# Update on erosion experiments

Magnus Hedström, Emelie Hansen

Clay Technology AB

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# The initial problem

- SR-97 (TR-99-07) Erosion (colloid) neglected
  - Concentrations of divalent ions, especially Ca2+, in deep Swedish groundwaters are generally fully adequate. If the concentration is over 0.1 mM (4 ppm), a stable clay gel is obtained. **Base scenario:** The above discussion suggests that erosion of the buffer is not of significance for the long-term performance of the repository. The process is neglected in SR 97 but should be further studied. **Misinterpretation of Le Bell 1978** (KBS TR 97)

- RD&D Programme 2001 (TR-01-30)
  - ***Conclusions in RD&D 98 and its review*** Not dealt with.
  - The authorities consider that erosion of the buffer should be taken into account as a potential source of colloids. **But the actual problem of loss of bentonite is not identified**

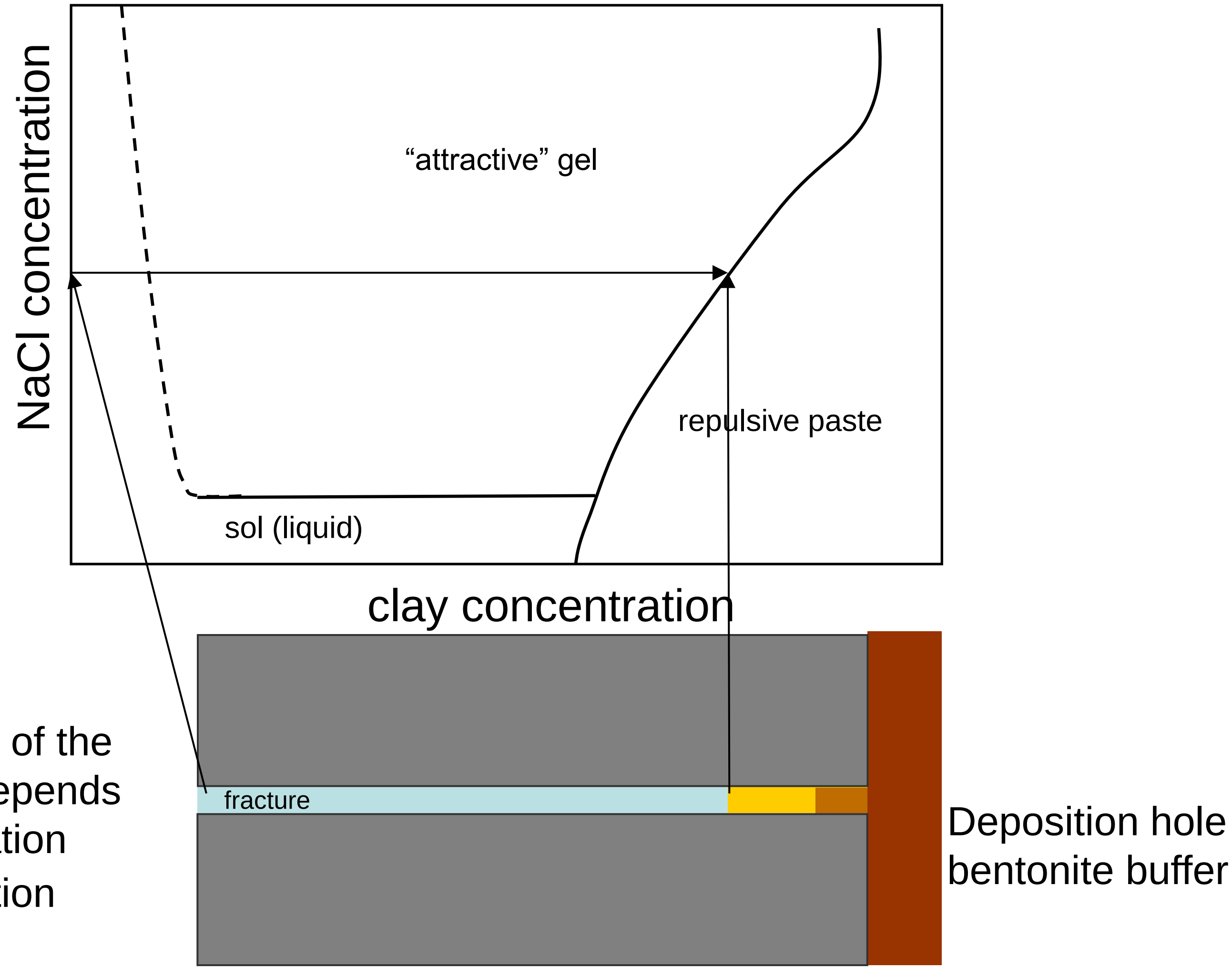
# The initial problem

- RD&D Programme 2004
  - On swelling, the buffer penetrates out into the fractures in the surrounding rock, where it can form colloids which can be carried away by the groundwater
  - The estimates in SR 97 suggest that there is little risk of erosion, whether chemical or mechanical, of large quantities of bentonite. However, the process should be further studied. One remaining question concerns the importance of very low ionic strengths in the groundwater
  - **Conclusions in RD&D 2001 and its review** SKI notes that erosion of the buffer material is not mentioned in the RD&D-Programme, but is of the opinion that SKB has taken the necessary initiatives to move forward in the colloid issue (for example by means of the Colloid Project in the Äspö HRL).
- Systematic work arranged by SKB
  - Misinterpretation of Le Bell (1978) identified. No basis for the limit of 0.1 mM Ca2+. Ion exchange neglected. Erosion of Na-montmorillonite in DI water identified as a problem in experiments at Claytech since long. **Ola Karnland, CT**.
  - CCC for Na-mmt tested for DI, 1, 10 100 and 1000 mM

# The initial problem

- SR-Can (TR-06-18) Impact of first SKB measurements of CCC
  – The critical coagulation concentration (CCC) may be determined for different solutions, and used as a conservative value for spontaneous colloid formation. Groundwater concentration has to be at least 0.1 M with respect to sodium (monovalent) ions or 0.001 M calcium ions (divalent ions) in order to neglect colloid formation. If this is not achieved mass transport modelling, including diffusive and flow transport, has to be made.
- SKB application March 16 2011
  – What are the weakest points in the application?
  – Colloid erosion is one of the weakest points in the application (of two identified weak points) Claes Thegerström CEO at the press conference held in connection with the formal application
- Present day: The process cannot be dismissed yet.

