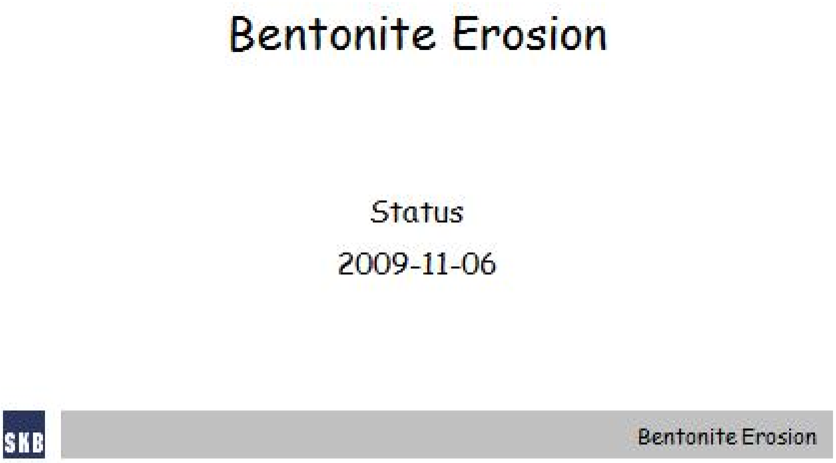
SSM/BRITE: Do you have understanding of the situation where $X_{Ca}>0.9$. SKB: Yes, it is controlled by attractive forces between the flakes. These are correlation forces. Bo Jönsson shows in TR-09-06 (Fig 5-6) that at X=0.9 correlation forces dominate so that the swelling pressure is negative. At X=0.8 the swelling pressure is always positive so the system will disperse to become a sol in deionized water. The mapping of the sol formation zone shows that the system behaves as pure Ca montmorillonite when X > 0.9. The release of colloids from such system is negligible.

SSM/BRITE: What is the cause of the difference in CCC for different bentonites? SKB: The reasons are not well understood but it is likely that it is due to edge charges.

7 Close of meeting

Olle Olsson closed the meeting and thanked the participants for their contributions to the meeting.

Appendix 1

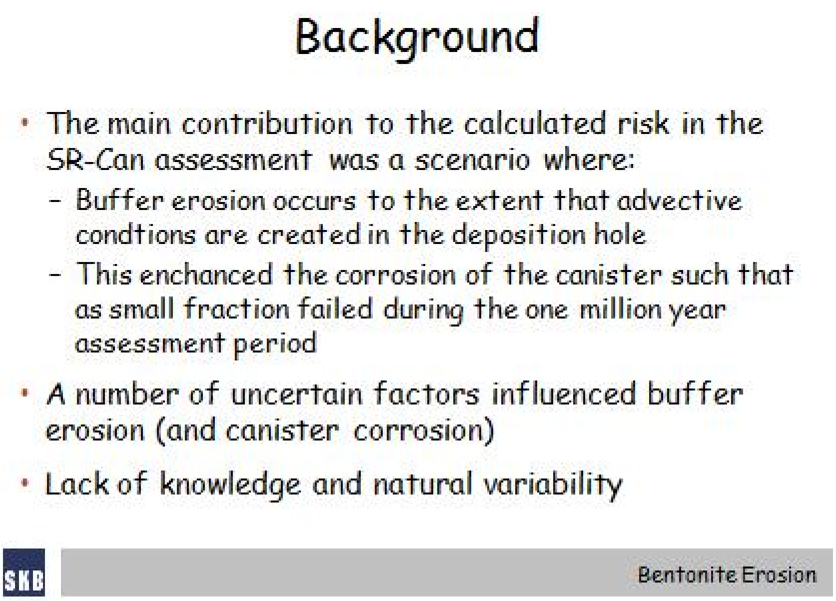


Bentonite Erosion

Status

2009-11-06

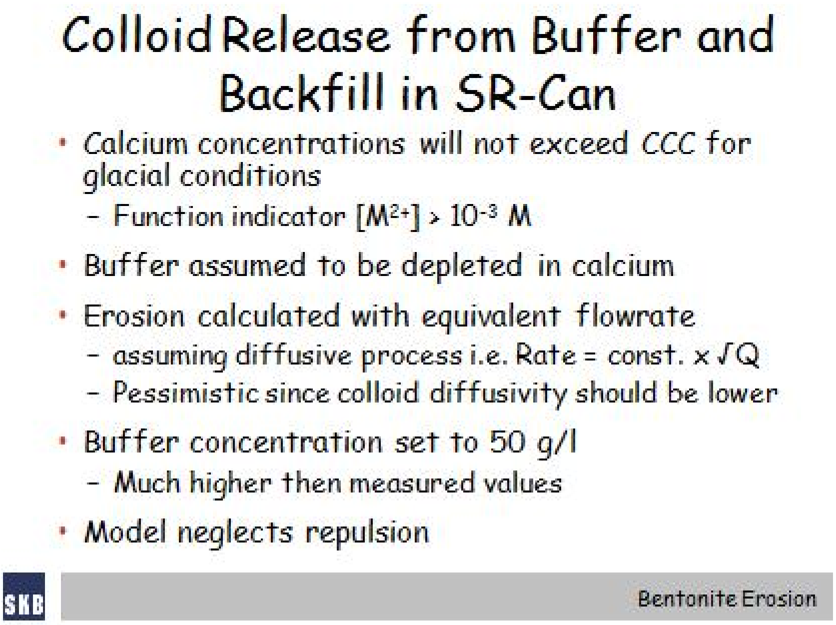
SKB Bentonite Erosion



Background

- The main contribution to the calculated risk in the SR-Can assessment was a scenario where:
  - Buffer erosion occurs to the extent that advective condtions are created in the deposition hole
  - This enchanced the corrosion of the canister such that as small fraction failed during the one million year assessment period
- A number of uncertain factors influenced buffer erosion (and canister corrosion)
- Lack of knowledge and natural variability

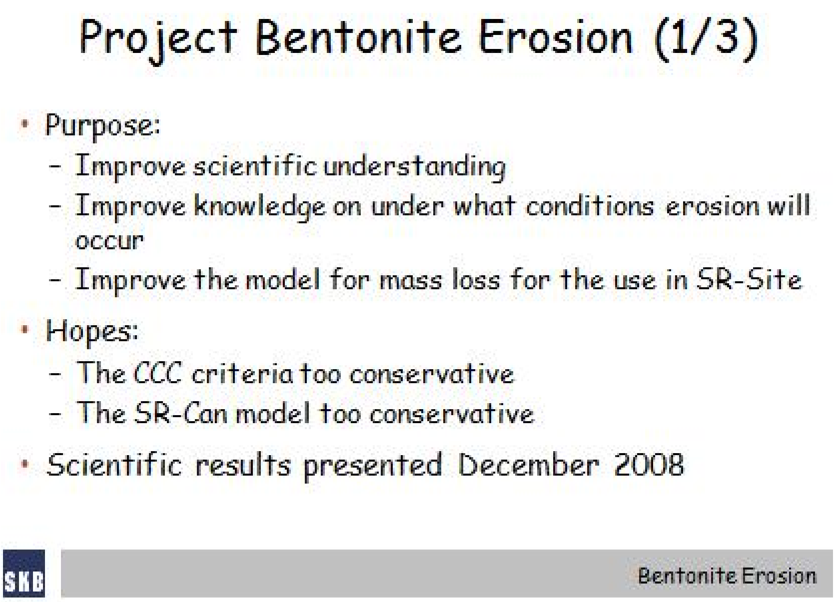
SKB Bentonite Erosion



Colloid Release from Buffer and Backfill in SR-Can

- *Calcium concentrations will not exceed CCC for glacial conditions*
  - Function indicator $[M^{2+}] > 10^{-3}$ M
- Buffer assumed to be depleted in calcium
- Erosion calculated with equivalent flowrate
  - assuming diffusive process i.e. Rate = const. x $\sqrt{Q}$
  - Pessimistic since colloid diffusivity should be lower
- Buffer concentration set to 50 g/l
  - Much higher then measured values
- Model neglects repulsion

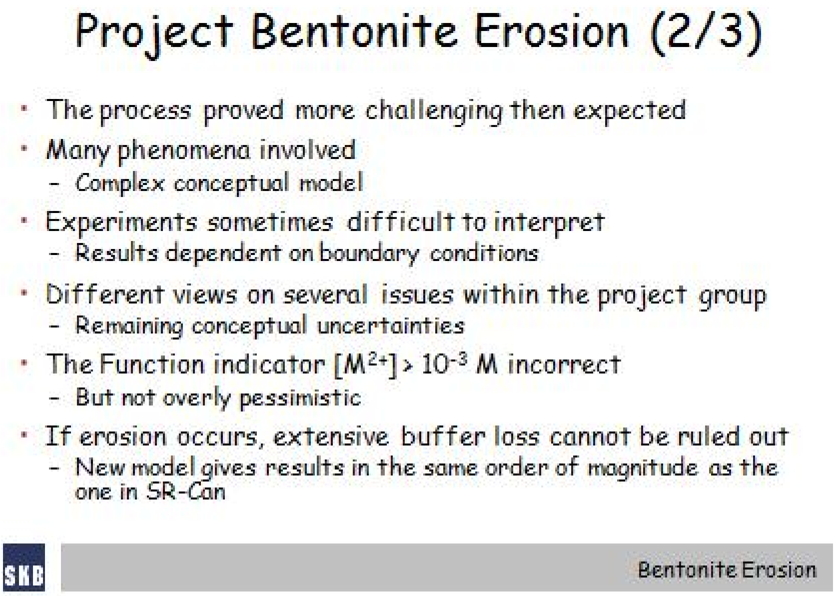
Bentonite Erosion



Project Bentonite Erosion (1/3)

- Purpose:
  - Improve scientific understanding
  - Improve knowledge on under what conditions erosion will occur
  - Improve the model for mass loss for the use in SR-Site
- Hopes:
  - The *CCC* criteria too conservative
  - The SR-Can model too conservative
- Scientific results presented December 2008

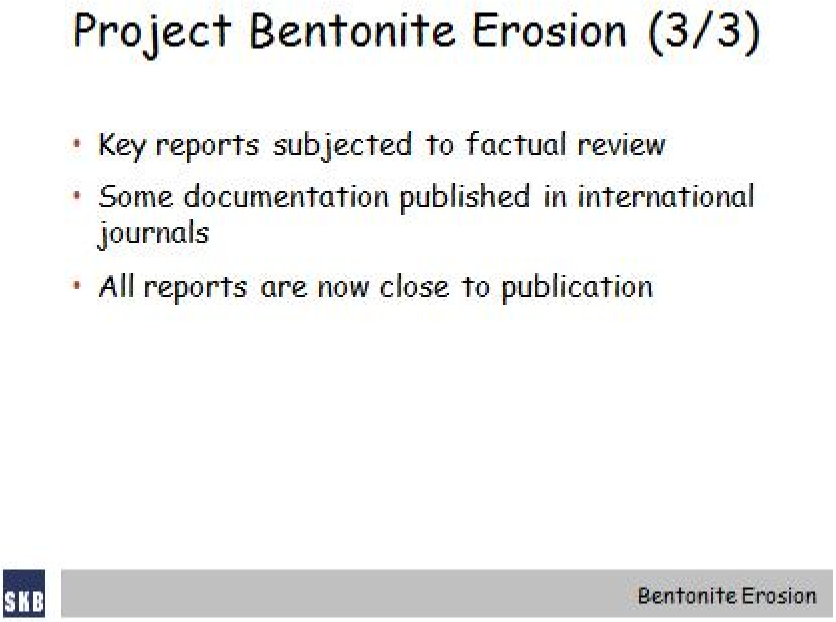
Bentonite Erosion



Project Bentonite Erosion (2/3)

- The process proved more challenging then expected
- Many phenomena involved
  - Complex conceptual model
- Experiments sometimes difficult to interpret
  - Results dependent on boundary conditions
- Different views on several issues within the project group
  - Remaining conceptual uncertainties
- The Function indicator $[M^{2+}] > 10^{-3}$ M incorrect
  - But not overly pessimistic
- If erosion occurs, extensive buffer loss cannot be ruled out
  - New model gives results in the same order of magnitude as the one in SR-Can

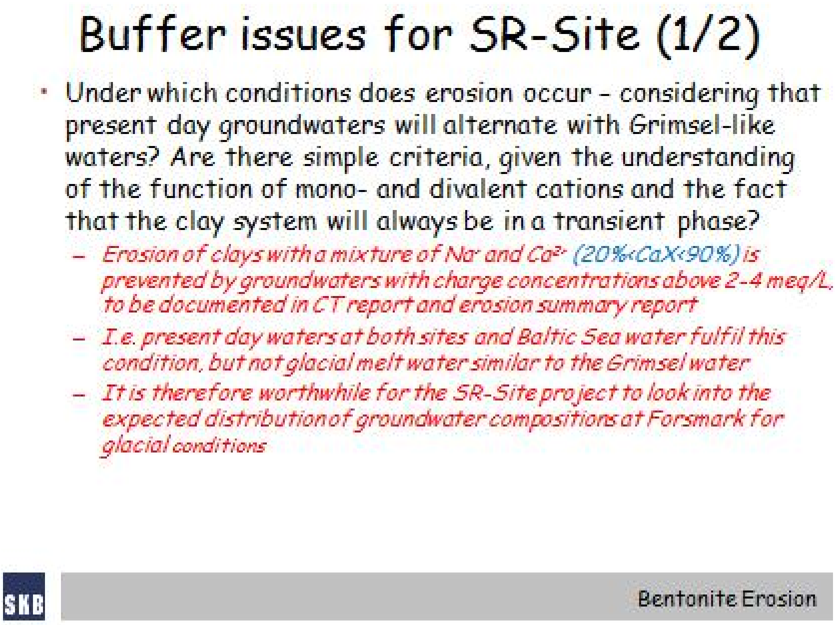
Bentonite Erosion



Project Bentonite Erosion (3/3)

- Key reports subjected to factual review
- Some documentation published in international journals
- All reports are now close to publication

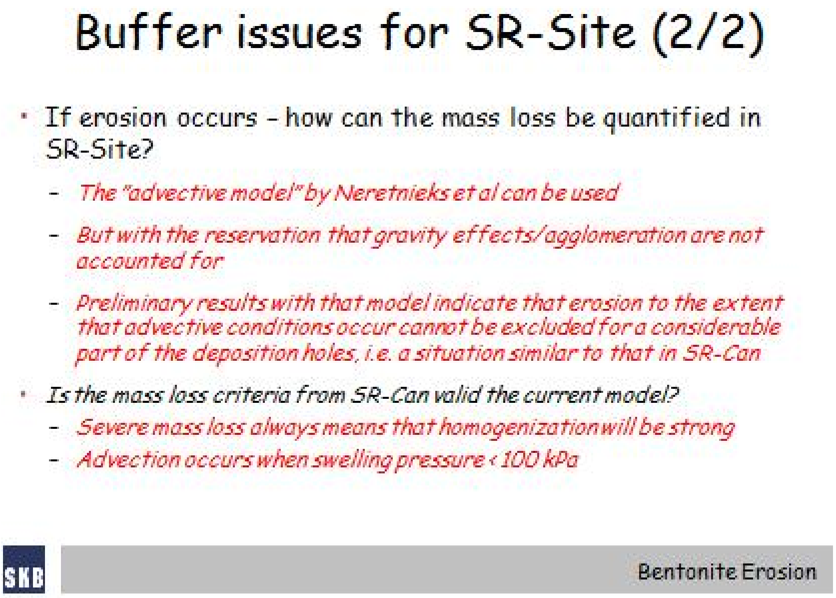
Bentonite Erosion



Buffer issues for SR-Site (1/2)

- Under which conditions does erosion occur – considering that present day groundwaters will alternate with Grimsel-like waters? Are there simple criteria, given the understanding of the function of mono- and divalent cations and the fact that the clay system will always be in a transient phase?
  - *Erosion of clays with a mixture of* Na^+ *and* Ca^{2+} *(20%<CaX<90%) is prevented by groundwaters with charge concentrations above 2-4 meq/L, to be documented in CT report and erosion summary report*
  - *I.e. present day waters at both sites and Baltic Sea water fulfil this condition, but not glacial melt water similar to the Grimsel water*
  - *It is therefore worthwhile for the SR-Site project to look into the expected distribution of groundwater compositions at Forsmark for glacial conditions*

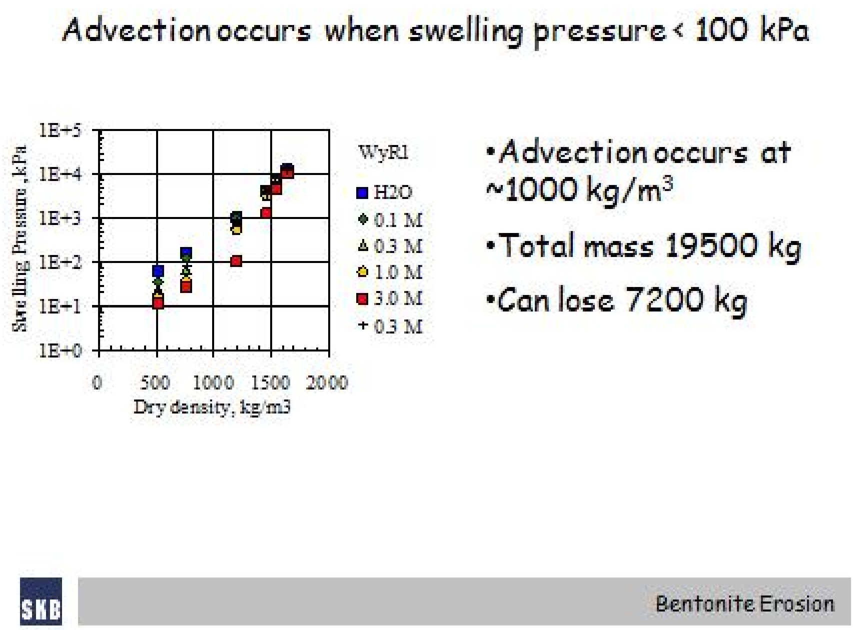
Bentonite Erosion



Buffer issues for SR-Site (2/2)

- If erosion occurs – how can the mass loss be quantified in SR-Site?
  - *The "advective model" by Neretnieks et al can be used*
  - *But with the reservation that gravity effects/agglomeration are not accounted for*
  - *Preliminary results with that model indicate that erosion to the extent that advective conditions occur cannot be excluded for a considerable part of the deposition holes, i.e. a situation similar to that in SR-Can*
- *Is the mass loss criteria from SR-Can valid the current model?*
  - *Severe mass loss always means that homogenization will be strong*
  - *Advection occurs when swelling pressure < 100 kPa*