# Montmorillonite state/phase diagram




The integrity of the repository depends on gel formation and wall friction

# Behaviour of montmorillonite at low ionic strength

decreasing salinity →

montmorillonite

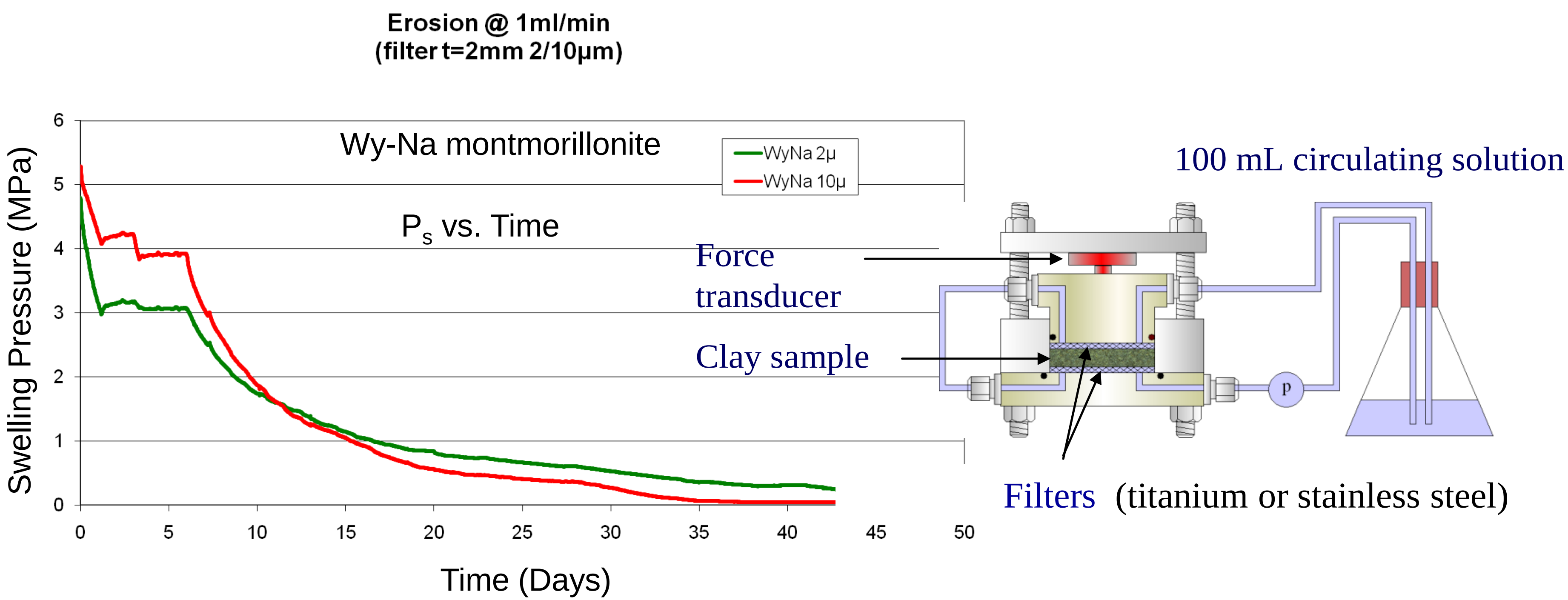
attractive gel — sol (liquid)

yield strength — viscosity

withstand flow — break due to flow — transport by flow

no erosion — erosion

# The problem of erosion due to sol formation




Sodium montmorillonite disperses easily

Filter pore size of 2 µm not enough to hinder erosion

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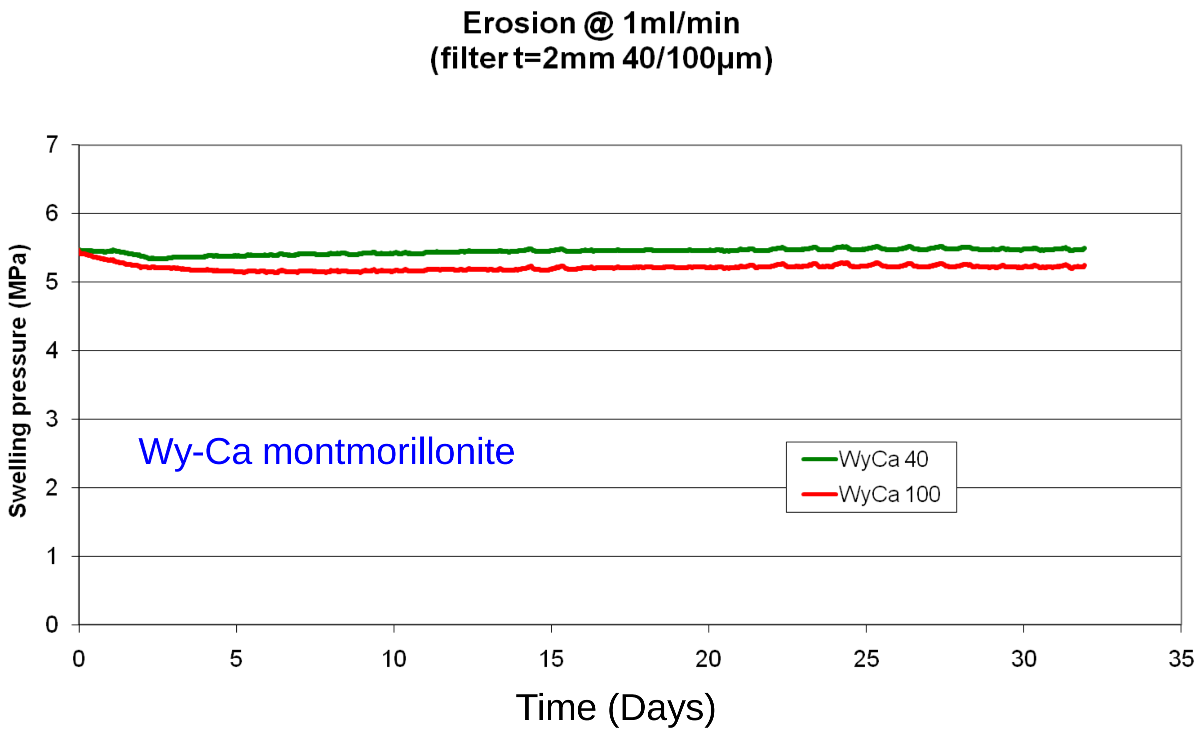
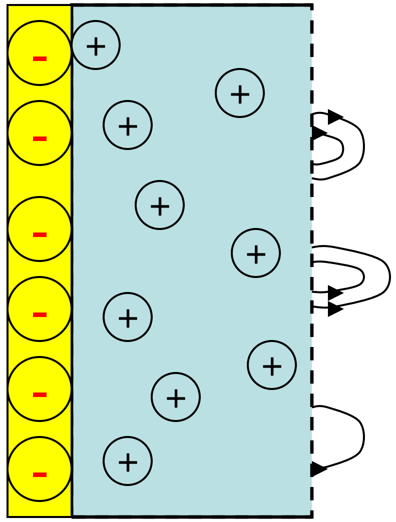
# No erosion with Ca-montmorillonite




Ion correlation important for divalent counterions



Cartoon adapted from Evans & Wennerström

No loss of Ca-montmorillonite even when pore size = 100µm

Ca-montmorillonite is not sol forming even in DI water

CCC for Ca-montmorillonite is not a meaningful concept

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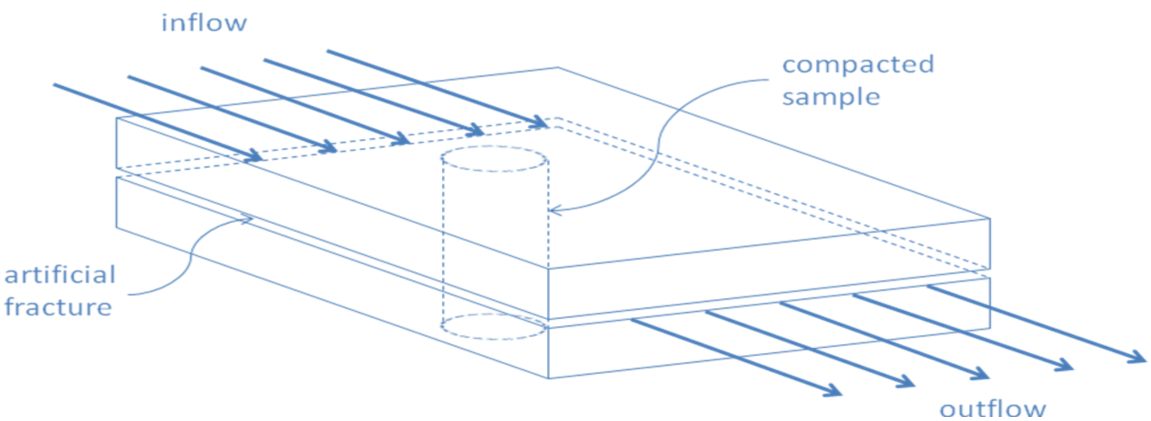
# Focus on Na-montmorillonite

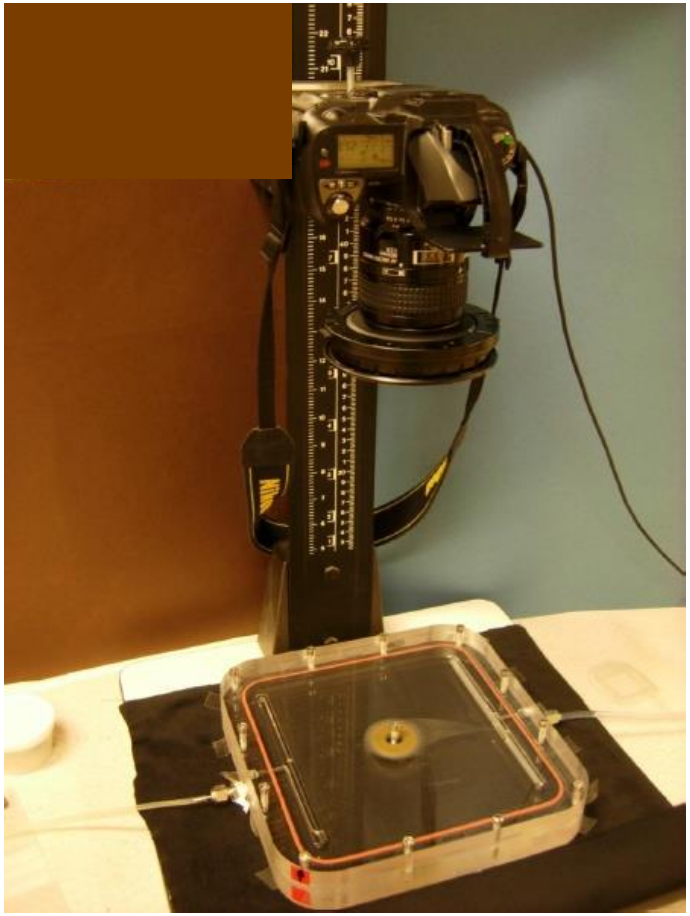
Wy-Na from MX-80

DI water, NaCl solution,
Sometimes NaOH added to give pH 9-10
No effect of pH on erosion or formation of attractive gel

# Erosion in artificial fractures

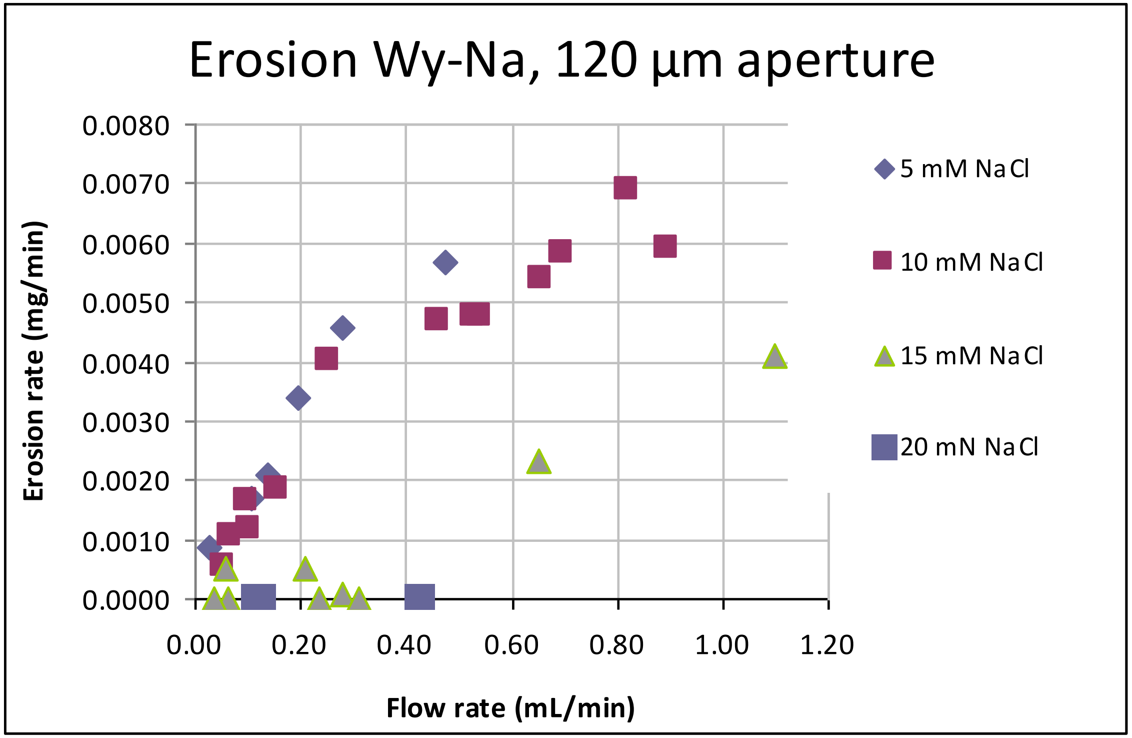



Schatz et al. POSIVA 2012-44.