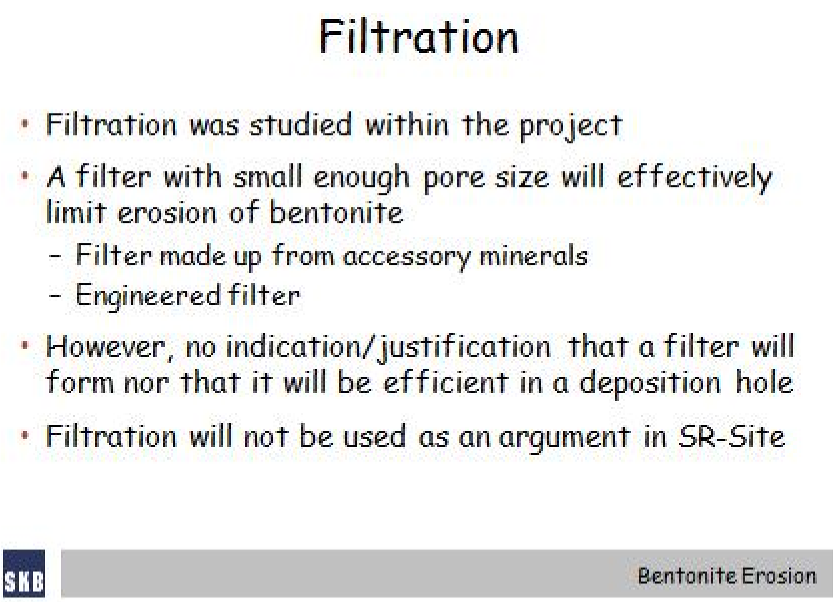
Bentonite Erosion



Advection occurs when swelling pressure < 100 kPa

- Advection occurs at ~1000 kg/m^3
- Total mass 19500 kg
- Can lose 7200 kg

Bentonite Erosion

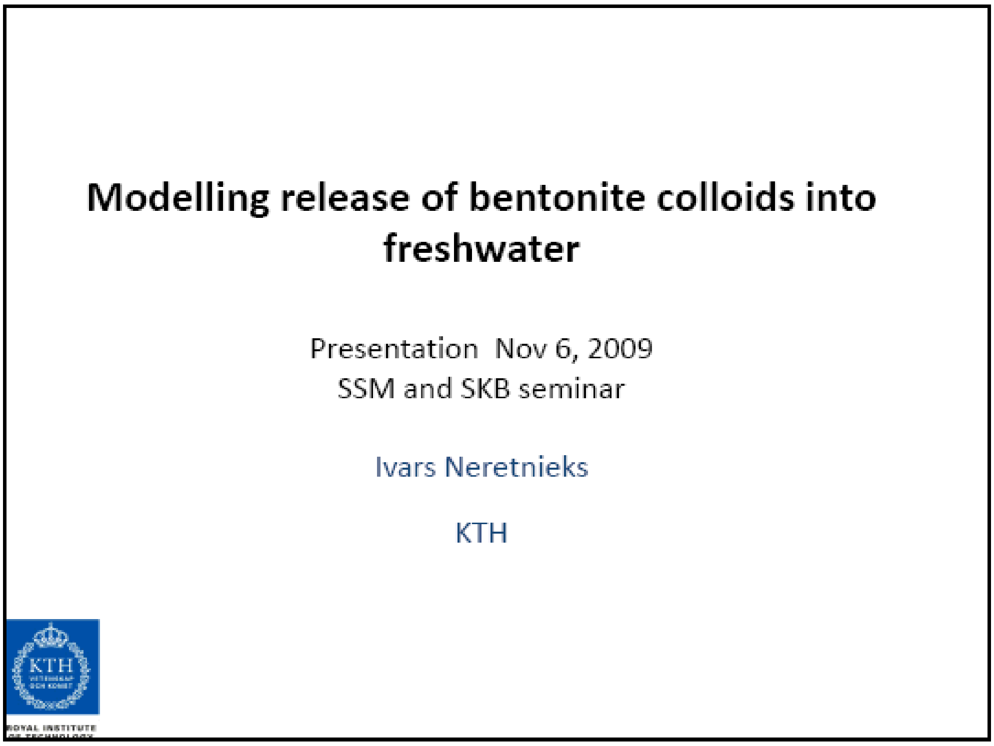


Filtration

- Filtration was studied within the project
- A filter with small enough pore size will effectively limit erosion of bentonite
  - Filter made up from accessory minerals
  - Engineered filter
- However, no indication/justification that a filter will form nor that it will be efficient in a deposition hole
- Filtration will not be used as an argument in SR-Site

Bentonite Erosion

Appendix 2

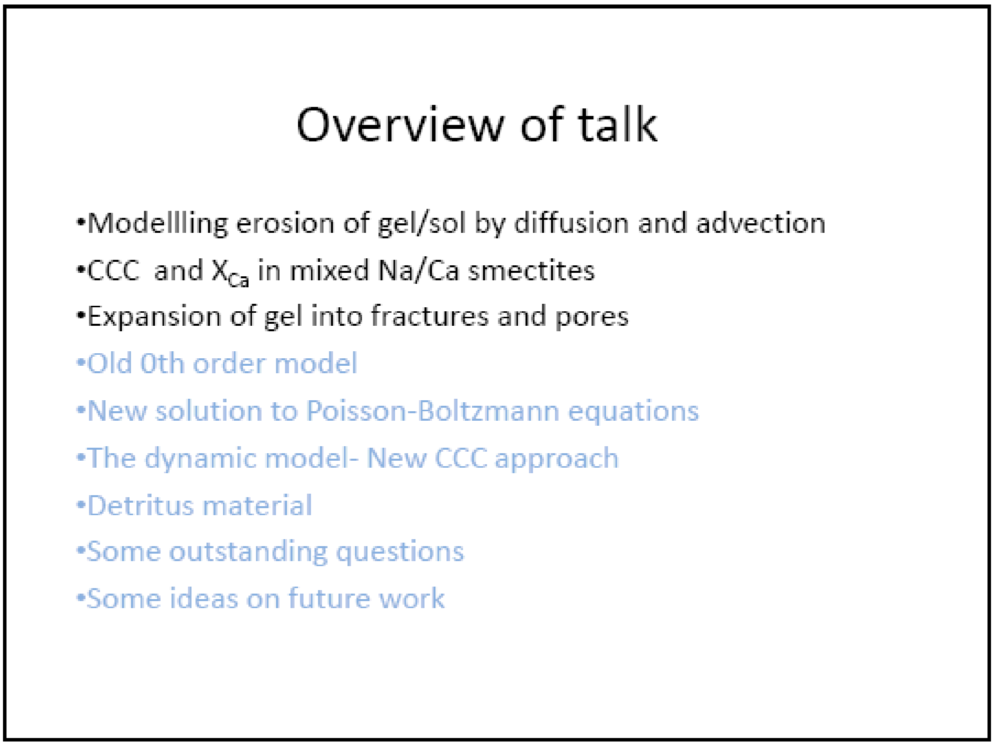


Modelling release of bentonite colloids into freshwater

Presentation Nov 6, 2009
SSM and SKB seminar

Ivars Neretnieks

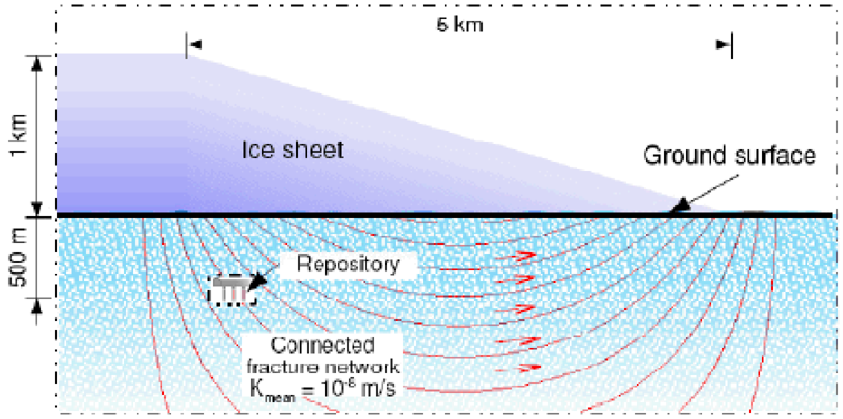
KTH



Overview of talk

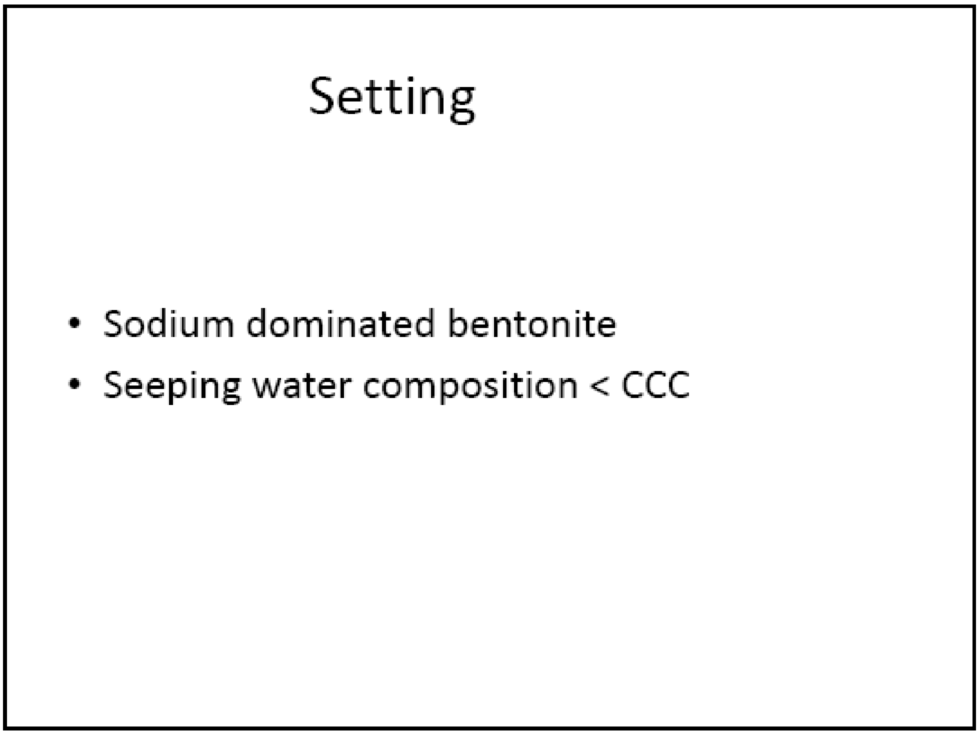
- Modellling erosion of gel/sol by diffusion and advection
- CCC and X_{Ca} in mixed Na/Ca smectites
- Expansion of gel into fractures and pores
- Old 0th order model
- New solution to Poisson-Boltzmann equations
- The dynamic model- New CCC approach
- Detritus material
- Some outstanding questions
- Some ideas on future work

High flowrates of meltwater



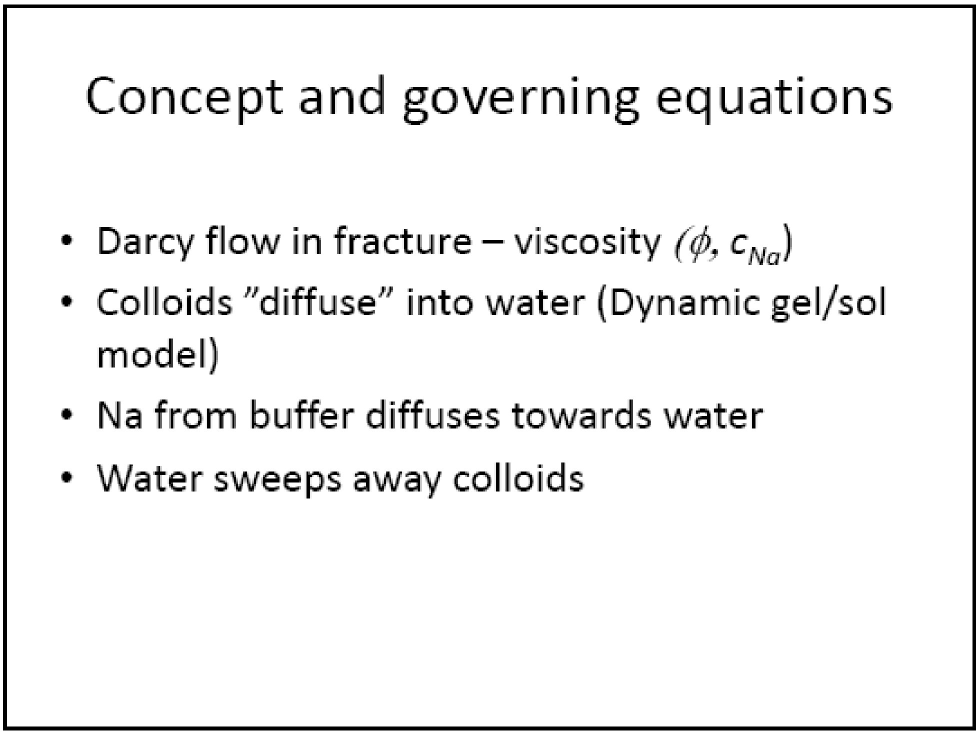
Our present erosion model

- No detritus material present
- Gel expands by water uptake out into fractures
- As the ϕ decreases with distance, gel viscosity decreases and gel can flow downstream while continuing to expand



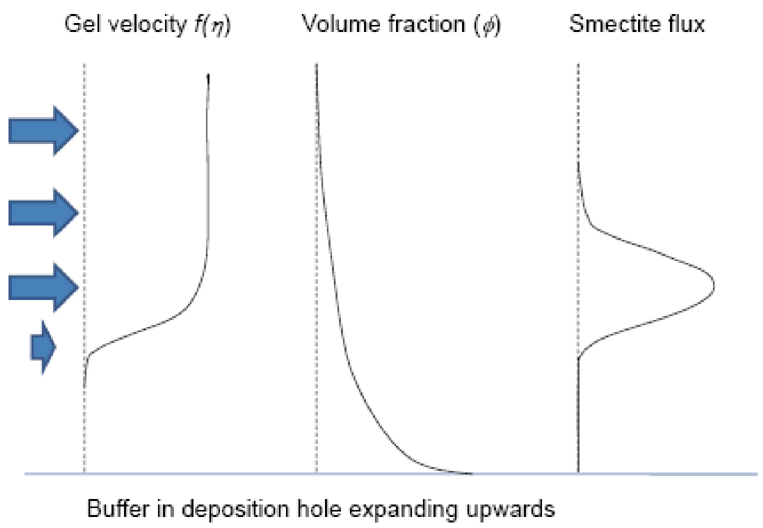
Setting

- Sodium dominated bentonite
- Seeping water composition < CCC



Concept and governing equations

- Darcy flow in fracture – viscosity (ϕ, c_{Na})
- Colloids ”diffuse” into water (Dynamic gel/sol model)
- Na from buffer diffuses towards water
- Water sweeps away colloids



Gel/sol viscosity

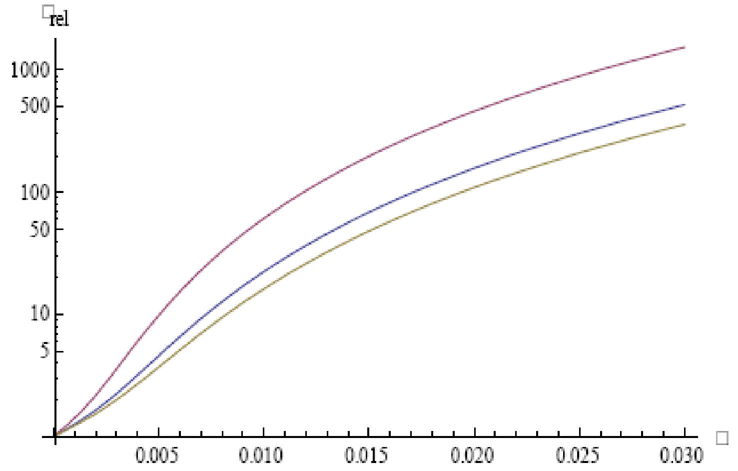
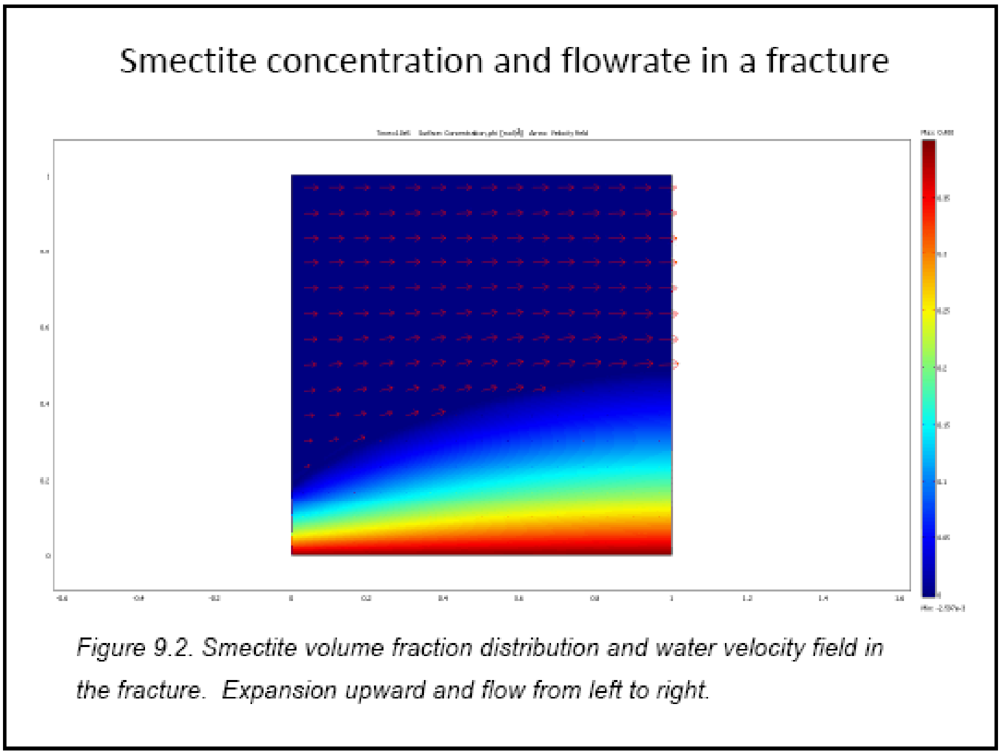
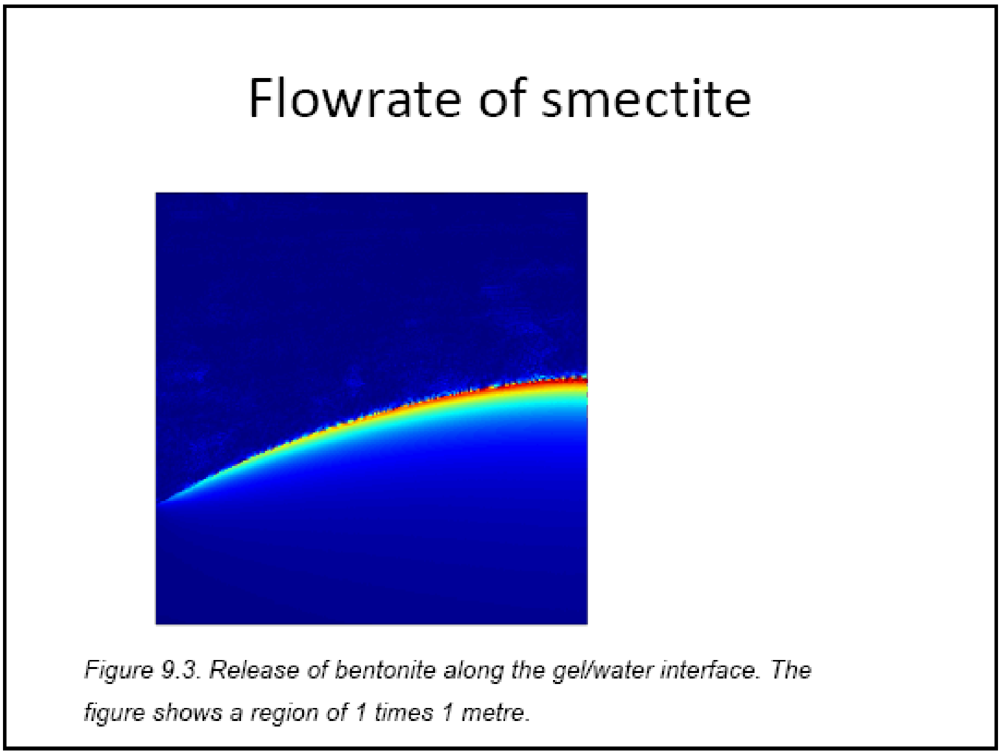


Figure 9.1. Relative viscosity for the base case as a function of bentonite volume fraction. Curves from bottom and up for 10, 1 and 0.1 mM monovalent ion.