The amount of montmorillonite in the effluent is determined from its turbidity
Lower limit 0.1 mg/l

# Results 120μm aperture




Salinity from low to higher

Eventually erosion stops at 15 mM NaCl

Never any erosion for 20 mM

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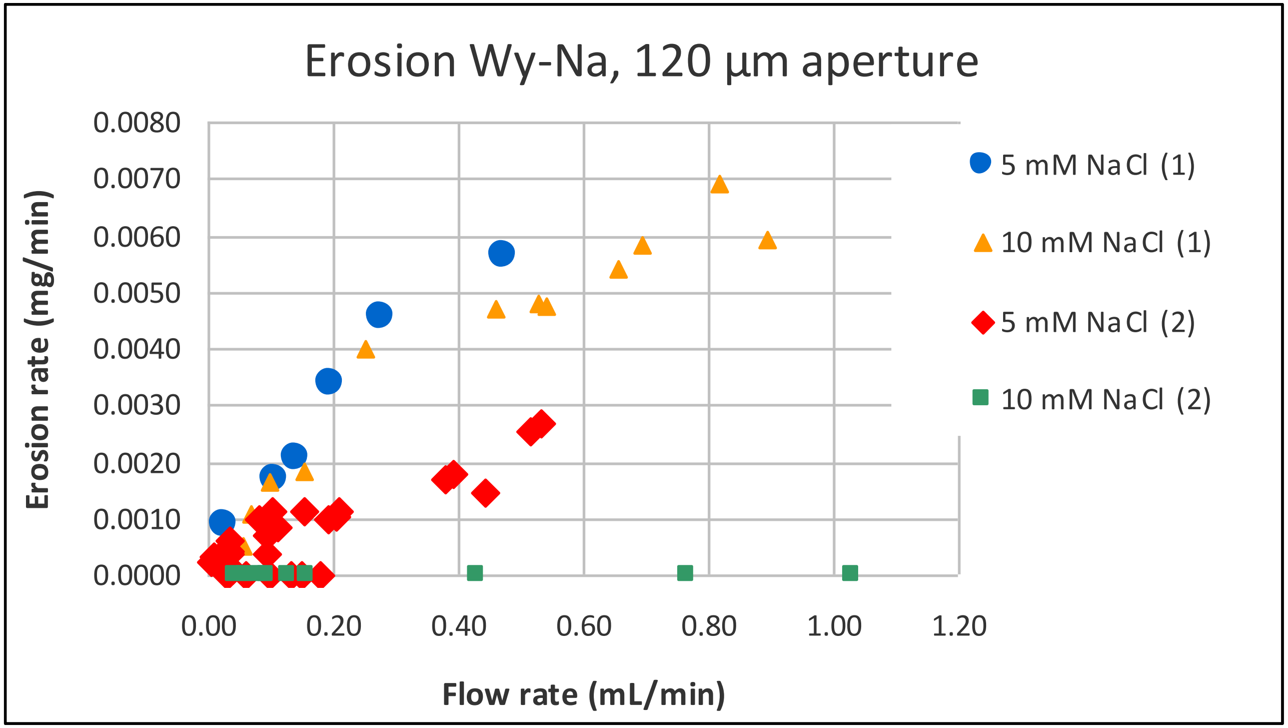
# A case of mis-identity
# Comparison of erosion rates




When coming from higher to lower concentrations (2), no erosion at 10 mM

Hysteresis effect: There is more to erosion than CCC

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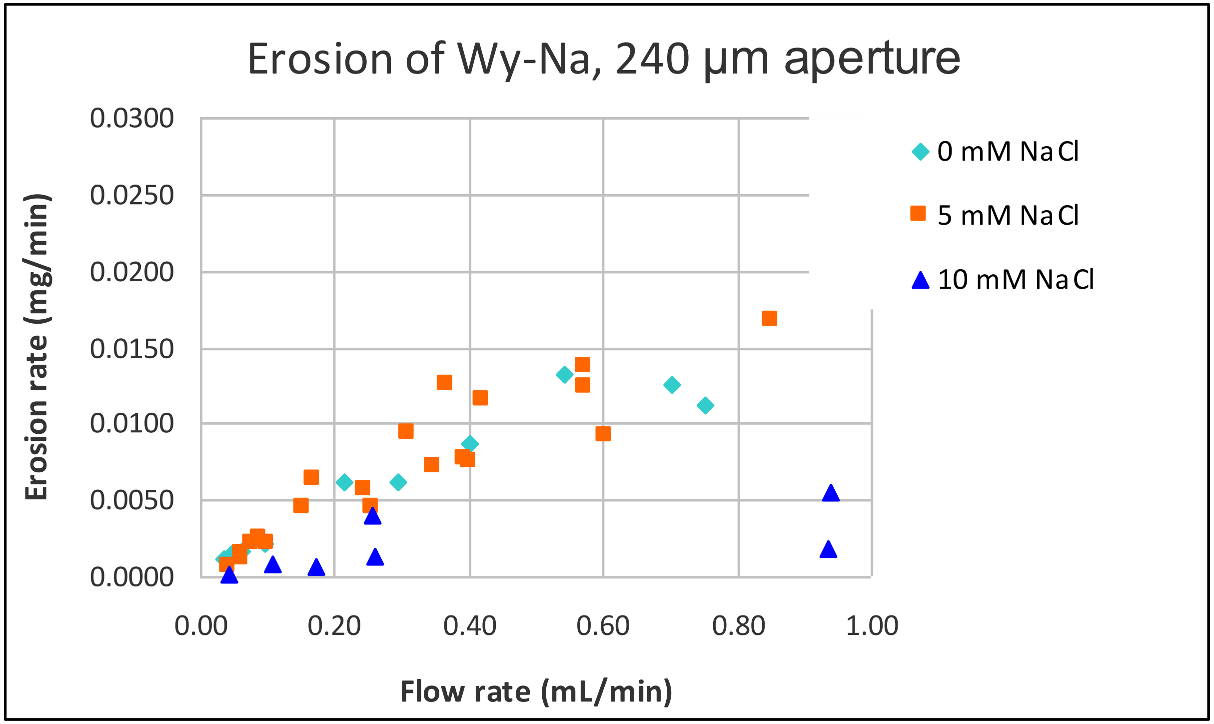
# Results 240µm aperture




Salinity from low to higher
No difference between DI and 5 mM.

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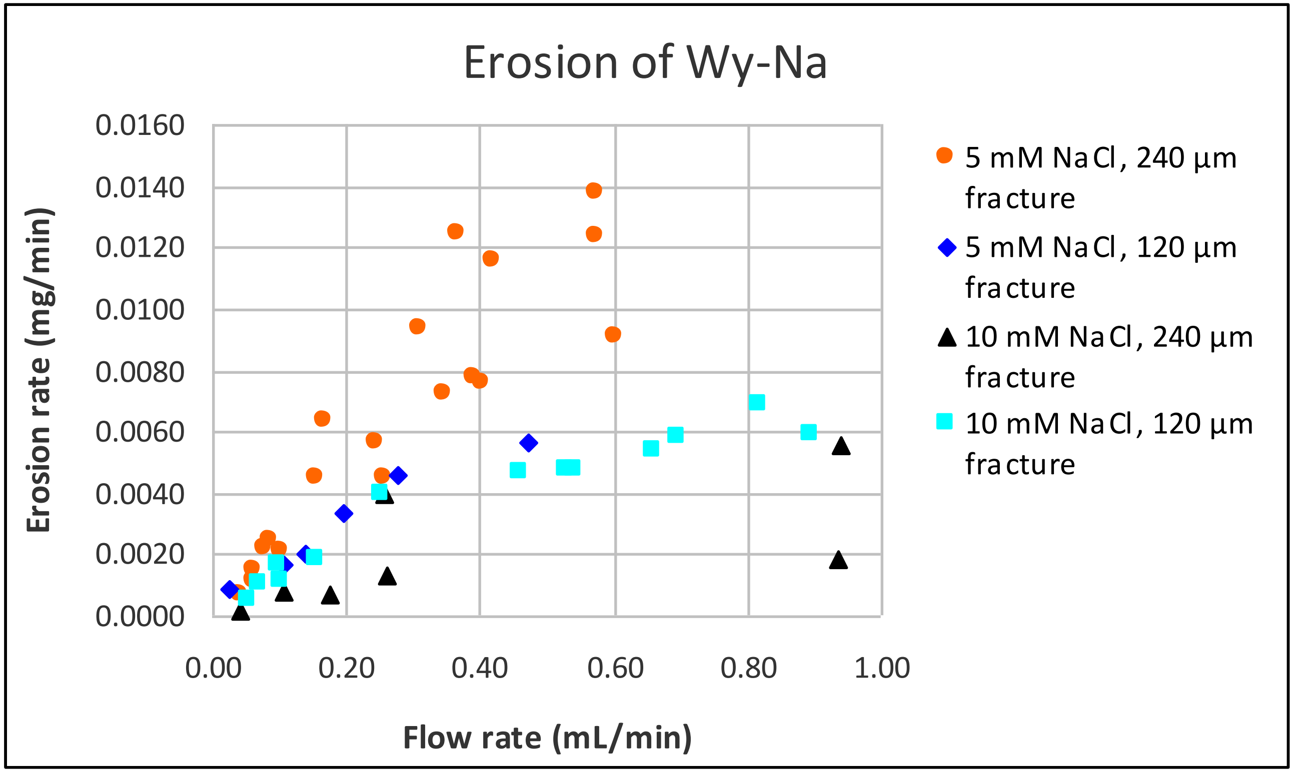
# Comparison: 120 and 240µm aperture




At 5 mM erosion rate is higher for the wider fracture

At 10 mM erosion rates are the same if flow rate is converted to velocity

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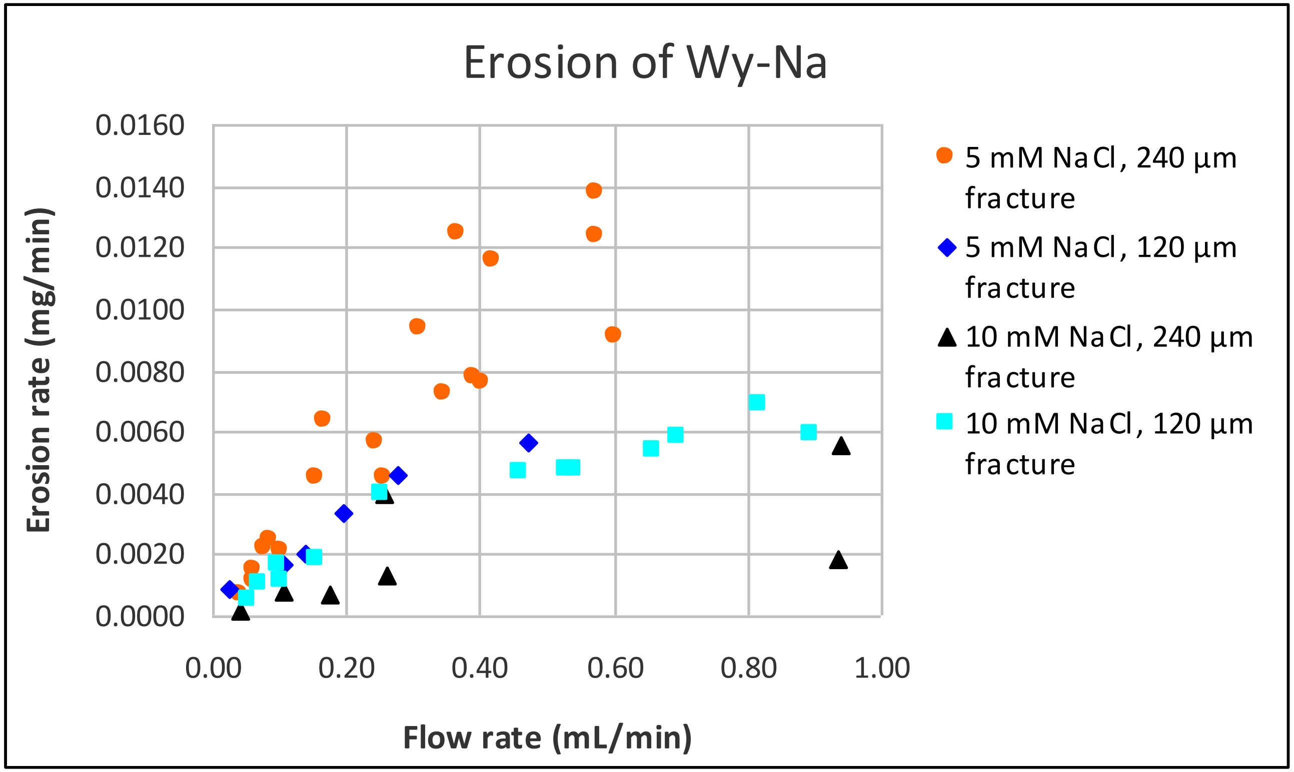
# Comparison: 120 and 240µm aperture