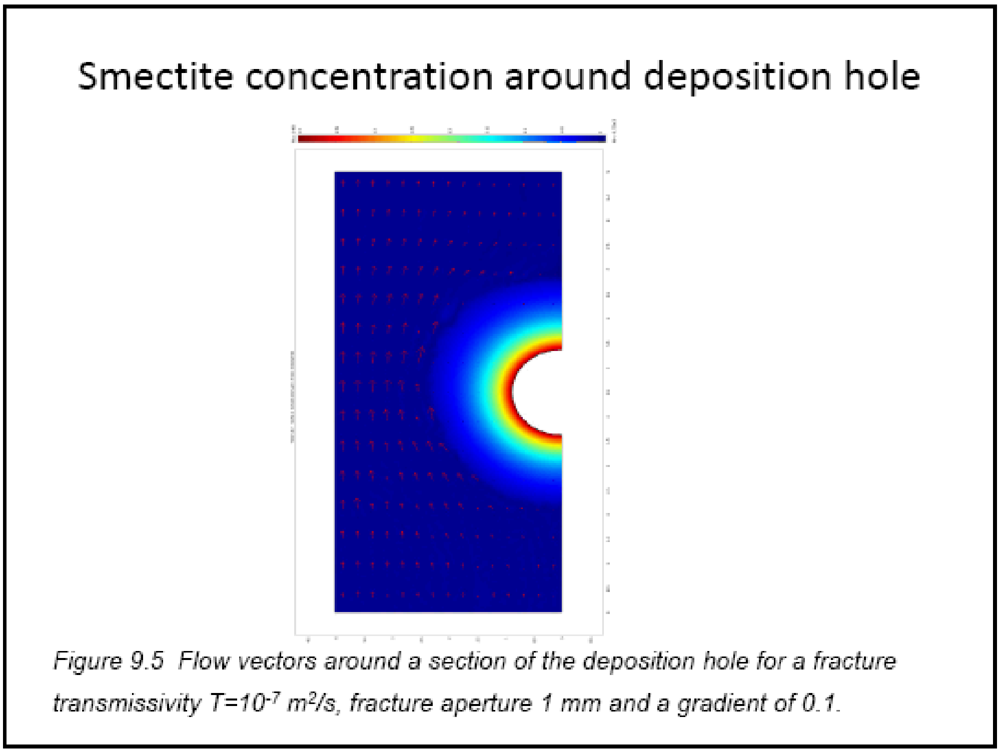
Smectite concentration and flowrate in a fracture

Figure 9.2. Smectite volume fraction distribution and water velocity field in the fracture. Expansion upward and flow from left to right.



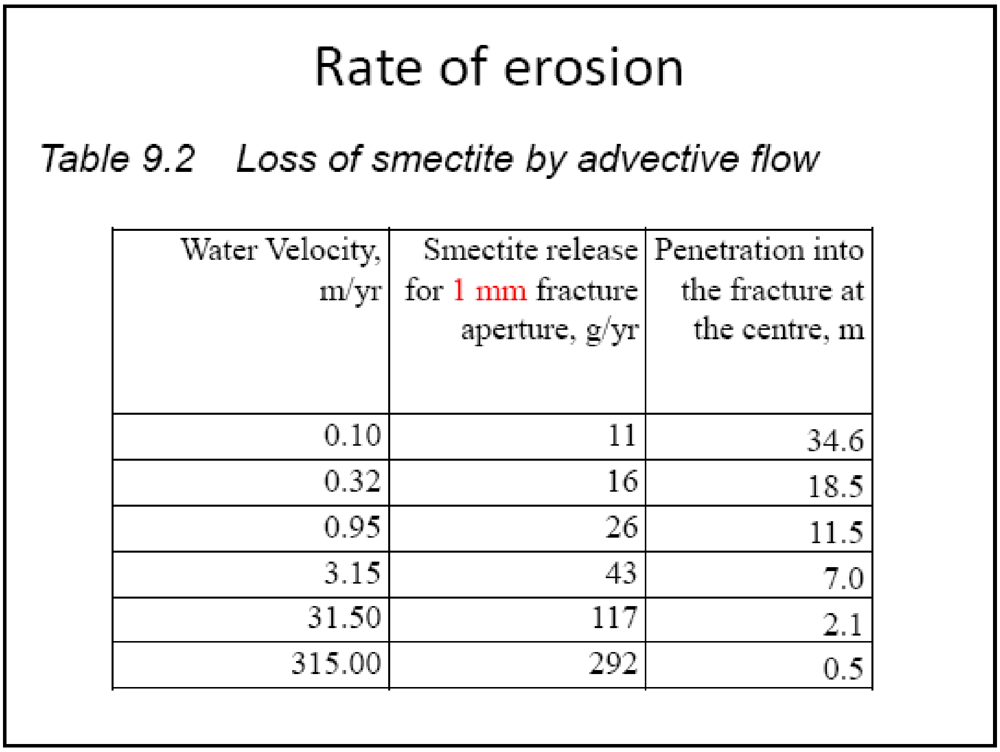
Flowrate of smectite

Figure 9.3. Release of bentonite along the gel/water interface. The figure shows a region of 1 times 1 metre.



Smectite concentration around deposition hole

Figure 9.5 Flow vectors around a section of the deposition hole for a fracture transmissivity T=10^{-7} m^2/s, fracture aperture 1 mm and a gradient of 0.1.



Rate of erosion

Table 9.2 Loss of smectite by advective flow

Water Velocity, m/yr	Smectite release for 1 mm fracture aperture, g/yr	Penetration into the fracture at the centre, m
0.10	11	34.6
0.32	16	18.5
0.95	26	11.5
3.15	43	7.0
31.50	117	2.1
315.00	292	0.5

Smectite loss in fracture by advection and ”diffusion”

$$N_{Smectite} = Const \cdot \delta \cdot u^{0.41}$$

Velocity u and aperture δ are obtained from fracture network hydraulic calculations

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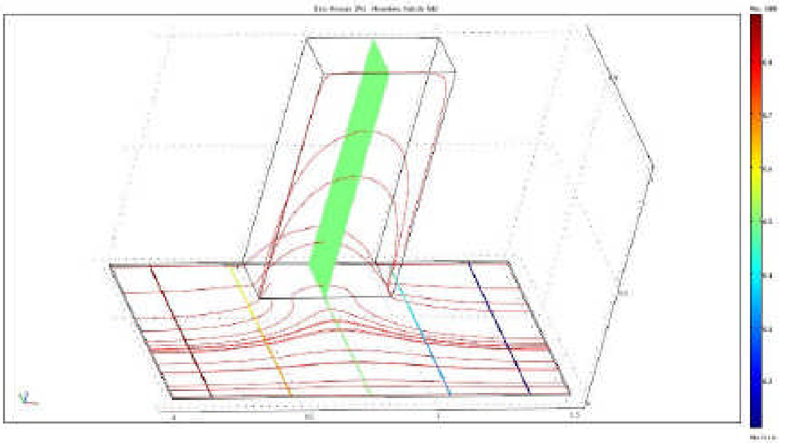
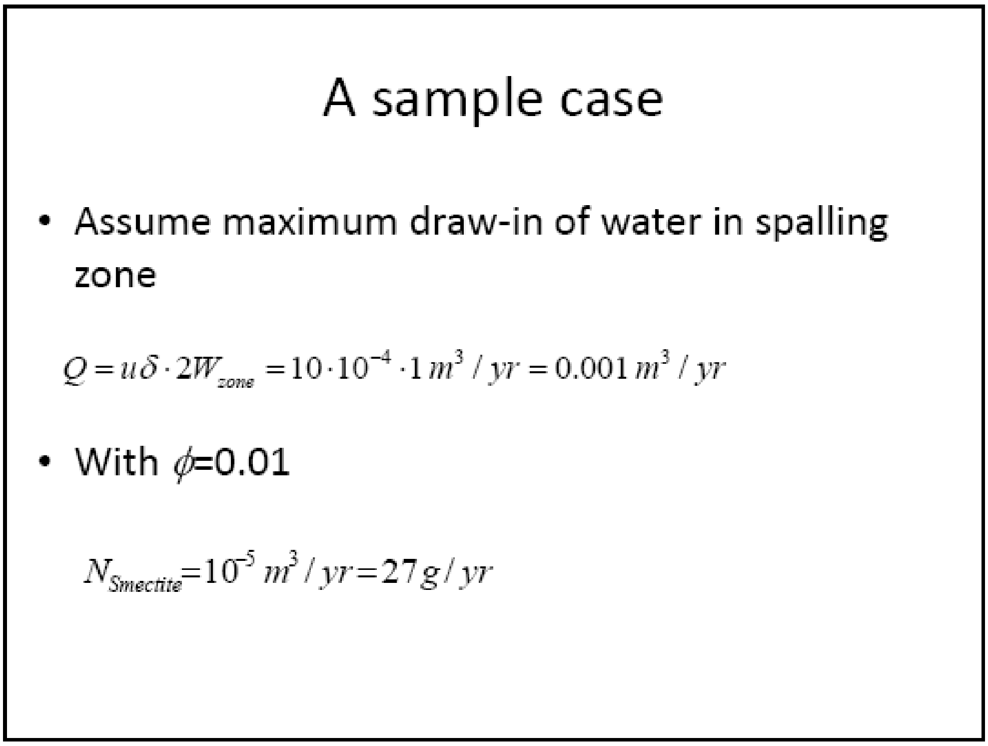
Spalling





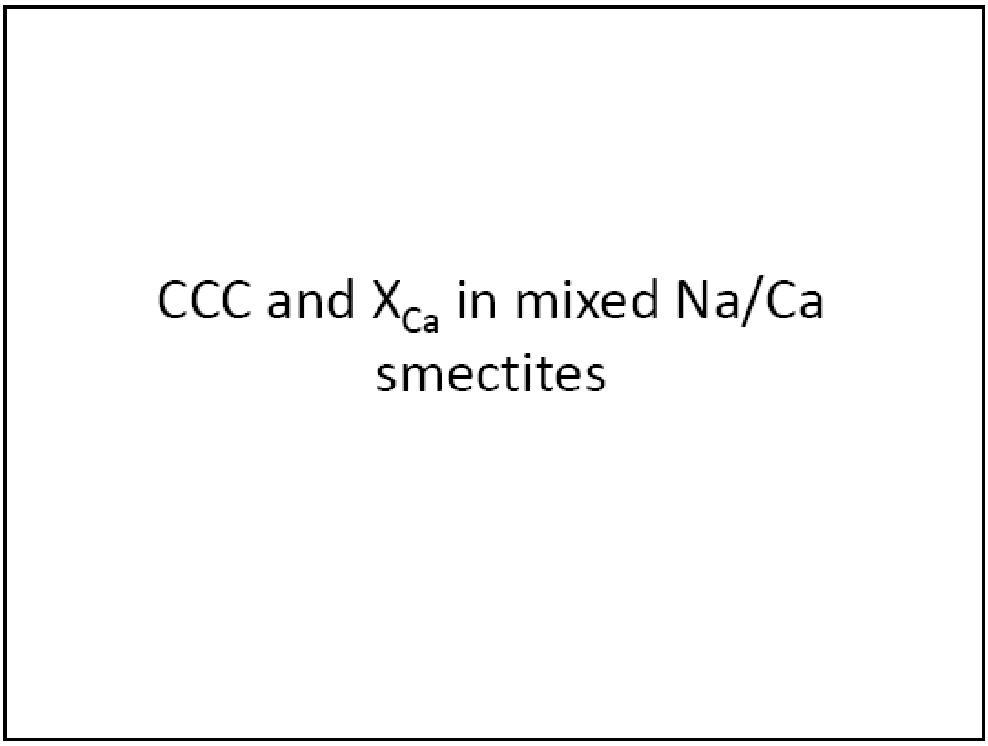
A sample case

- Assume maximum draw-in of water in spalling zone

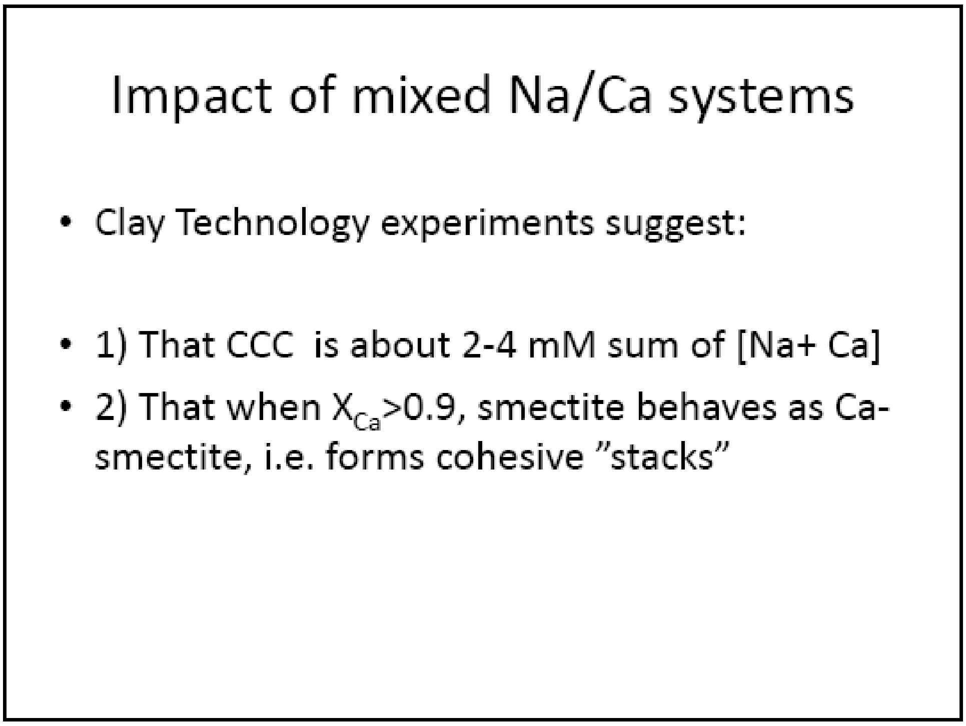
$$Q = u\delta \cdot 2W_{zone} = 10 \cdot 10^{-4} \cdot 1\, m^3 / yr = 0.001\, m^3 / yr$$

- With ϕ=0.01

$$N_{Smectite} = 10^{-5}\, m^3 / yr = 27\, g / yr$$



CCC and X_{Ca} in mixed Na/Ca smectites



Impact of mixed Na/Ca systems

- Clay Technology experiments suggest:

- 1) That CCC is about 2-4 mM sum of [Na+ Ca]
- 2) That when X_{Ca}>0.9, smectite behaves as Ca-smectite, i.e. forms cohesive ”stacks”

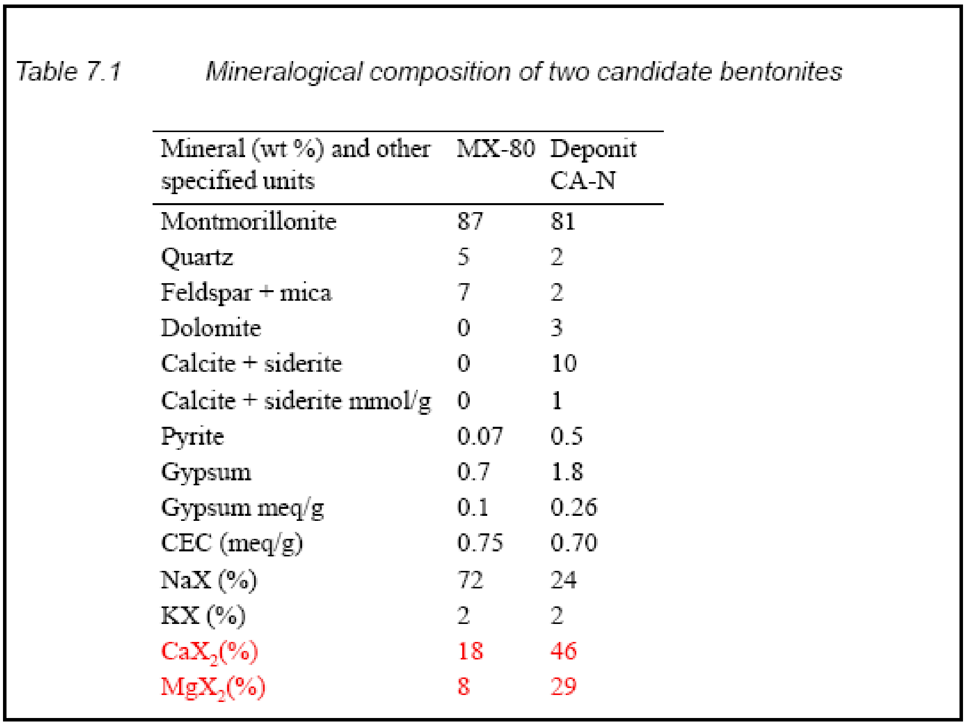
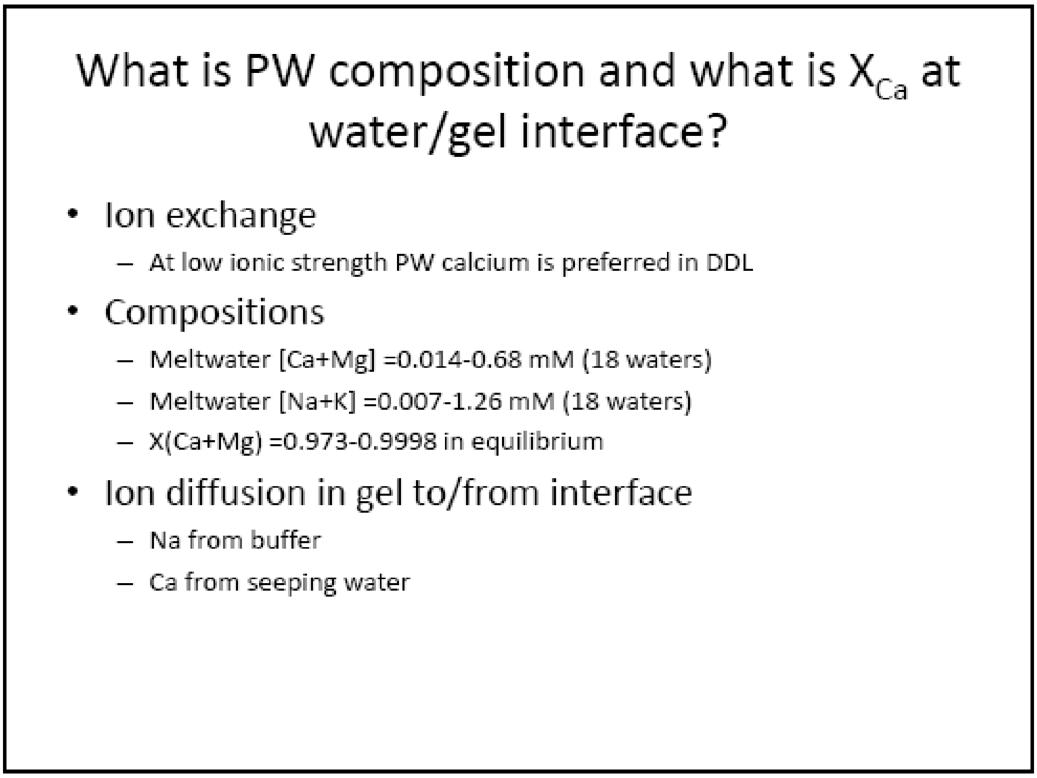


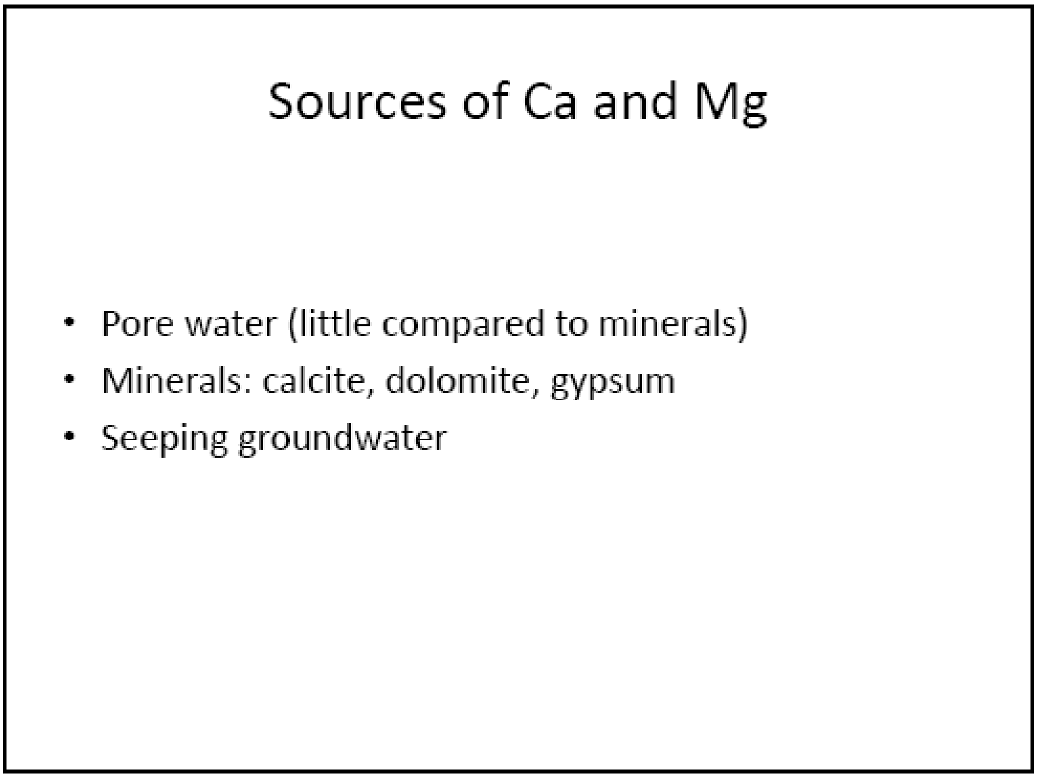
Table 7.1 *Mineralogical composition of two candidate bentonites*

Mineral (wt %) and other specified units	MX-80	Deponit CA-N
Montmorillonite	87	81
Quartz	5	2
Feldspar + mica	7	2
Dolomite	0	3
Calcite + siderite	0	10
Calcite + siderite mmol/g	0	1
Pyrite	0.07	0.5
Gypsum	0.7	1.8
Gypsum meq/g	0.1	0.26
CEC (meq/g)	0.75	0.70
NaX (%)	72	24
KX (%)	2	2
CaX_2(%)	18	46
MgX_2(%)	8	29



What is PW composition and what is X_{Ca} at water/gel interface?