Unit erosion rate (normalized to area) for the lowest flow rate at 5 mM

120 µm:23 kg/m$^2$/yr

240 µm: 4-6 kg/m$^2$/yr

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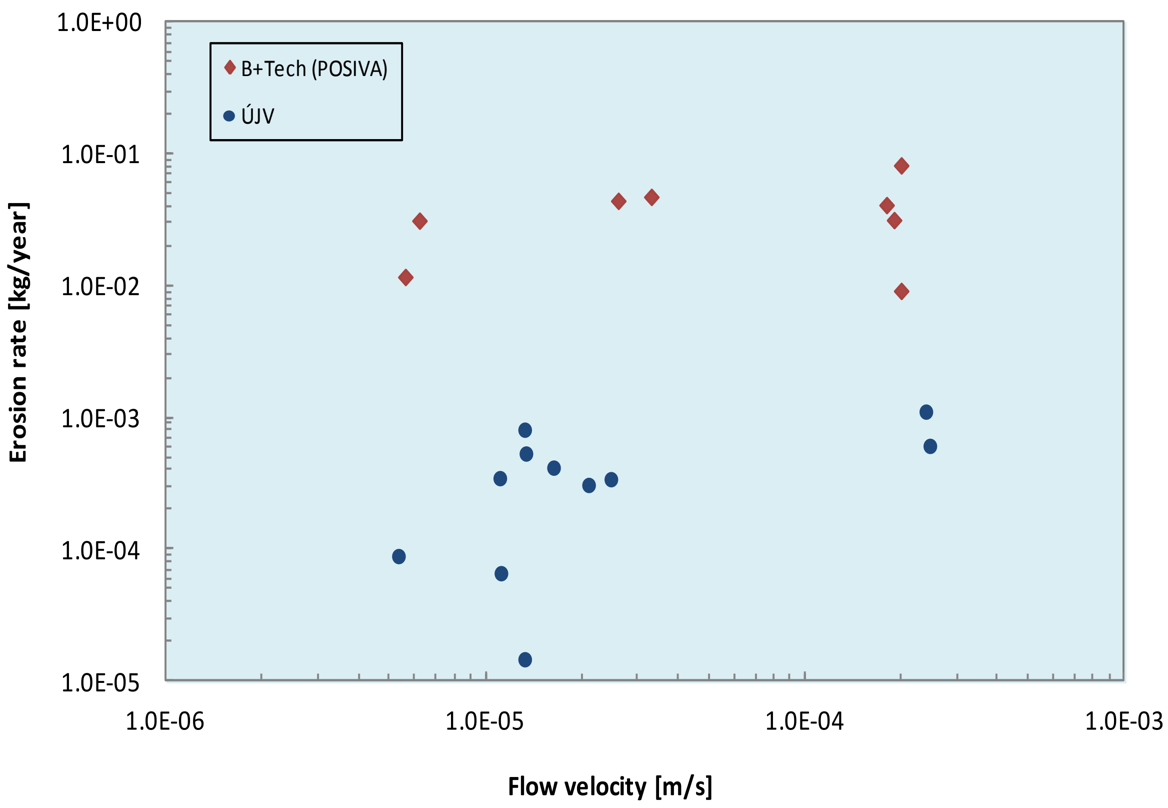
# Unit erosion rates: CT;B+Tech; ÚJV Řež

CT: 23 kg/m$^2$/yr:  Wy-Na, 5 mM NaCl, 120 µm
CT: 4-6 kg/m$^2$/yr: Wy-Na, 5 mM NaCl, 240 µm

B+Tech: 3.2x10$^{-5}$ kg/m$^2$/s: Wy-Na, Grimsel GW, 45° slope angle, 1 mm(D2.5)
B+Tech: 1000 kg/m$^2$/yr: Wy-Na, Grimsel GW, 45° slope angle, 1 mm (D2.5)

ÚJV Řež : 0.4-55 kg/m$^2$/yr: B75 bentonite, DI, velocity 200-9000 m/a, 0.15-2 mm (D2.5)

# Comparison:B+Tech; ÚJV Řež (D2.5)




Wy-Na, WyNa/Ca 1 mm

B75 bentonite 60% mmt
Lower CEC than Wy-mmt
Significant content of Ca/Mg

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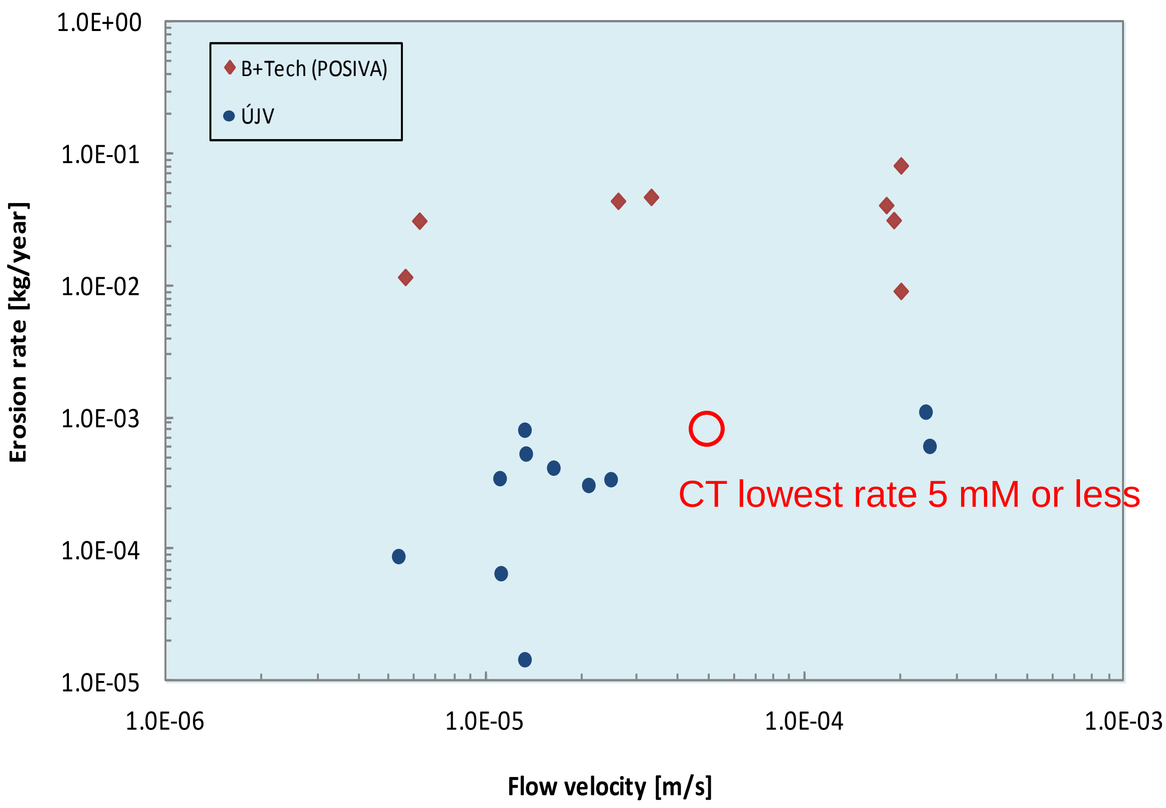
# Comparison:B+Tech; ÚJV Řež (D2.5)