- Ion exchange
  - At low ionic strength PW calcium is preferred in DDL
- Compositions
  - Meltwater [Ca+Mg] =0.014-0.68 mM (18 waters)
  - Meltwater [Na+K] =0.007-1.26 mM (18 waters)
  - X(Ca+Mg) =0.973-0.9998 in equilibrium
- Ion diffusion in gel to/from interface
  - Na from buffer
  - Ca from seeping water



Sources of Ca and Mg

- Pore water (little compared to minerals)
- Minerals: calcite, dolomite, gypsum
- Seeping groundwater

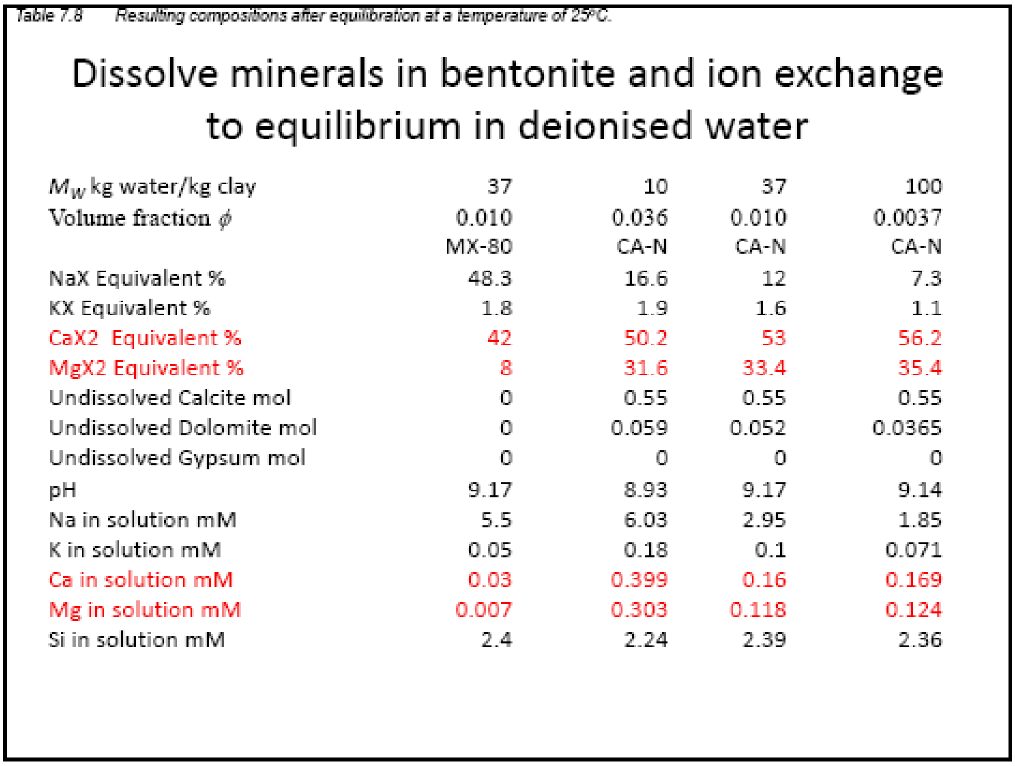
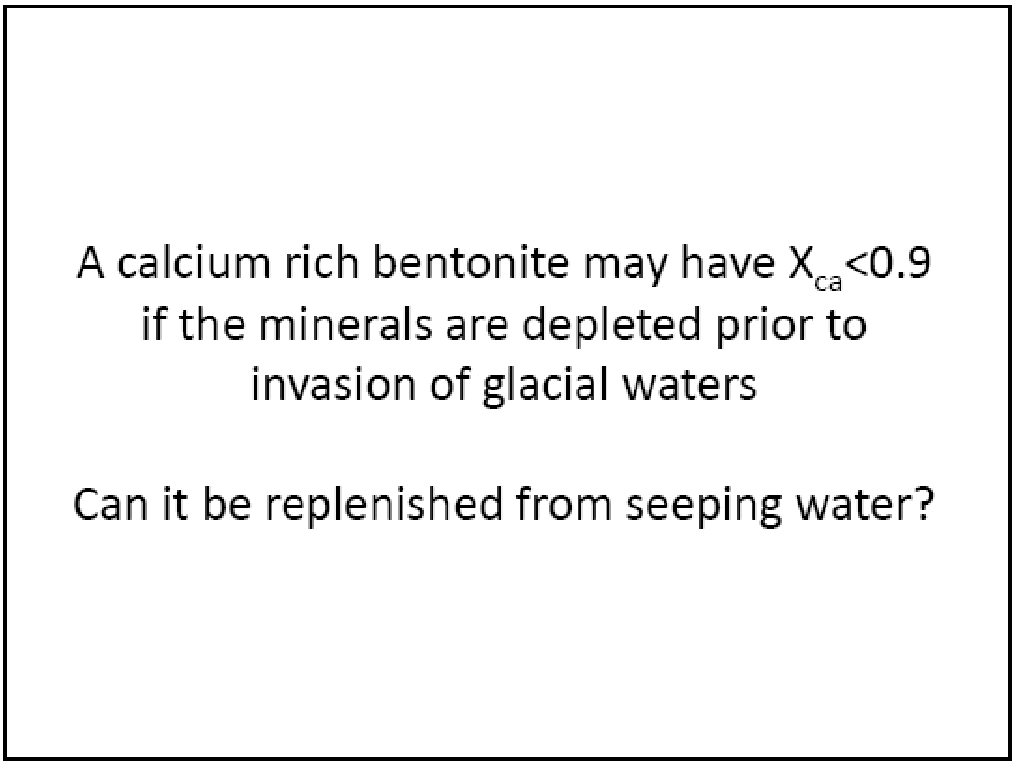


Table 7.8 Resulting compositions after equilibration at a temperature of 25°C.

Dissolve minerals in bentonite and ion exchange to equilibrium in deionised water

M_W kg water/kg clay	37	10	37	100
Volume fraction ϕ	0.010	0.036	0.010	0.0037
	MX-80	CA-N	CA-N	CA-N
NaX Equivalent %	48.3	16.6	12	7.3
KX Equivalent %	1.8	1.9	1.6	1.1
CaX2 Equivalent %	42	50.2	53	56.2
MgX2 Equivalent %	8	31.6	33.4	35.4
Undissolved Calcite mol	0	0.55	0.55	0.55
Undissolved Dolomite mol	0	0.059	0.052	0.0365
Undissolved Gypsum mol	0	0	0	0
pH	9.17	8.93	9.17	9.14
Na in solution mM	5.5	6.03	2.95	1.85
K in solution mM	0.05	0.18	0.1	0.071
Ca in solution mM	0.03	0.399	0.16	0.169
Mg in solution mM	0.007	0.303	0.118	0.124
Si in solution mM	2.4	2.24	2.39	2.36



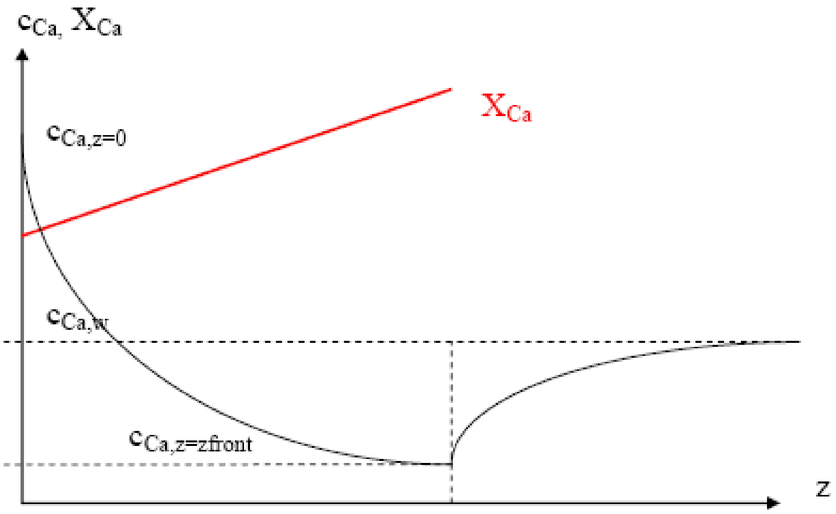
A calcium rich bentonite may have X_{ca}<0.9 if the minerals are depleted prior to invasion of glacial waters

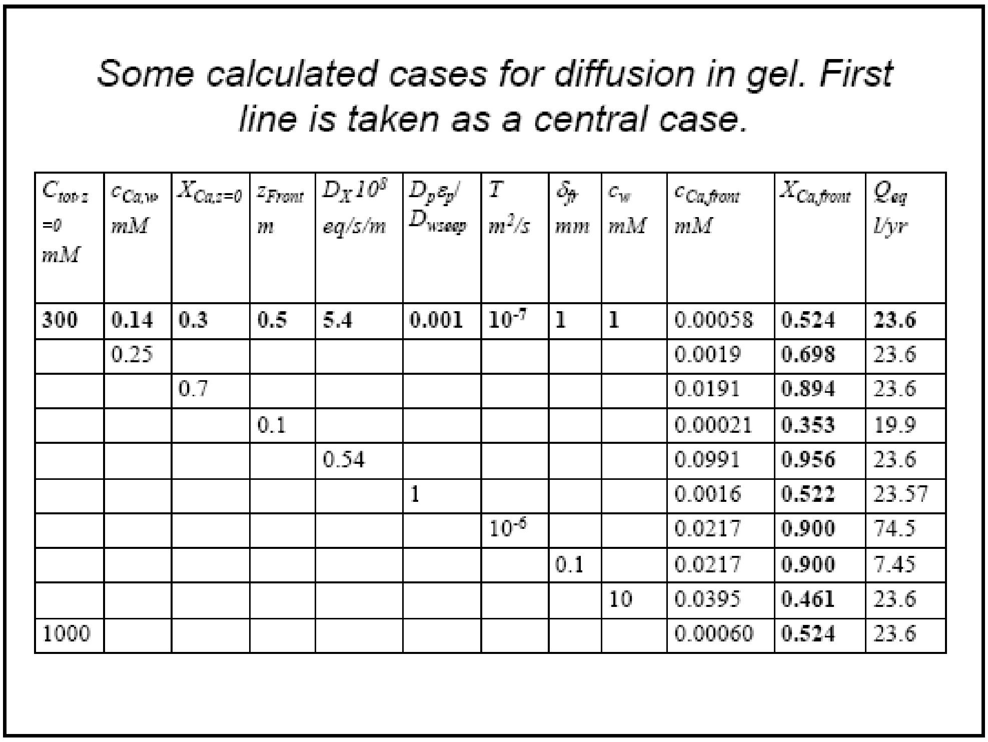
Can it be replenished from seeping water?

What if minerals are lost and the starting point is X_{Ca}=0.5
How much water with Ca+Mg is needed to raise to X_{Ca}=0.9 in 1 g of bentonite?

	Water volume l/g	Volume fraction ϕ
Grimsel water	1.45	0.00026
Laxemar	0.31	0.0012
Other waters	0.29 to14.2	0.0012 to 0.000026

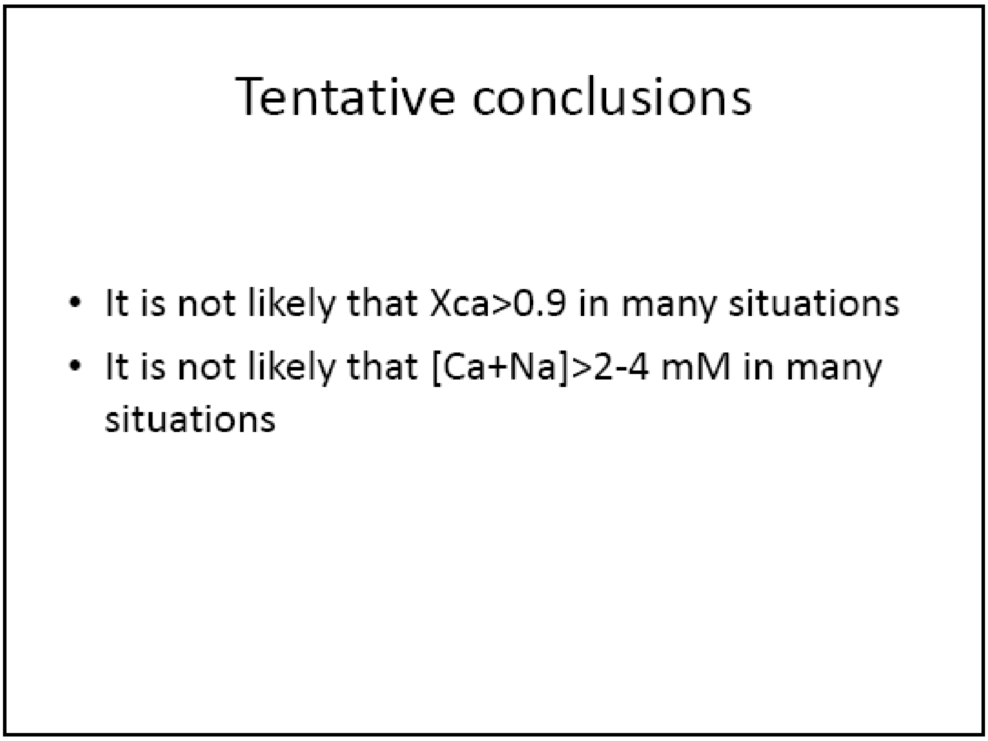
Supply of Ca from water and buffer by diffusion





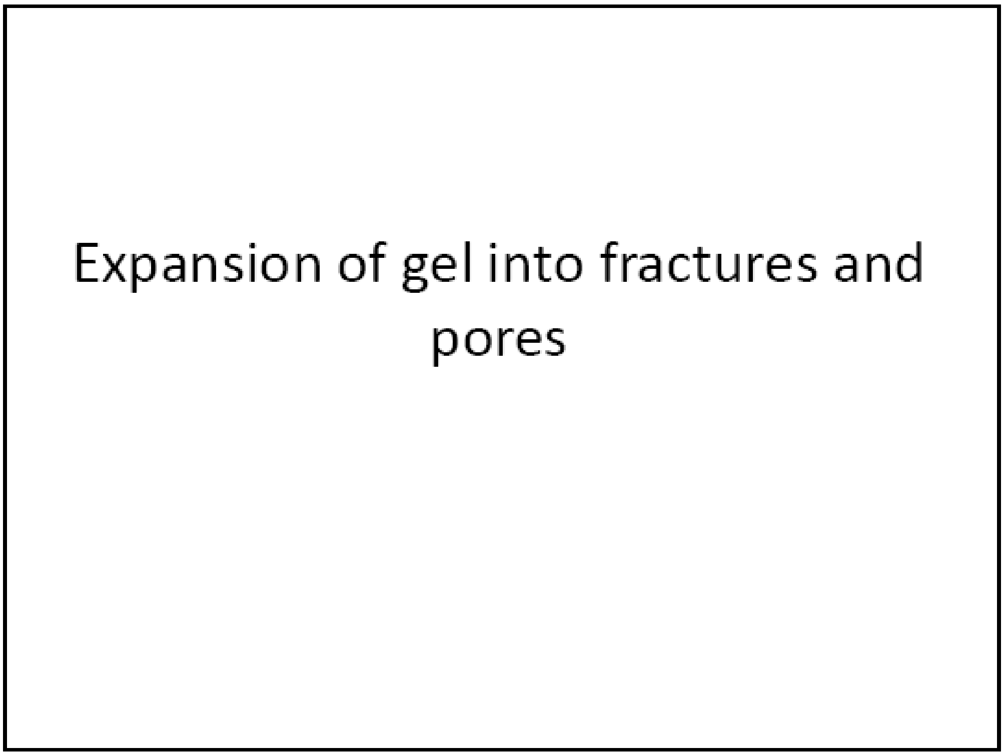
Some calculated cases for diffusion in gel. First line is taken as a central case.