Wy-Na, WyNa/Ca 1 mm

B75 bentonite 60% mmt
Lower CEC than Wy-mmt
Significant content of Ca/Mg

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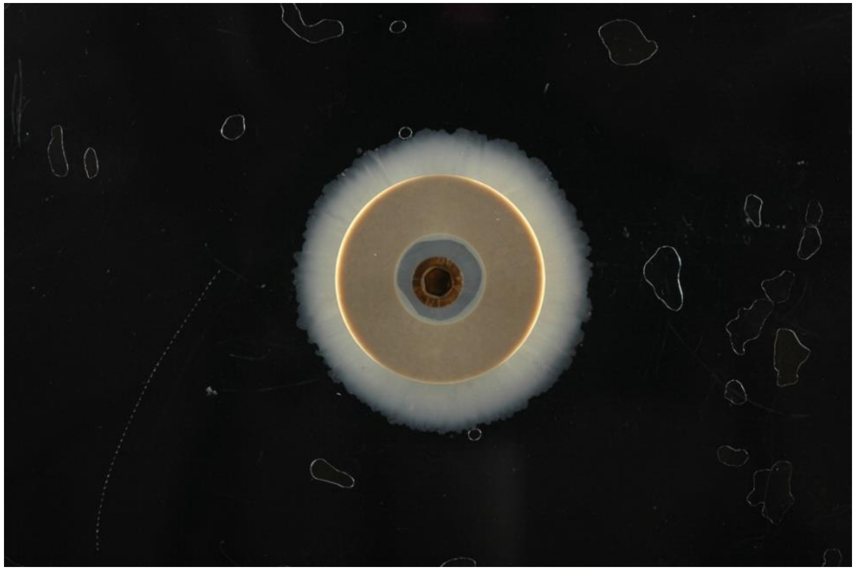
# Hysteresis effects

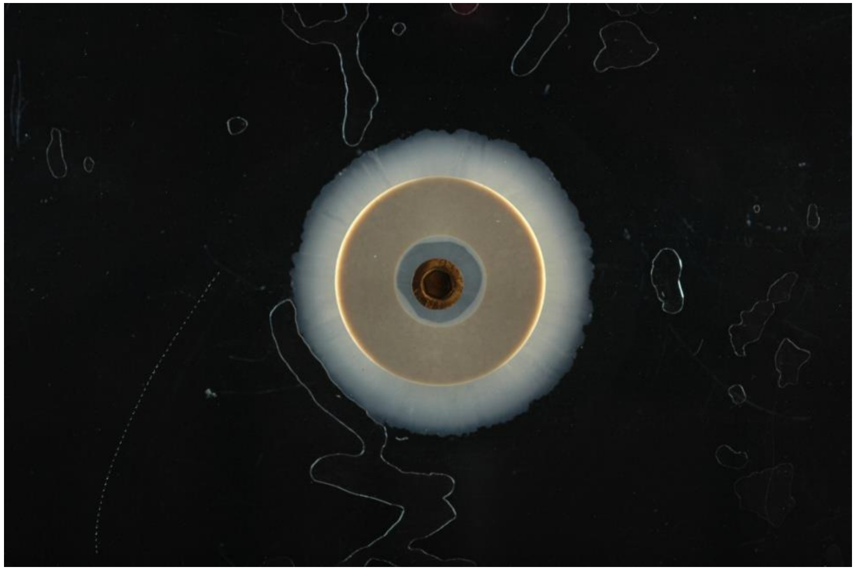
Increasing NaCl conc.

25 mM NaCl No erosion



Decreasing NaCl conc.

5 mM NaCl limited erosion starts



Wy Na with NaCl solution

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# Hysteresis effects


Preparation

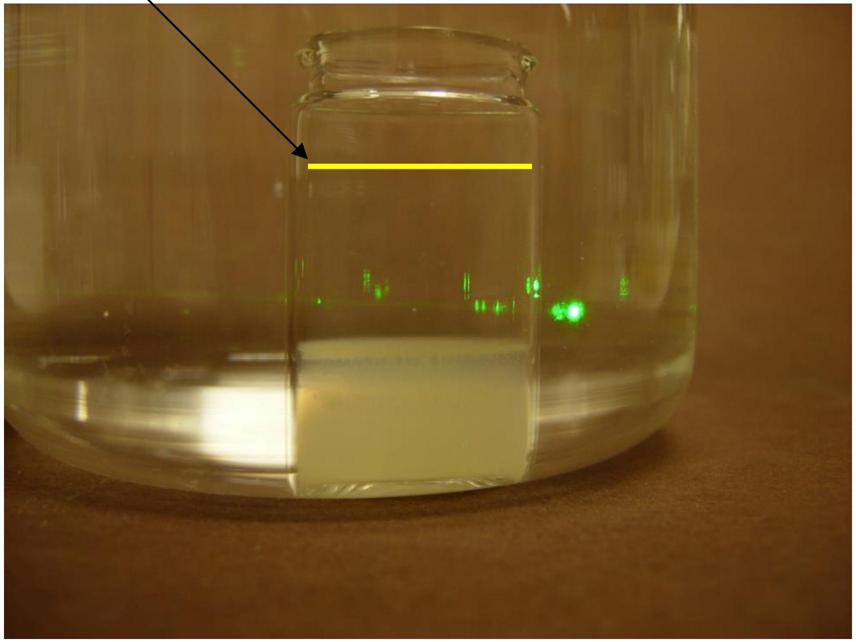
0.05 g Wy-Na in 10 ml 100 mM NaCl

The whole vial is put in 500 ml DI water

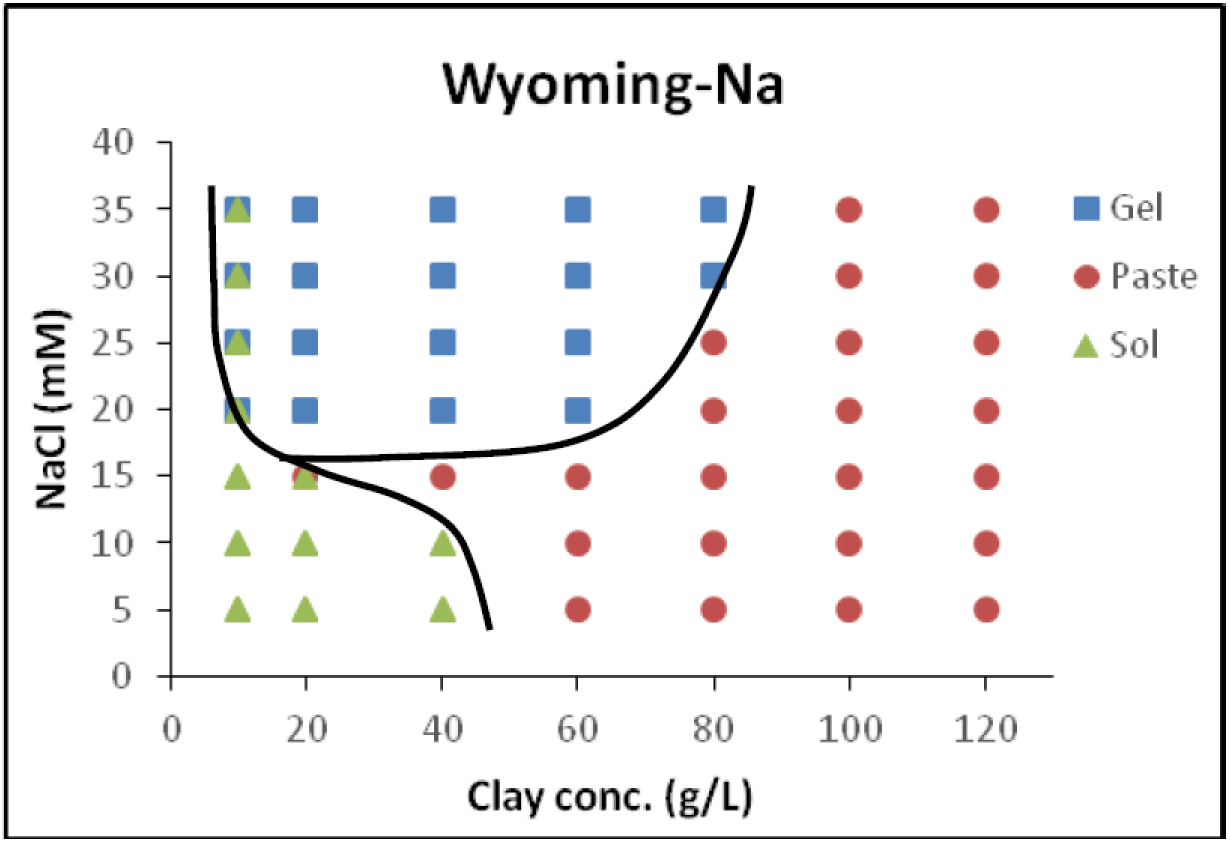
Gel is still there after 5 years albeit NaCl concentration is only 2 mM