$C_{tot,z=0}$ mM	$c_{Ca,w}$ mM	$X_{Ca,z=0}$	z_{Front} m	$D_X 10^8$ eq/s/m	$D_p \varepsilon_p / D_{wseep}$	T m^2/s	δ_{fr} mm	c_w mM	$c_{Ca,front}$ mM	$X_{Ca,front}$	Q_{eq} l/yr
300	**0.14**	**0.3**	**0.5**	**5.4**	**0.001**	**10^{-7}**	**1**	**1**	0.00058	**0.524**	**23.6**
	0.25								0.0019	**0.698**	23.6
		0.7							0.0191	**0.894**	23.6
			0.1						0.00021	**0.353**	19.9
				0.54					0.0991	**0.956**	23.6
					1				0.0016	**0.522**	23.57
						10^{-6}			0.0217	**0.900**	74.5
							0.1		0.0217	**0.900**	7.45
								10	0.0395	**0.461**	23.6
1000									0.00060	**0.524**	23.6

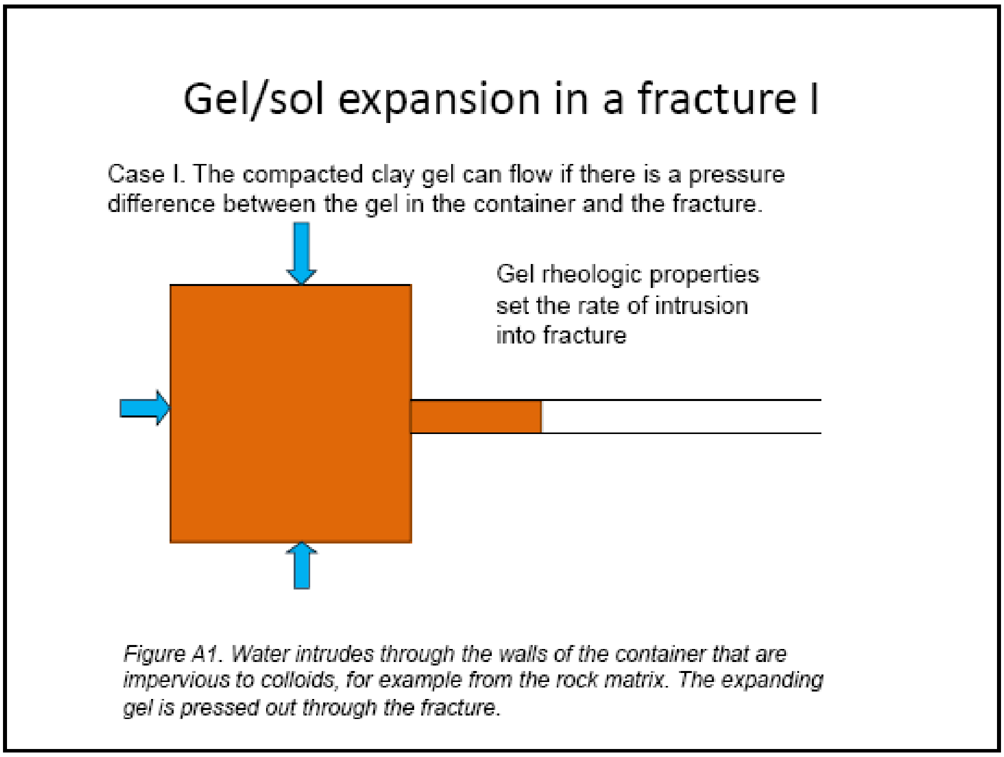


Tentative conclusions

- It is not likely that Xca>0.9 in many situations
- It is not likely that [Ca+Na]>2-4 mM in many situations



Expansion of gel into fractures and pores

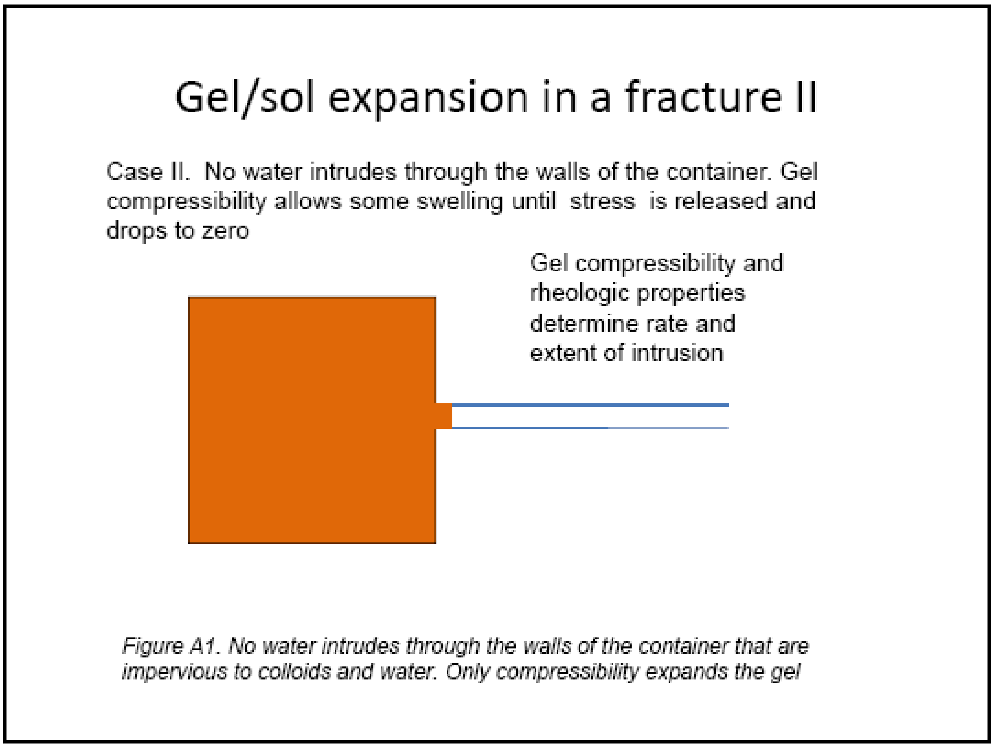


Gel/sol expansion in a fracture I

Case I. The compacted clay gel can flow if there is a pressure difference between the gel in the container and the fracture.

Gel rheologic properties set the rate of intrusion into fracture

Figure A1. Water intrudes through the walls of the container that are impervious to colloids, for example from the rock matrix. The expanding gel is pressed out through the fracture.

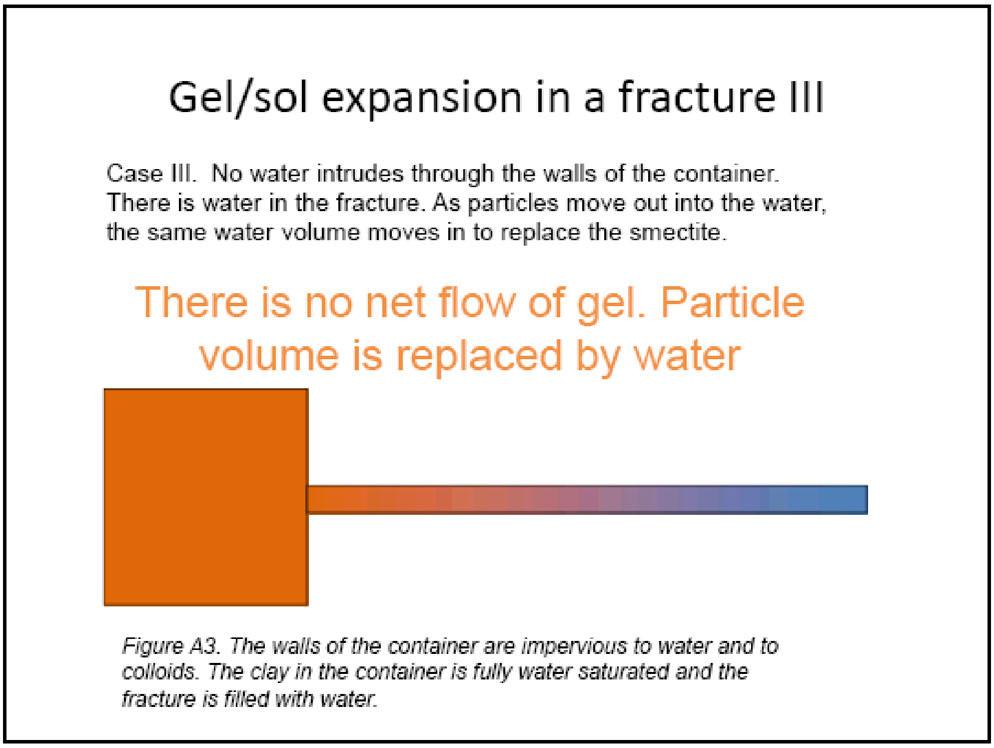


Gel/sol expansion in a fracture II

Case II. No water intrudes through the walls of the container. Gel compressibility allows some swelling until stress is released and drops to zero

Gel compressibility and rheologic properties determine rate and extent of intrusion

Figure A1. No water intrudes through the walls of the container that are impervious to colloids and water. Only compressibility expands the gel



Gel/sol expansion in a fracture III

Case III. No water intrudes through the walls of the container. There is water in the fracture. As particles move out into the water, the same water volume moves in to replace the smectite.

There is no net flow of gel. Particle volume is replaced by water

Figure A3. The walls of the container are impervious to water and to colloids. The clay in the container is fully water saturated and the fracture is filled with water.

Penetration through narrow pores in filters
ClayTechnology experiments

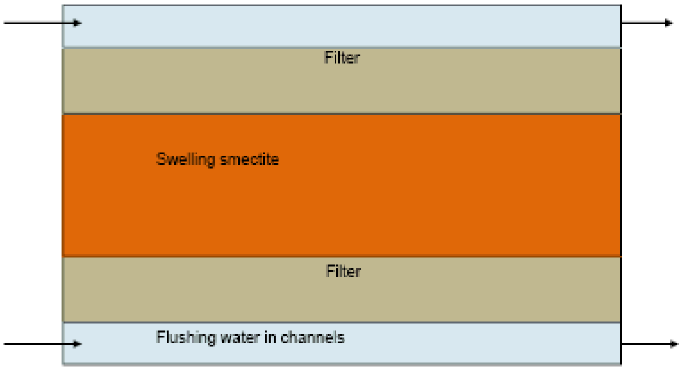


Figure 8.8. Compacted smectite is confined between filters that on their outsides are flushed by water. Swelling pressure is monitored over time. The water in the channels only contacts about 27 % of the filter surface.

Swelling of Na smectite through filters

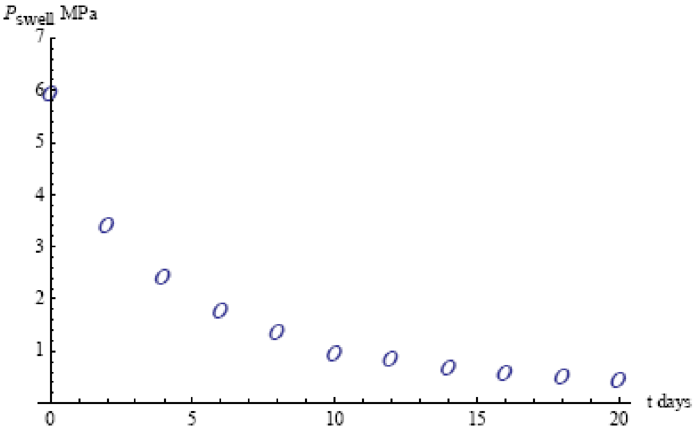


*Figure 8.9. Swelling pressure drop for purified WyNa smectite with 2 micrometer filters marked with * and 10 micrometer filters marked with o.*

10 micrometer filters

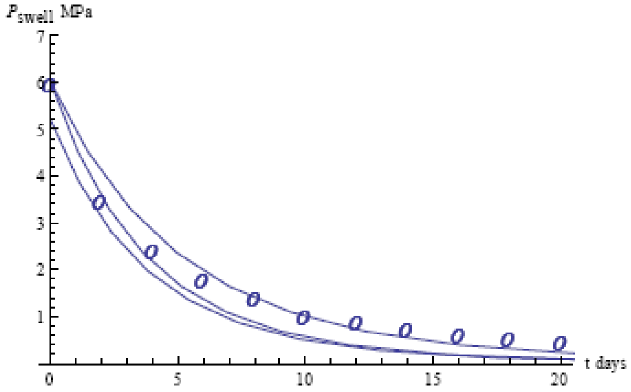


Figure 8.10. Swelling pressure for purified WyNa smectite with 10 micrometer filters. Lower curve with equipment factor=3.7 and no adjustment of starting volume fraction. Middle curve with equipment factor=3.7 and 5 % increase in starting volume fraction. Upper curve with equipment factor=5 and 5 % increase in starting volume fraction.

2 micrometer filters.

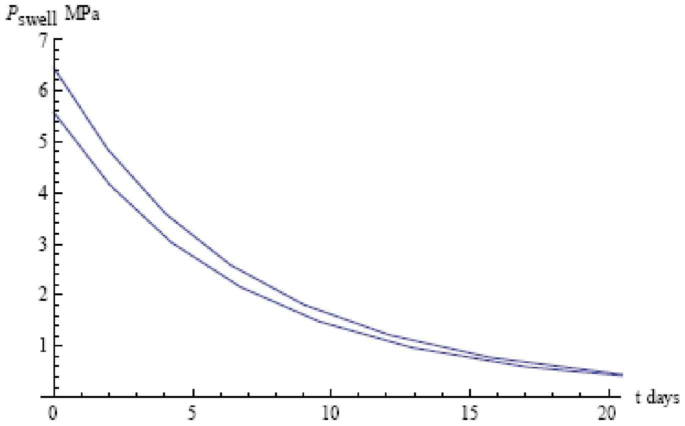
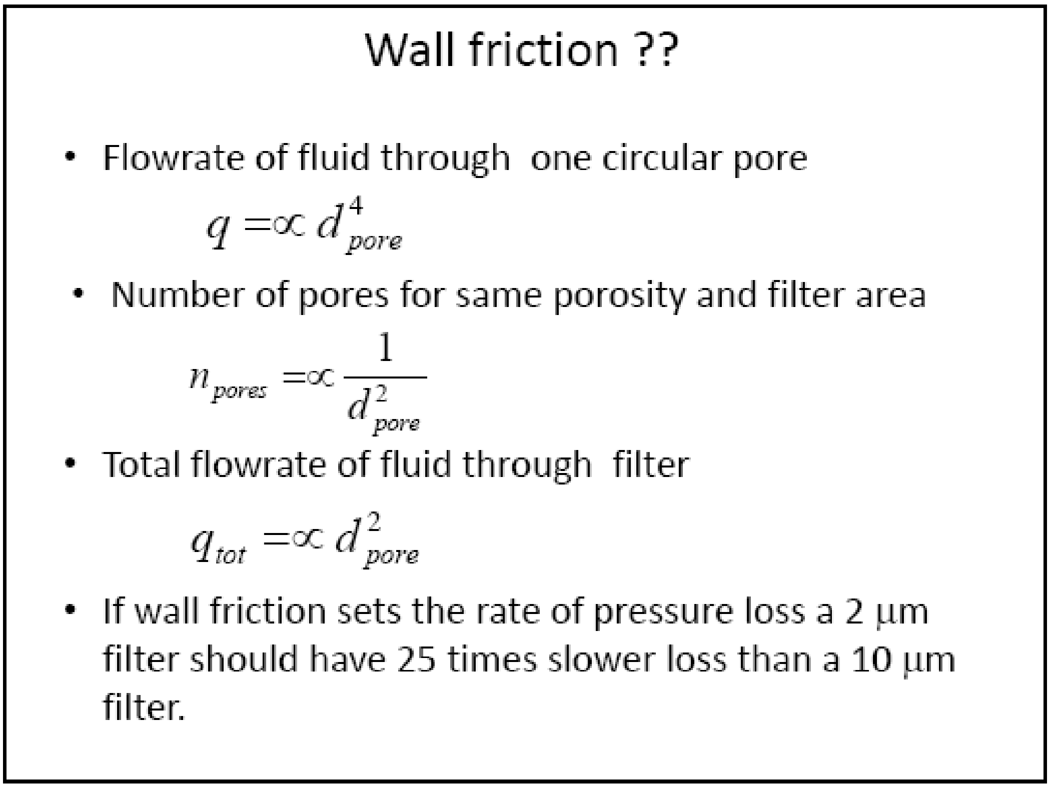


Figure 8.11. Swelling pressure for purified WyNa smectite with 2 micrometer filters. Equipment factor =5. Lower curve, no adjustment of starting volume fraction, upper with 5 % increase.



Wall friction ??

- Flowrate of fluid through one circular pore

$$q = \propto d_{pore}^{4}$$

- Number of pores for same porosity and filter area

$$n_{pores} = \propto \frac{1}{d_{pore}^{2}}$$

- Total flowrate of fluid through filter

$$q_{tot} = \propto d_{pore}^{2}$$

- If wall friction sets the rate of pressure loss a 2 µm filter should have 25 times slower loss than a 10 µm filter.

Appendix 3

Justification of the “CCC”

Martin Birgersson
Lennart Börgesson
Magnus Hedström
Ola Karnland
Ulf Nilsson

CLAY TECHNOLOGY AB

Expert Meeting- Buffer Erosion
Stockholm, November 6, 2009

SKB

Critical Charge Concentration for Coagulation

- Under which conditions does erosion occur – considering that present day groundwaters will alternate with Grimsel-like glacial waters?
  - *Erosion of clays with a mixture of Na^+ and Ca^{2+} ($20\% < X_{Ca} < 90\%$) is prevented by groundwaters with charge concentrations above 2-4 mmol/L*
    - *$X_{Ca} > 20\ \%$ always fulfilled. $X_{Ca} > 90$ difficult to prove, but more favourable criteria apply then.*
- *Consequence*
  - *Present day waters at both sites as well as Baltic Sea water fulfil this condition, but not glacial melt water similar to the Grimsel water*

X_{Ca} = Charge fraction of Ca^{2+} in the clay

Physical properties of the investigated montmorillonites

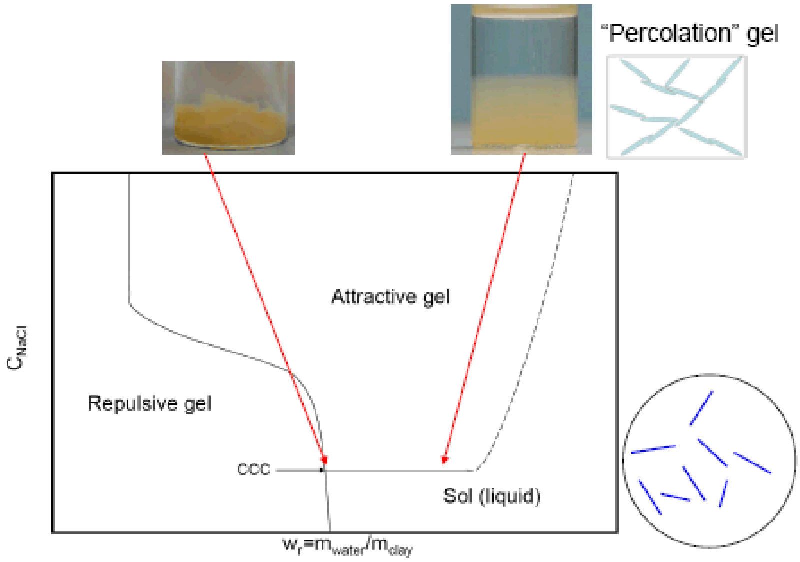
Homo-ionic Na-montmorillonite

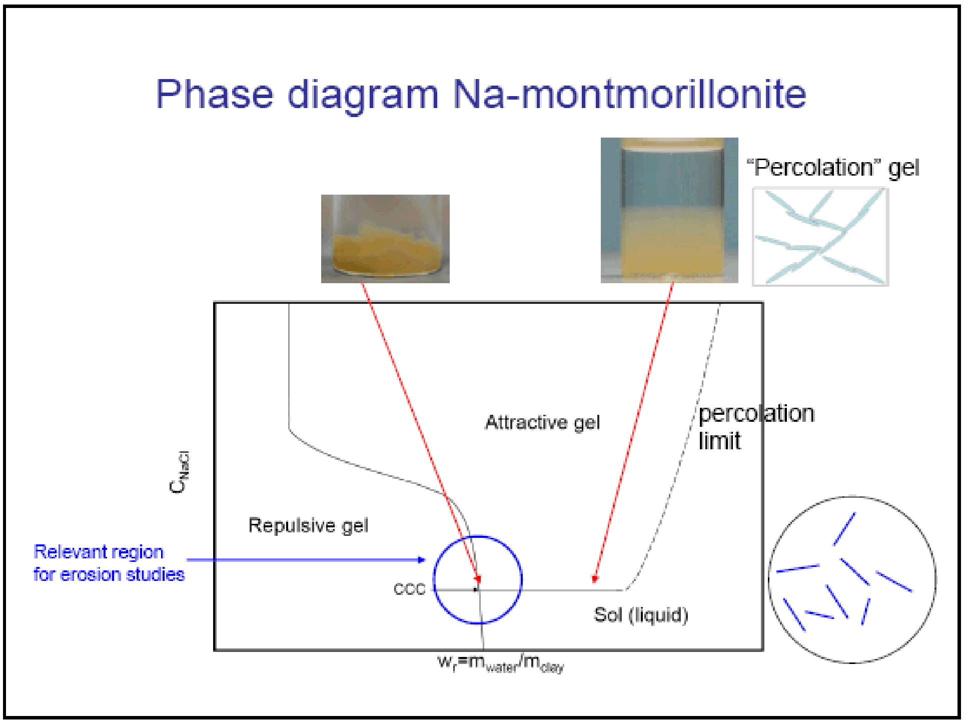
	Wy-Na1	Wy-Na2	Mi-Na1	Mi-Na2	Ku-39-Na
CEC [eq/kg]	0.87	0.88	0.97	1.09	1.04
σ [C/m^2]	-0.11(1)	-0.11(1)	-0.12(3)	-0.14(0)	-0.13(5)
Tetr. Charge [e]	-0.11	-0.05	-0.15	-0.27	-0.38
Octa. Charge [e]	-0.54	-0.60	-0.57	-0.55	-0.42
Total Charge [e]	-0.65	-0.65	-0.72	-0.82	-0.79

$$\sigma = \frac{q}{a \cdot b}$$

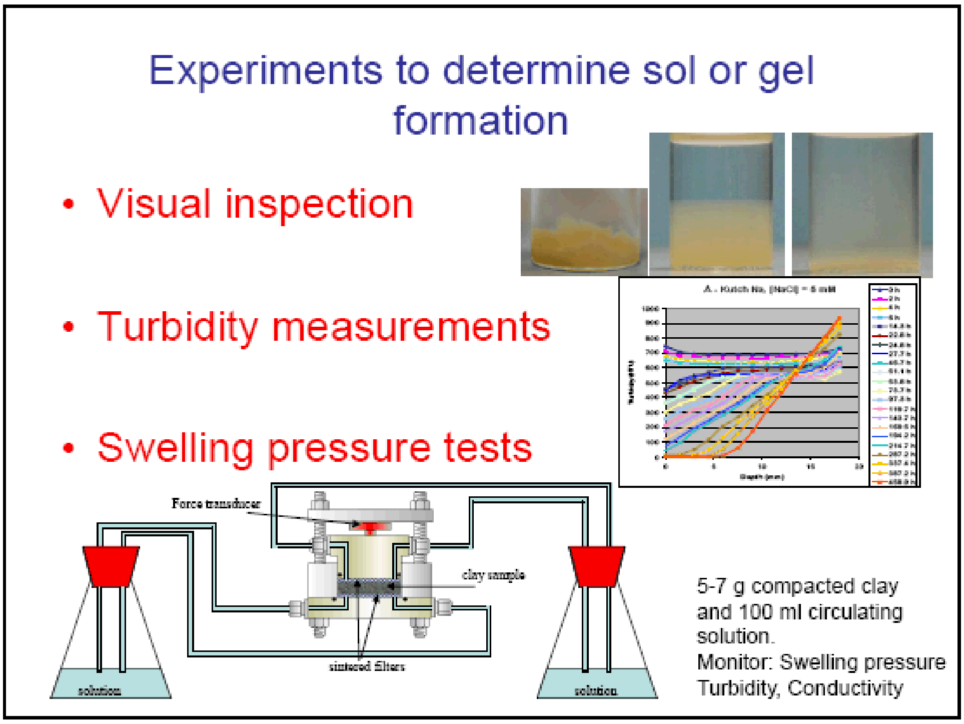
Wyoming	MX-80
Milos	Deponit CA-N
Kutch	Asha-505

Phase diagram Na-montmorillonite





Phase diagram Na-montmorillonite

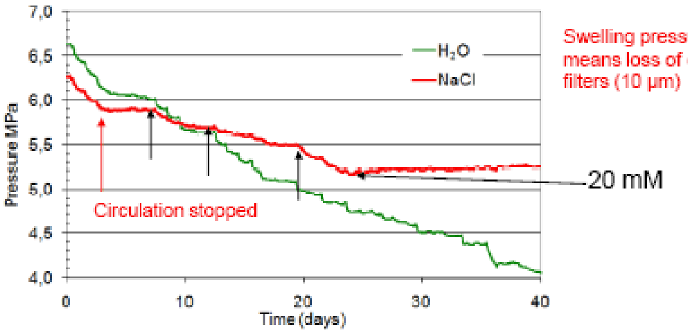


Experiments to determine sol or gel formation

- Visual inspection
- Turbidity measurements
- Swelling pressure tests

5-7 g compacted clay and 100 ml circulating solution.
Monitor: Swelling pressure
Turbidity, Conductivity

CCC Homoionic Wy-Na Montmorillonite



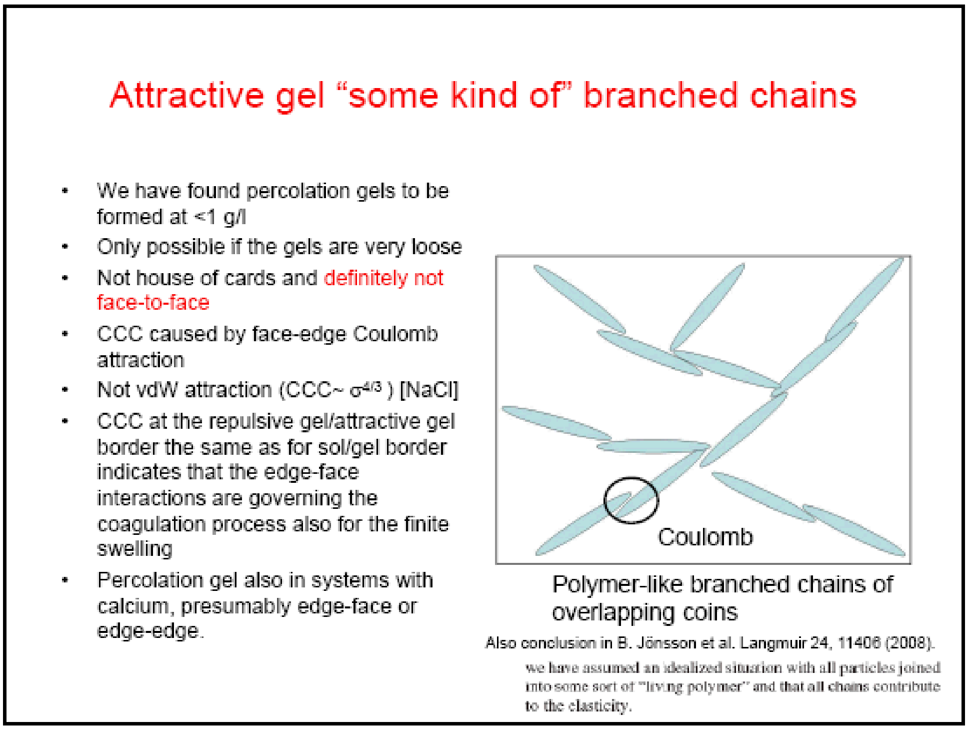
Swelling pressure drop means loss of clay through filters (10 µm)

Solution exchange w. increasing NaCl concentration

Turbidity and visual inspection of small 10 ml vials give
CCC = 25 mM NaCl for Wy-Na. 2, 5 and 10 g Wy-Na per litre.
Both sedimentation and swelling → horizontal "CCC" line in phase diagram

CCC for Na-Montmorillonite

- CCC (NaCl) Wy-Na 20-25 mM, Mi-Na 10 mM, Ku-Na 5 mM
- In PB theory for parallel surfaces the CCC is caused by vdW attraction at high ionic strengths [NaCl]~1 M. CCC depends on the layer charge ~$\sigma^{4/3}$ (Evans and Wennerström, 1999)
- Consequence: CCC for Kutch should be higher than for Wy as Kutch has higher layer charge, instead it is 1/5 of the for Wy
- In PB/DLVO theory, CCC depends on ionic strength, thus NaOH or NaCl should have about the same effect.
- We have found that at pH 11.5 Ku-Na does not readily form a gel even when the Na concentration is about 20 mM.
- $Na_4P_2O_7$ and Calgon increases CCC by a factor of 10. (CT, Lagaly & Ziesmer 2003, several others)
- Coagulation at low ionic strength can only be explained by edge-face interactions so called hetero-coagulation



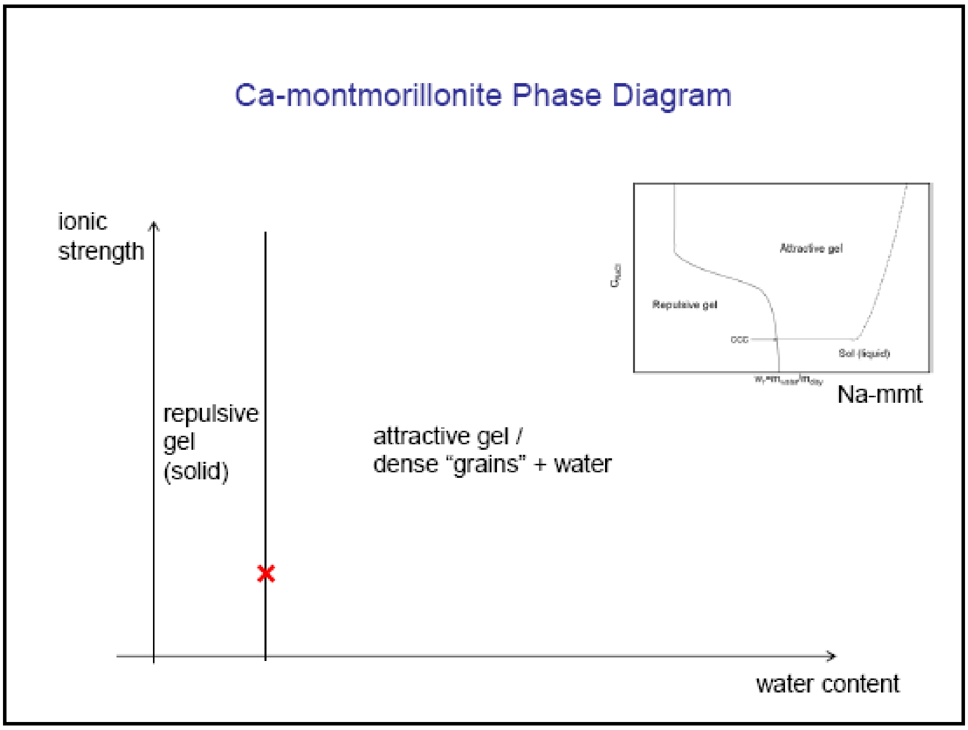
Attractive gel “some kind of” branched chains

- We have found percolation gels to be formed at <1 g/l
- Only possible if the gels are very loose
- Not house of cards and definitely not face-to-face
- CCC caused by face-edge Coulomb attraction
- Not vdW attraction (CCC~ $\sigma^{4/3}$) [NaCl]
- CCC at the repulsive gel/attractive gel border the same as for sol/gel border indicates that the edge-face interactions are governing the coagulation process also for the finite swelling
- Percolation gel also in systems with calcium, presumably edge-face or edge-edge.

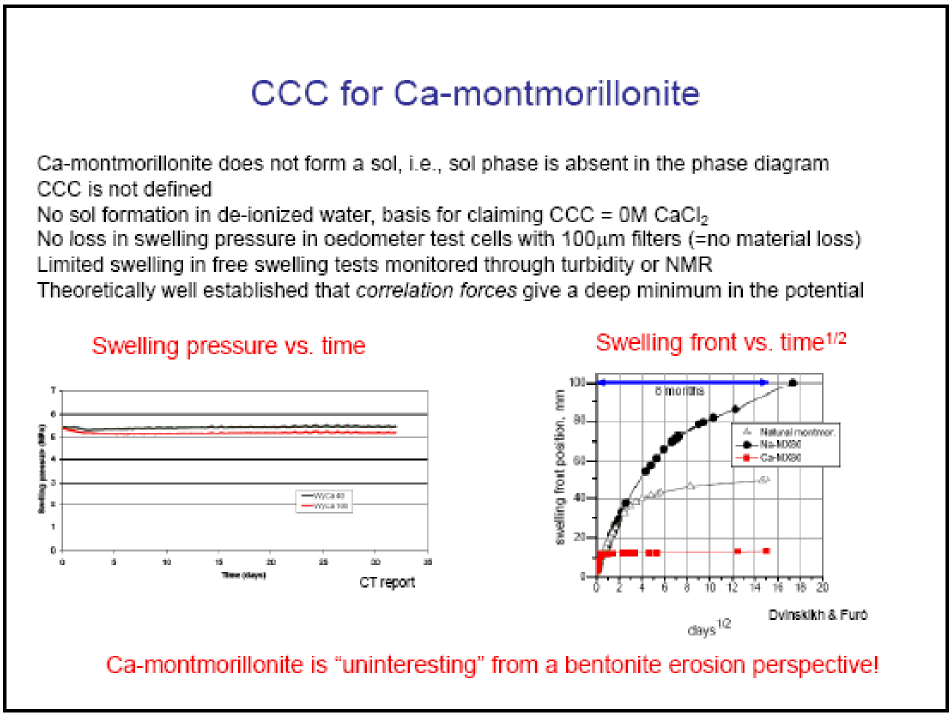
Polymer-like branched chains of overlapping coins

Also conclusion in B. Jönsson et al. Langmuir 24, 11406 (2008).

we have assumed an idealized situation with all particles joined into some sort of “living polymer” and that all chains contribute to the elasticity.



Ca-montmorillonite Phase Diagram



CCC for Ca-montmorillonite

Ca-montmorillonite does not form a sol, i.e., sol phase is absent in the phase diagram
CCC is not defined
No sol formation in de-ionized water, basis for claiming CCC = 0M $CaCl_2$
No loss in swelling pressure in oedometer test cells with 100µm filters (=no material loss)
Limited swelling in free swelling tests monitored through turbidity or NMR
Theoretically well established that *correlation forces* give a deep minimum in the potential

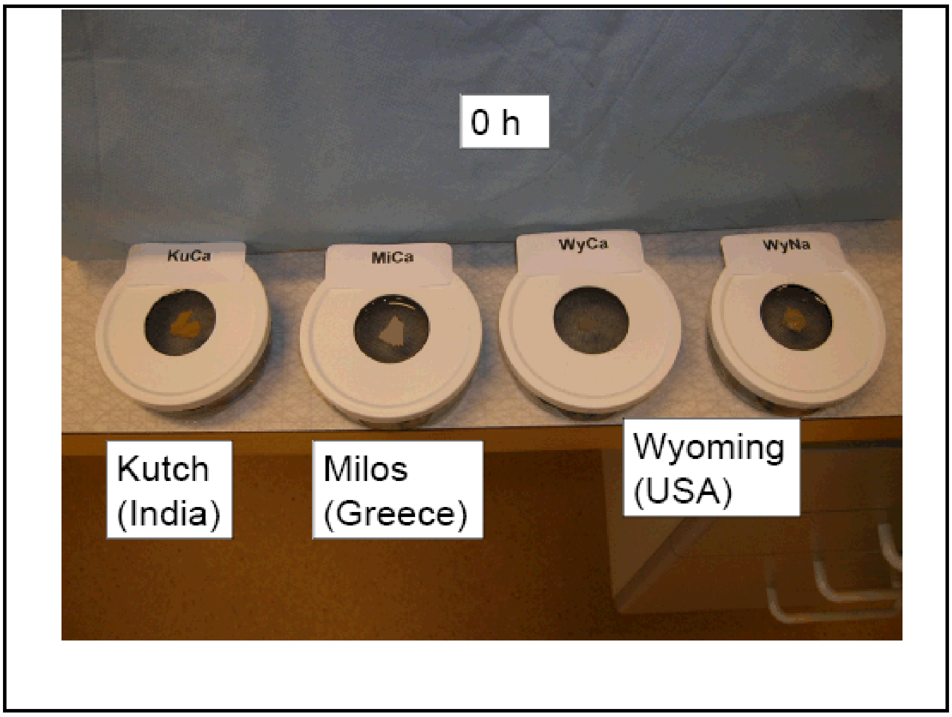
Swelling pressure vs. time

CT report

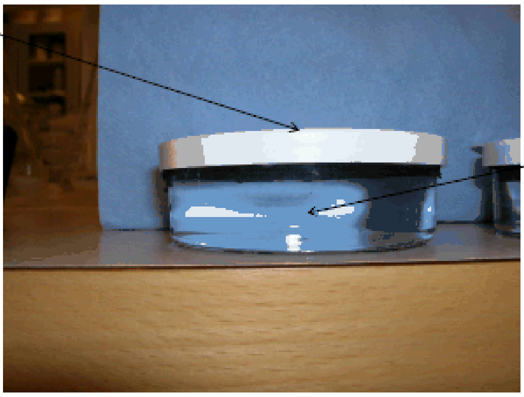
Swelling front vs. $time^{1/2}$

Dvinskikh & Furó

Ca-montmorillonite is “uninteresting” from a bentonite erosion perspective!

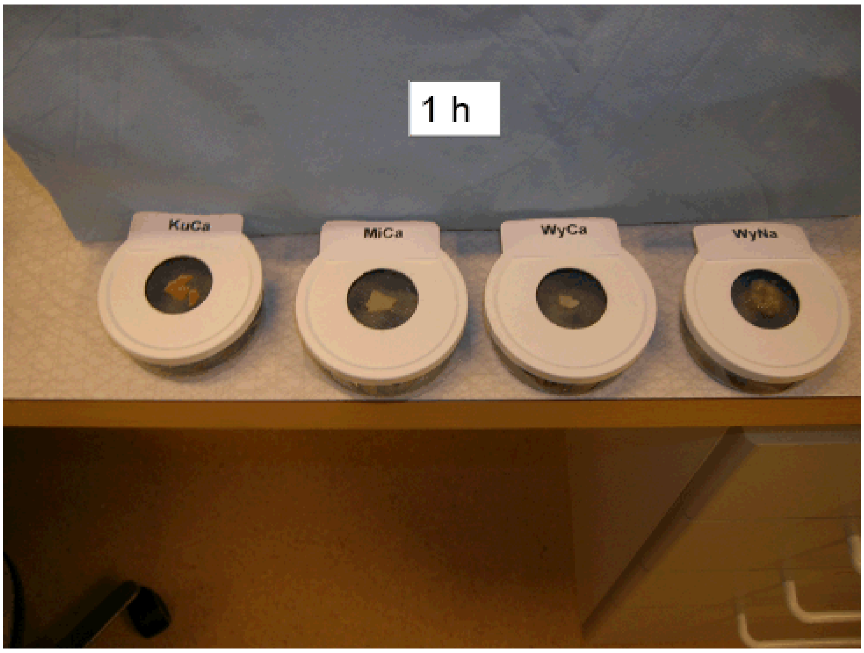


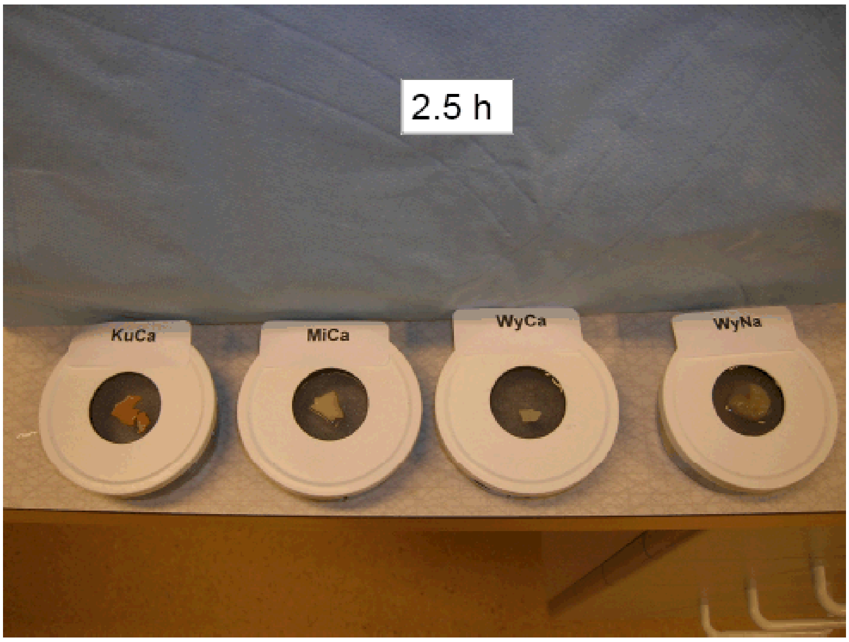
Side view



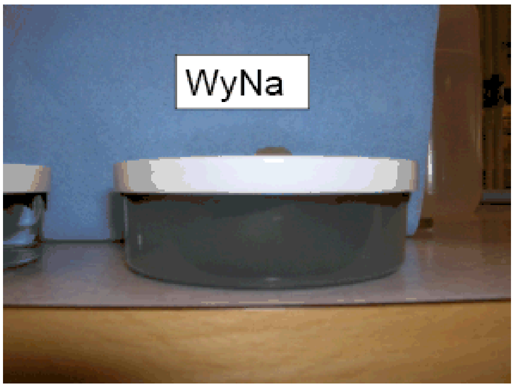
Clay sample

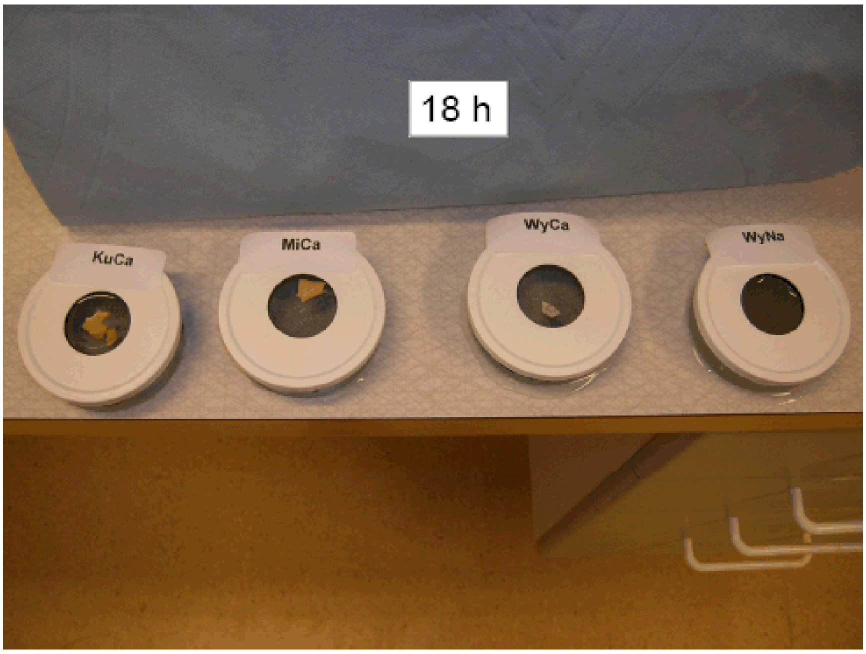
Deionized H_2O





2.5 h

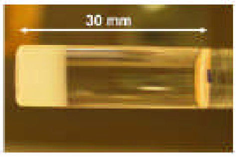




1 week

Is it so that there is no release of colloids occurs when claimed so?

Yes! Compare with data from Dvinskikh & Furó, system suggested by CT



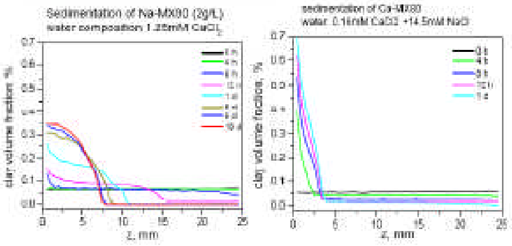
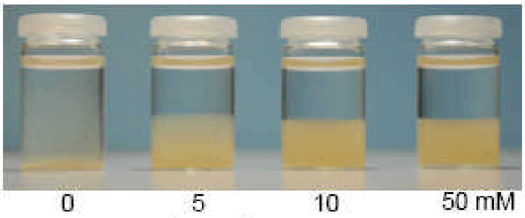
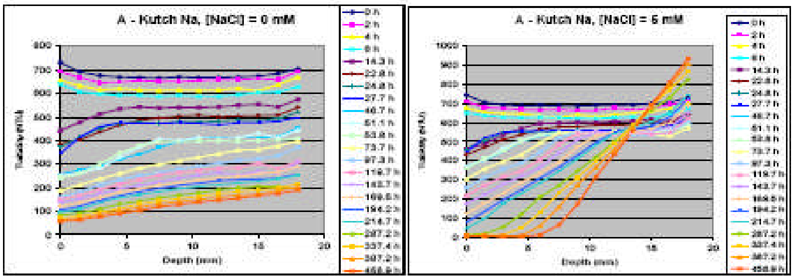


Figure 5.2 Profiles of bentonite volume fraction during sedimentation of different bentonite sorts.

Dvinskikh & Furó, 2009

Density profiles:Sediment Ku-Na 2 g/l





Turbidity is decreasing everywhere in the vial not just at the top. Aggregation.

Gel formation at 5 mM NaCl
Same concentration that limit swelling

pH and gel formation

- Investigated for Wy-Na, Ku-Na, (Mi-Na less) and Wy-Ca/Na (SFZ)
- Wy-Na CCC = 25 mM,2g/l pH 7.5(1), 10g/l pH 7.8(1)
- Ku-Na 2g/l, CCC = 5 mM, pH 7.5

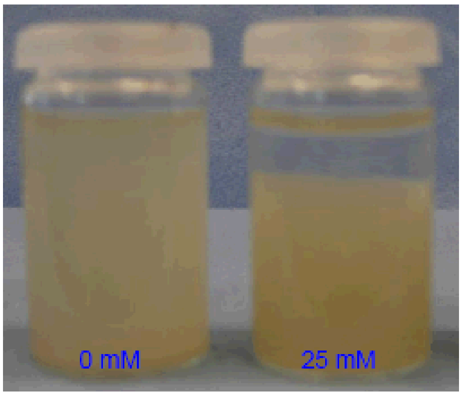
- Gelling (or settling of the gel) is a slow process and montmorillonite has high buffer capacity→ difficult to investigate this process as a function of added NaOH
- Method: Centrifugation at low frequency
- Wy-Na 2 g/l and 25 mM NaCl + NaOH → pH 8.9 , still forms a gel. Maybe weaker
- Ku-Na 2g/l and 5 mM NaCl + NaOH → pH 8.5(4), still forms a gel.

- The mixed Wy-Ca/Na systems have pH ranging from 6.5-7.9 No particular studies on altering pH. $Ca(OH)_2$ is a very powerful flocculating agent.
- Report by CT: "In the pH range 7-9 there are no dramatic changes in CCC, which is also the finding by Hetzel and Doner".

pH and gel formation (centrifugation)

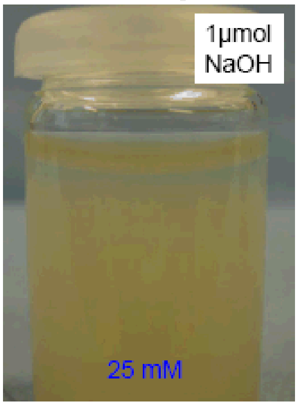
- Stronger percolation gel the more clay, test with 10 g/l
- Inhomogeneous force-field, e.g. 240g at top and 340g at the bottom due to the dimensions of the centrifuge. →Gel could be pulled apart.

10 min centrifugation @ 1600 rpm

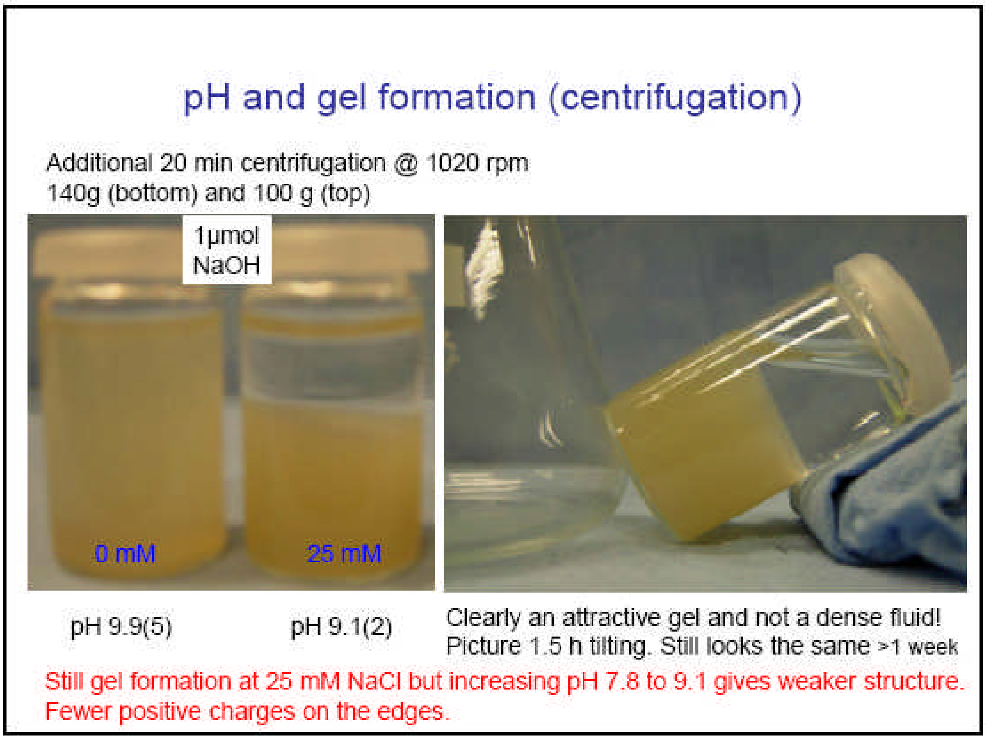


pH 9.8(6) pH 7.8(1)

10 min centrifugation @ 1600 rpm



pH 9.1(2)



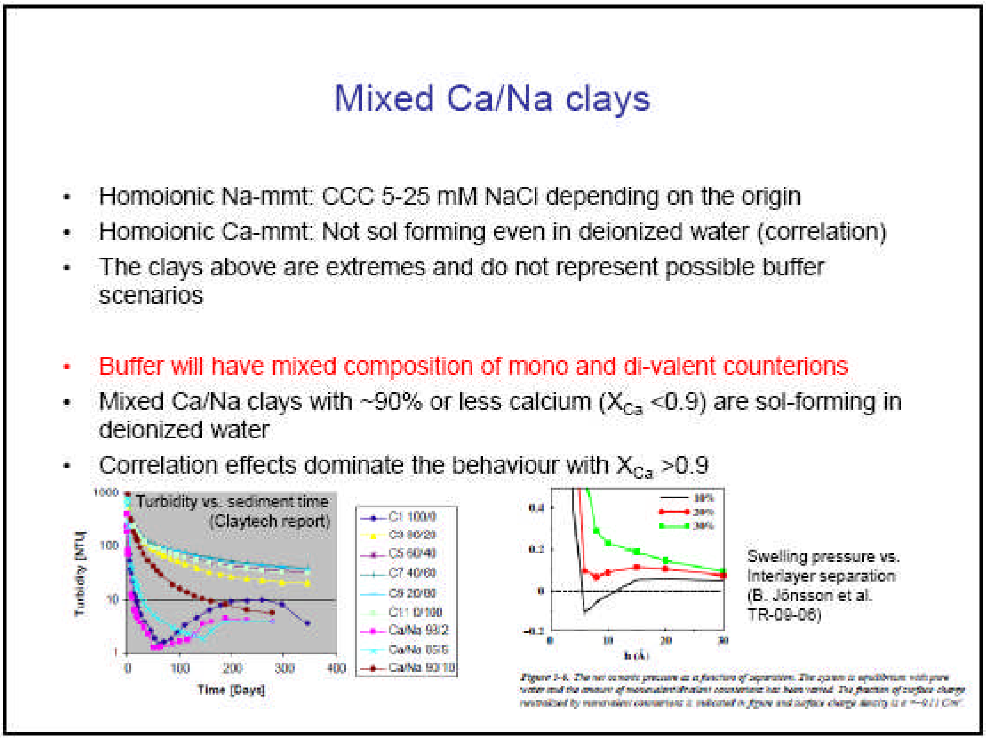
pH and gel formation (centrifugation)

Additional 20 min centrifugation @ 1020 rpm
140g (bottom) and 100 g (top)

pH 9.9(5)   pH 9.1(2)

Clearly an attractive gel and not a dense fluid!
Picture 1.5 h tilting. Still looks the same >1 week

Still gel formation at 25 mM NaCl but increasing pH 7.8 to 9.1 gives weaker structure. Fewer positive charges on the edges.



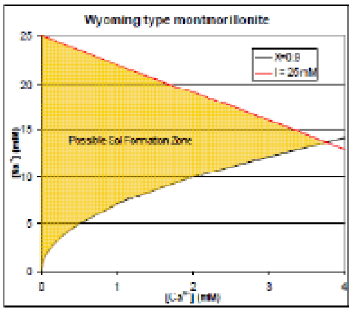
Mixed Ca/Na clays

- Homoionic Na-mmt: CCC 5-25 mM NaCl depending on the origin
- Homoionic Ca-mmt: Not sol forming even in deionized water (correlation)
- The clays above are extremes and do not represent possible buffer scenarios

- Buffer will have mixed composition of mono and di-valent counterions
- Mixed Ca/Na clays with ~90% or less calcium (X_{Ca} <0.9) are sol-forming in deionized water
- Correlation effects dominate the behaviour with X_{Ca} >0.9

Swelling pressure vs. Interlayer separation (B. Jönsson et al. TR-09-06)

Mixed Ca/Na clays with excess ions



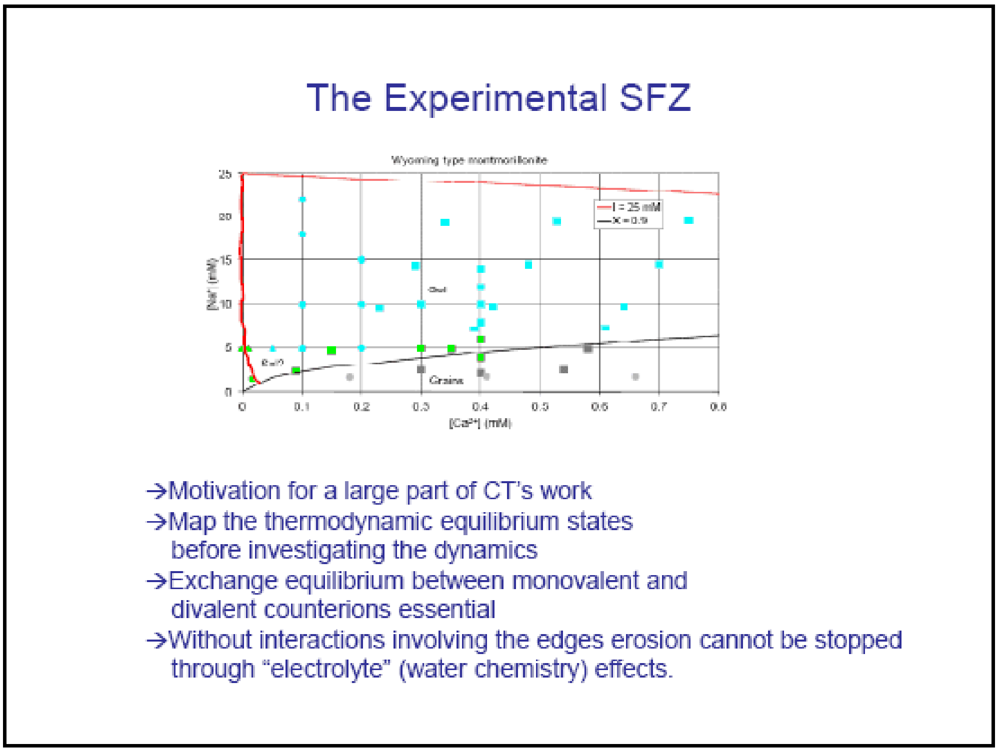
Beak-shaped sol formation zone

More complicated phase diagram
CCC is not a good variable
Needs both sodium and calcium
Concentration

Note that chloride is the anion

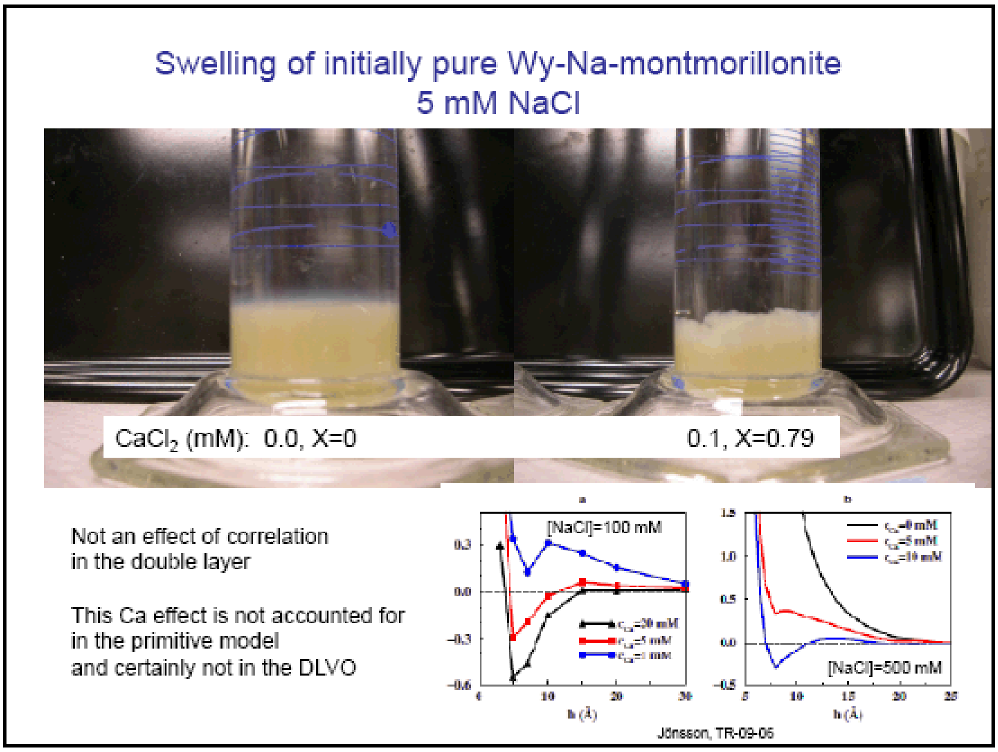
The new Ca-effect

- Beak-shaped sol formation zone (SFZ) formulated as a hypothesis based on CCC for NaCl and our experimental finding that montmorillonite with more than 90% Ca in the interlayer behaves similar to homoionic Ca-montmorillonite
- Experimentally we find a much smaller SFZ. This is good news!
- Small amounts of excess Ca promote gel formation. Believed to be related to edge-face or possibly edge-edge interactions. NB that the amounts of Ca in these systems are far below what is needed for having significant correlation effects.
- Not an effect of algae. One does not need to wait for months to judge whether the system is sol forming or not. In fact out of a total of more than 300 vials we have only noted algae in one of them (Ku-Na 5 used in pH tests, after more than a year)



The Experimental SFZ

→Motivation for a large part of CT's work
→Map the thermodynamic equilibrium states before investigating the dynamics
→Exchange equilibrium between monovalent and divalent counterions essential
→Without interactions involving the edges erosion cannot be stopped through "electrolyte" (water chemistry) effects.



Swelling of initially pure Wy-Na-montmorillonite 5 mM NaCl

$CaCl_2$ (mM): 0.0, X=0 0.1, X=0.79

Not an effect of correlation in the double layer

This Ca effect is not accounted for in the primitive model and certainly not in the DLVO

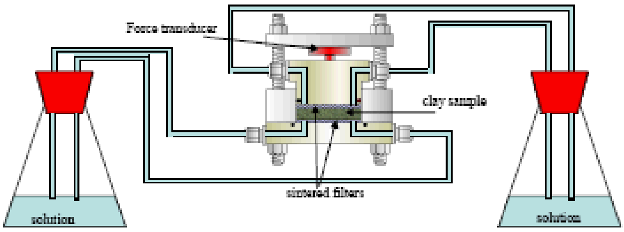
Jönsson, TR-09-06

For what equilibrium conditions could buffer erosion occur?

Two types of erosion:

- montmorillonite forms a sol at low ionic strength (liquid state)
  - ✓ applies only to systems with a Ca-population $X_{Ca} < 90\%$
  - ✓ depends on pH, anions, particle shape, etc.
  - ✓ occurs for Wyoming type Na-montmorillonite in NaCl below [NaCl] = 25 mM
  - ✓ occurs for Wyoming type Ca/Na-montmorillonite in NaCl/$CaCl_2$-solution below approximately [$CaCl_2$] < 0.1 mM, [NaCl] < 2 mM
- mechanical erosion of attractive gel
  - ✓ dependent on mechanical strength and external water flow

Erosion tests



Specified initial solution circulated
Amount of eroded material measured with turbidity
Pressure response monitored

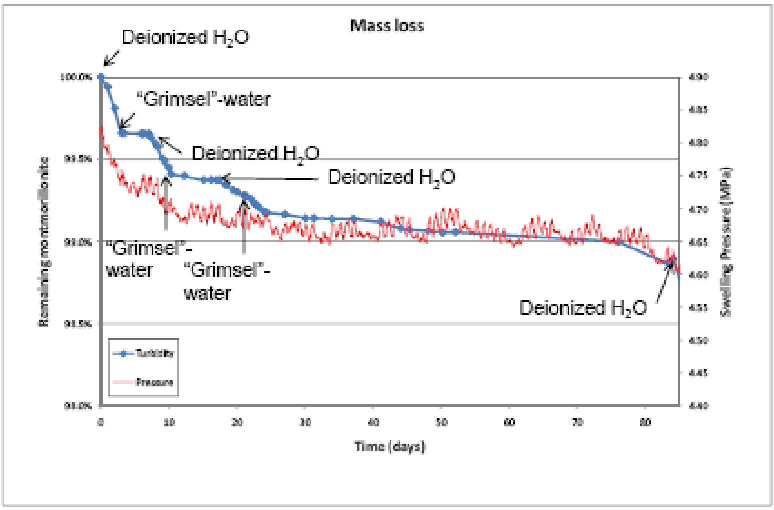
Erosion tests

Sample: MX-80 bentonite, gypsum depleted
Ca-population < 30%

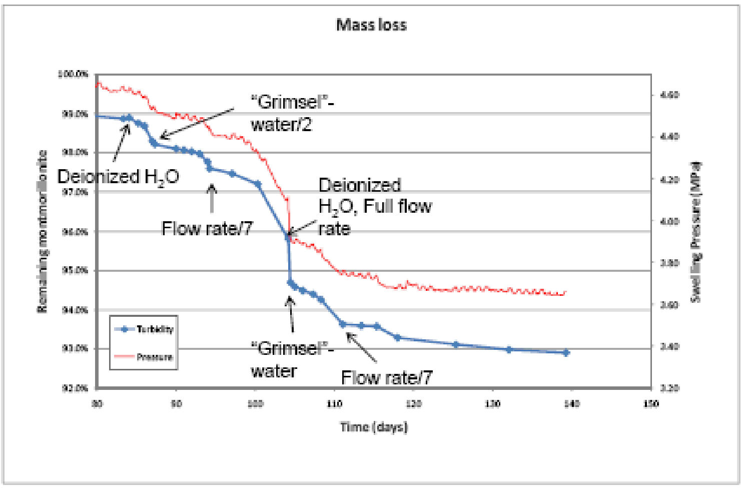
Solution(s): Deionized H_2O
"Grimsel"-water: $[CaCl_2] = 0.2$ mM , [NaCl]= 0.7 mM, $pH_{init} \approx 5.9$ (CO_2)

When (exchange) equilibrium between MX-80 and "Grimsel"-solution is established
[NaCl] ≈ 1.1 mM, only small amount of Ca

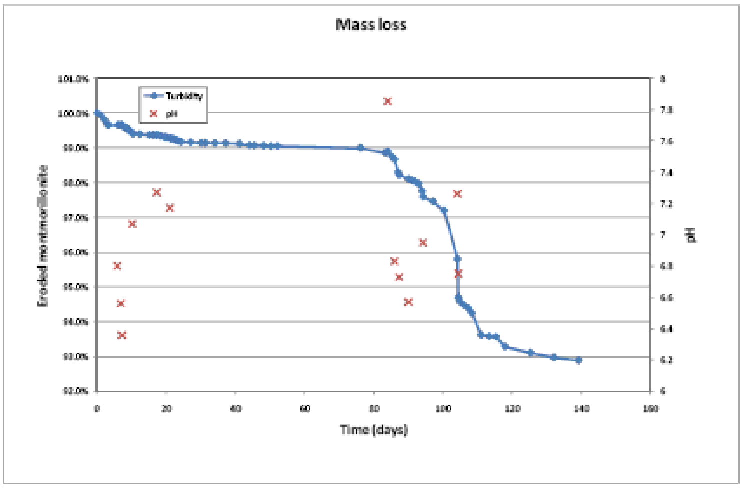
Erosion test of MX-80



Erosion test of MX-80



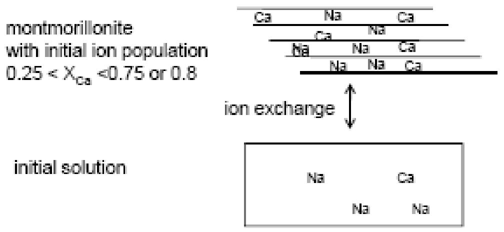
Erosion test of MX-80



Erosion test of MX-80

- Erosion can be turned on and off (and on!) (physico)chemically
- The concentration limit **in this test** ≈ 1 mM (NaCl)
- Flow rate influence behavior: component of mechanical erosion (~1ml/min here)
- pH not fully controlled, but erosion demonstrated at pH=5.9 and prohibited at pH=7.9

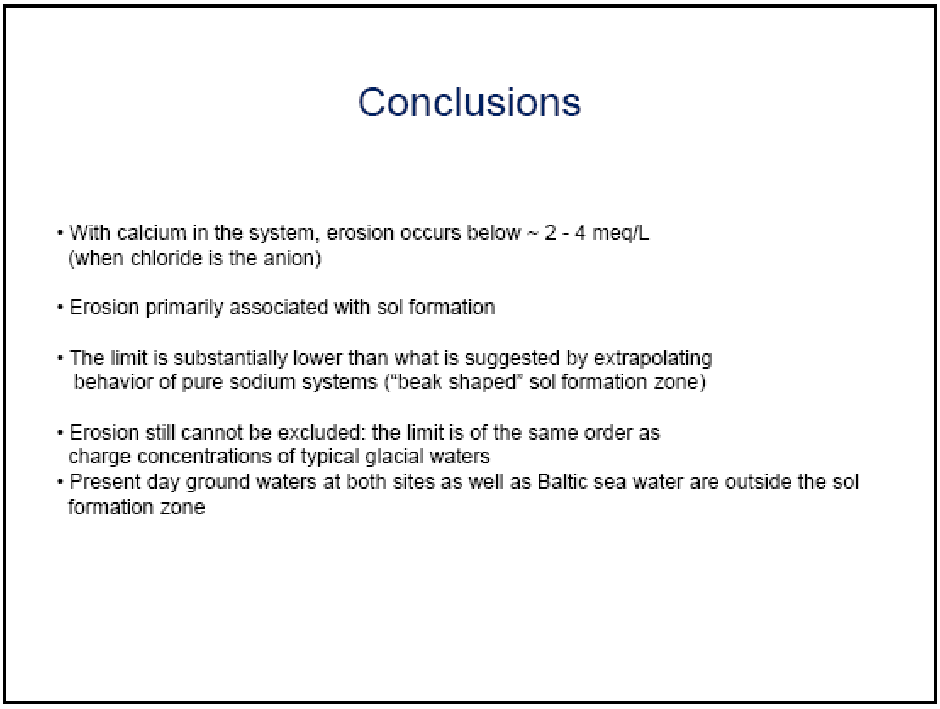
Erosion tests of pure montmorillonite



With the conditions the performed tests (low external concentrations, substantial amounts of both Ca and Na in the clay, and a high solid-to-water ratio), the external solution consists basically only of Na at equilibrium →CCC in terms of charge eq/mol

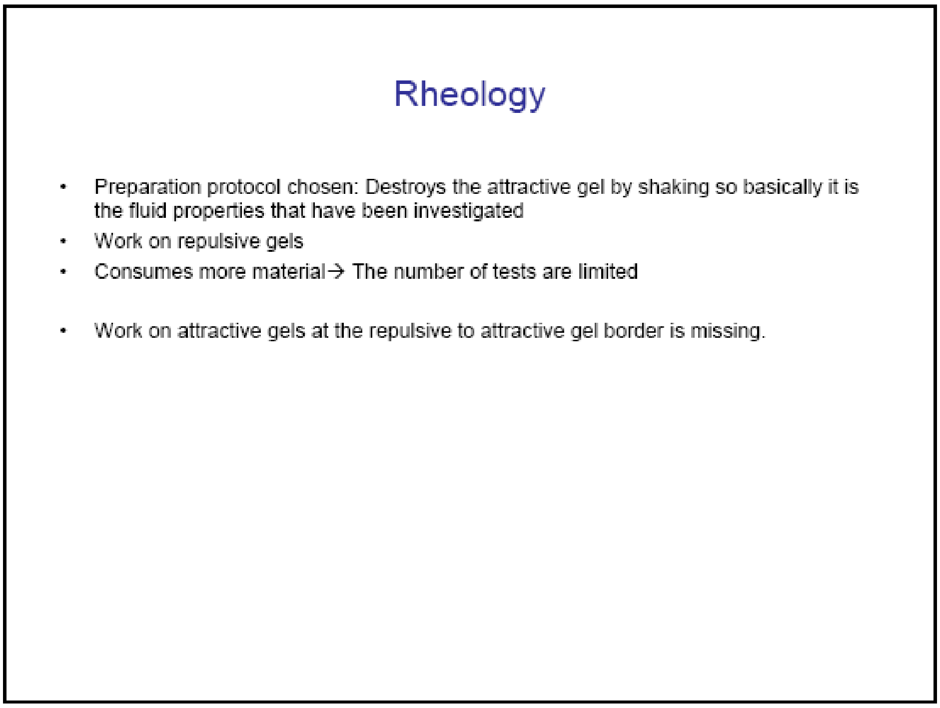
The tests on pure montmorillonite has pure NaCl solution initially, to be near equilbrium → tiny amount of Ca/Na exchange, Selectivity favours Ca^{2+} in the clay

In the real situation with a buffer, equilibrium is never reached



Conclusions

- With calcium in the system, erosion occurs below ~ 2 - 4 meq/L (when chloride is the anion)
- Erosion primarily associated with sol formation
- The limit is substantially lower than what is suggested by extrapolating behavior of pure sodium systems ("beak shaped" sol formation zone)
- Erosion still cannot be excluded: the limit is of the same order as charge concentrations of typical glacial waters
- Present day ground waters at both sites as well as Baltic sea water are outside the sol formation zone



Rheology

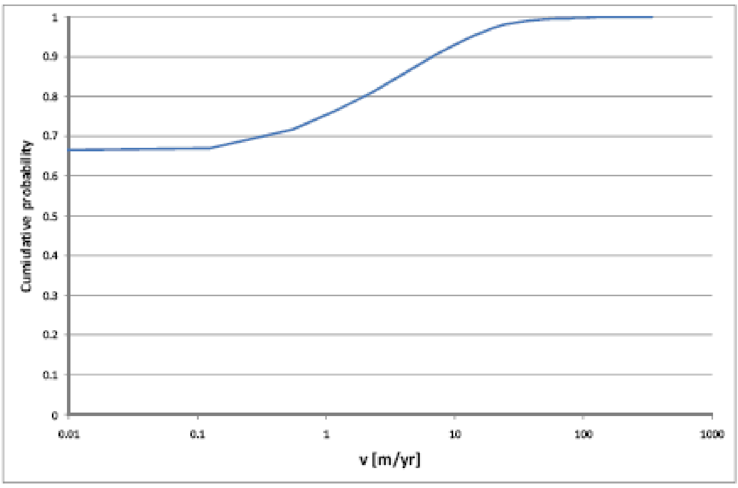
- Preparation protocol chosen: Destroys the attractive gel by shaking so basically it is the fluid properties that have been investigated
- Work on repulsive gels
- Consumes more material→ The number of tests are limited
- Work on attractive gels at the repulsive to attractive gel border is missing.

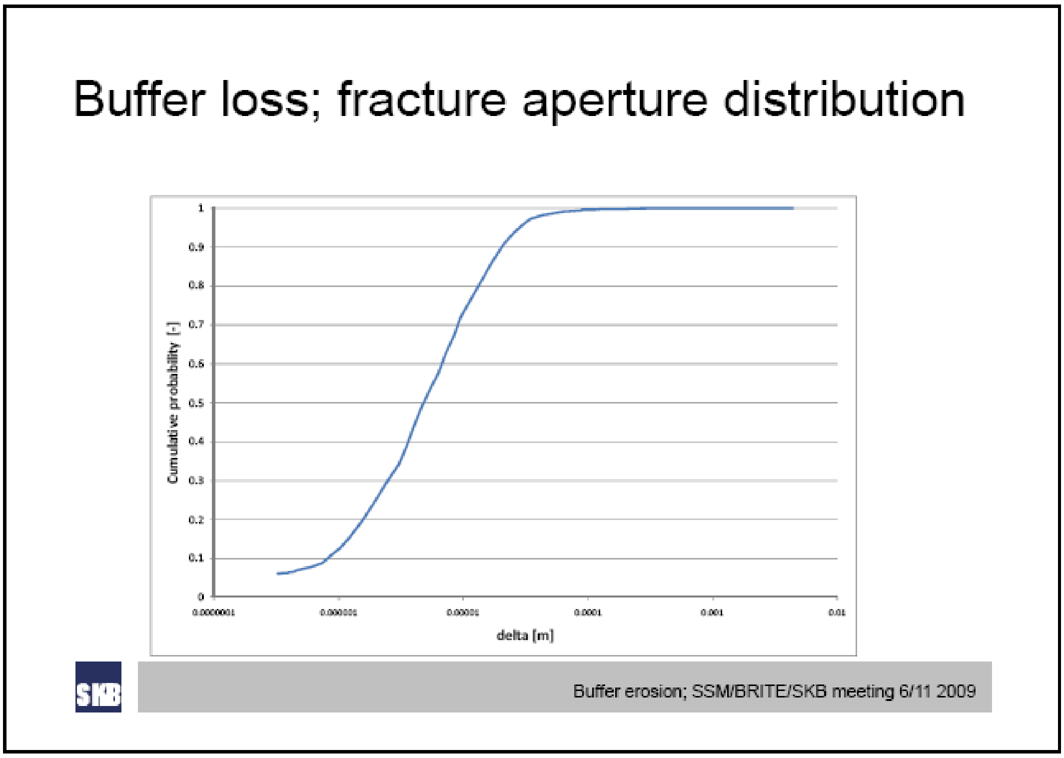
Appendix 4

Calculations of buffer loss - a first attempt for SR-Site

- Use model presented by Neretnieks
  - $dM/dt = 0.0272 \cdot \delta/0.001 \cdot v^{0.41}$ kg/yr
  - Water velocities v [m/yr] and fracture apertures δ [m] from hydrogeological calculations (same results as used for radionuclide transport)
  - Obtain results for ensemble of 6,916 modelled deposition holes
  - Filtered w.r.t. the so called FPI criterion (layout rule, excludes 402 positions)

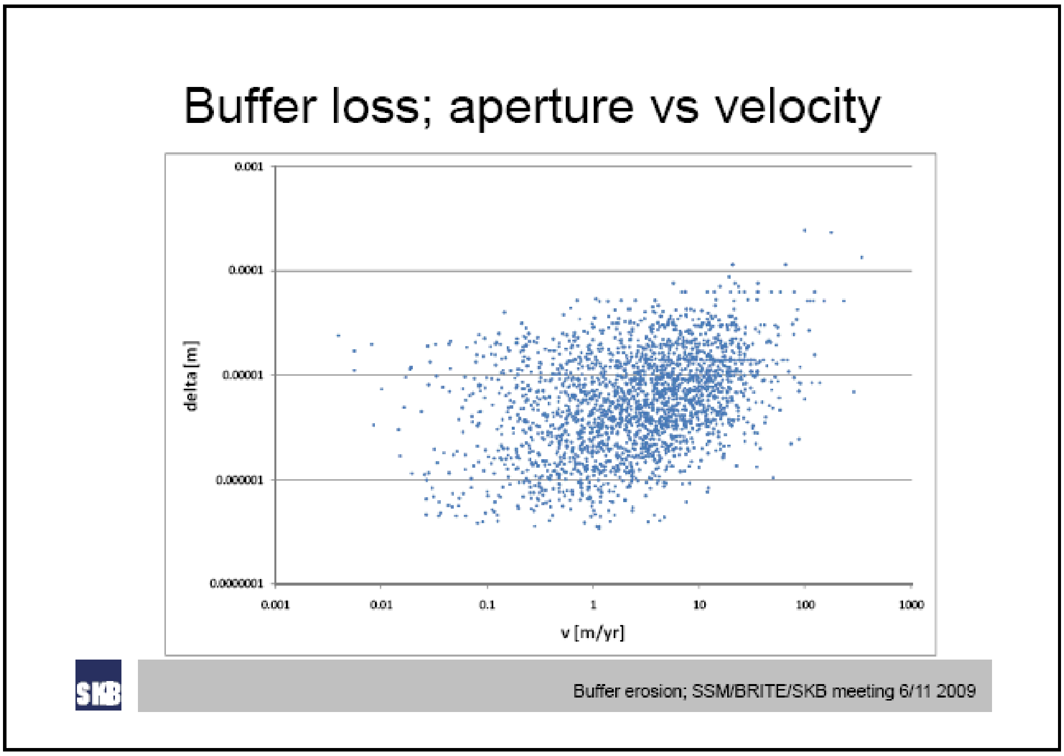
Buffer loss; water velocity distribution





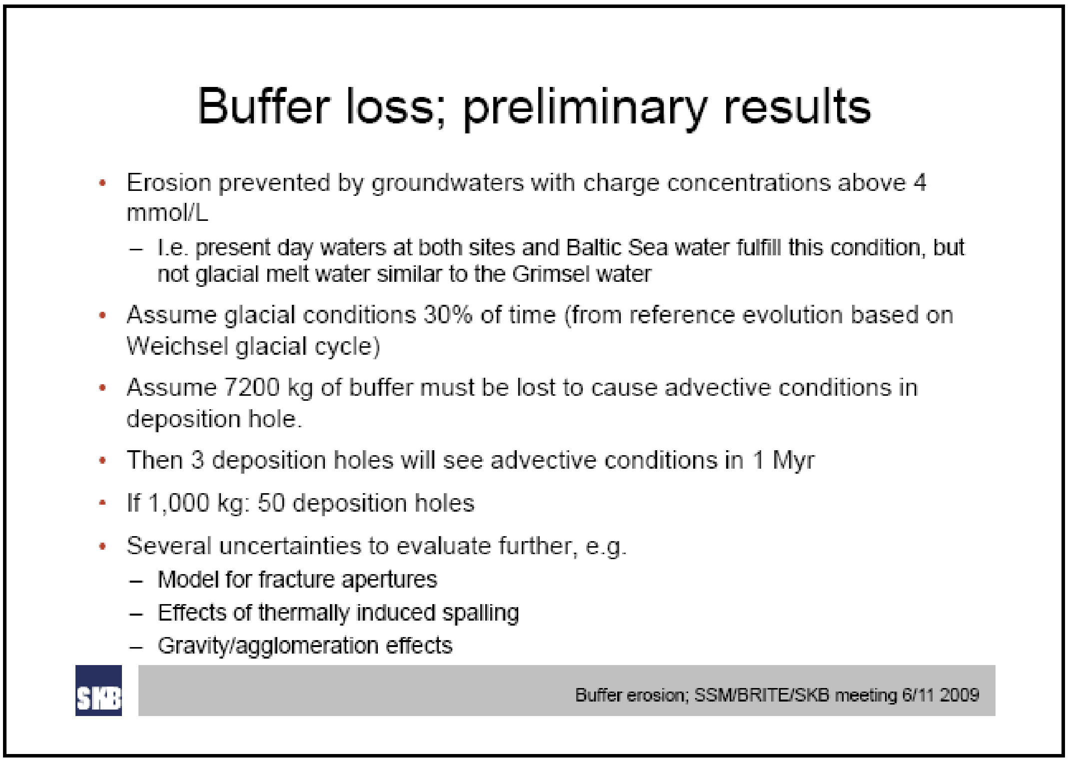
Buffer loss; fracture aperture distribution

Buffer erosion; SSM/BRITE/SKB meeting 6/11 2009



Buffer loss; aperture vs velocity

Buffer erosion; SSM/BRITE/SKB meeting 6/11 2009



Buffer loss; preliminary results

- Erosion prevented by groundwaters with charge concentrations above 4 mmol/L
  - I.e. present day waters at both sites and Baltic Sea water fulfill this condition, but not glacial melt water similar to the Grimsel water
- Assume glacial conditions 30% of time (from reference evolution based on Weichsel glacial cycle)
- Assume 7200 kg of buffer must be lost to cause advective conditions in deposition hole.
- Then 3 deposition holes will see advective conditions in 1 Myr
- If 1,000 kg: 50 deposition holes
- Several uncertainties to evaluate further, e.g.
  - Model for fracture apertures
  - Effects of thermally induced spalling
  - Gravity/agglomeration effects

Buffer erosion; SSM/BRITE/SKB meeting 6/11 2009