# Hysteresis effects


Approximate initial height of gel



# Wy-Na phase diagram



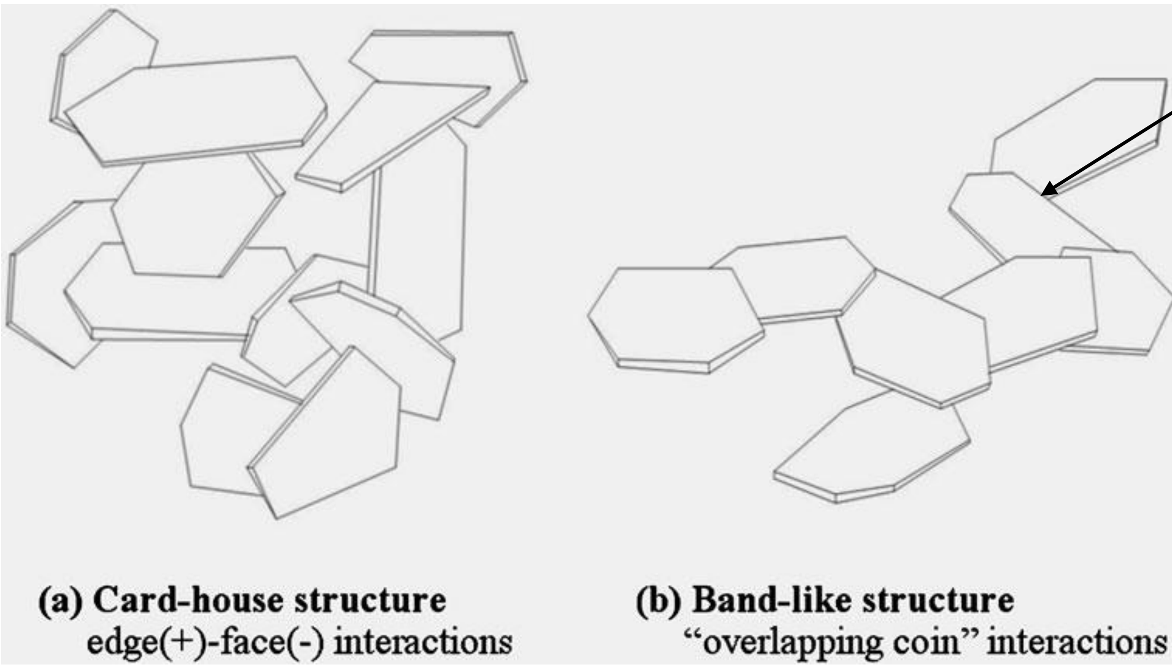


Hansen, Hedström 2014 to be submitted

Under increasing salinity conditions
erosion stops at the paste/gel border as expected

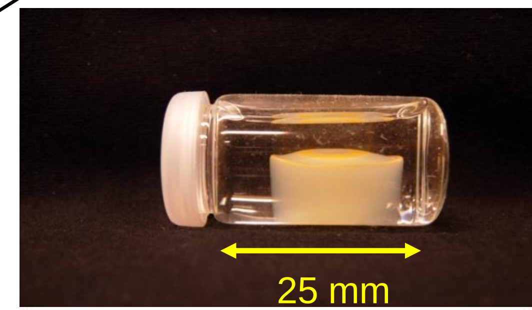
# Empty house or speckled band?

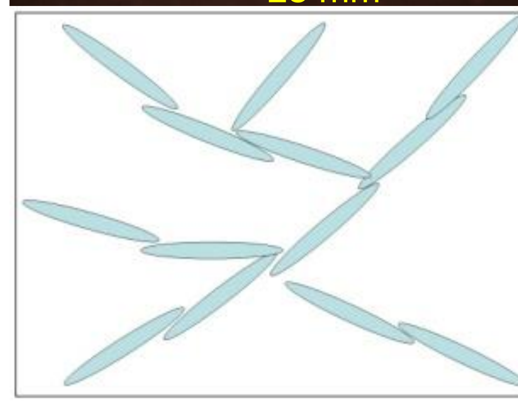
Hypothetical gel structures




Goh R., Leong Y.-K. & Lehane B..
*Rheol. Acta.* **50**, 29-38 (2011).

Possible interactions
edge(+) – face(-)
van der Waals



Branched band-like structure

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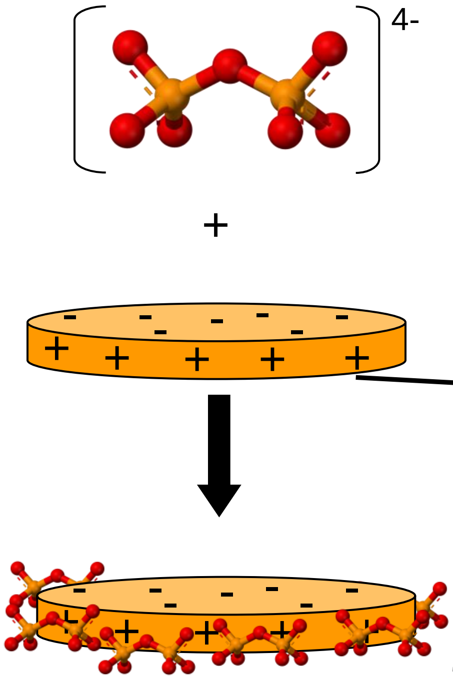
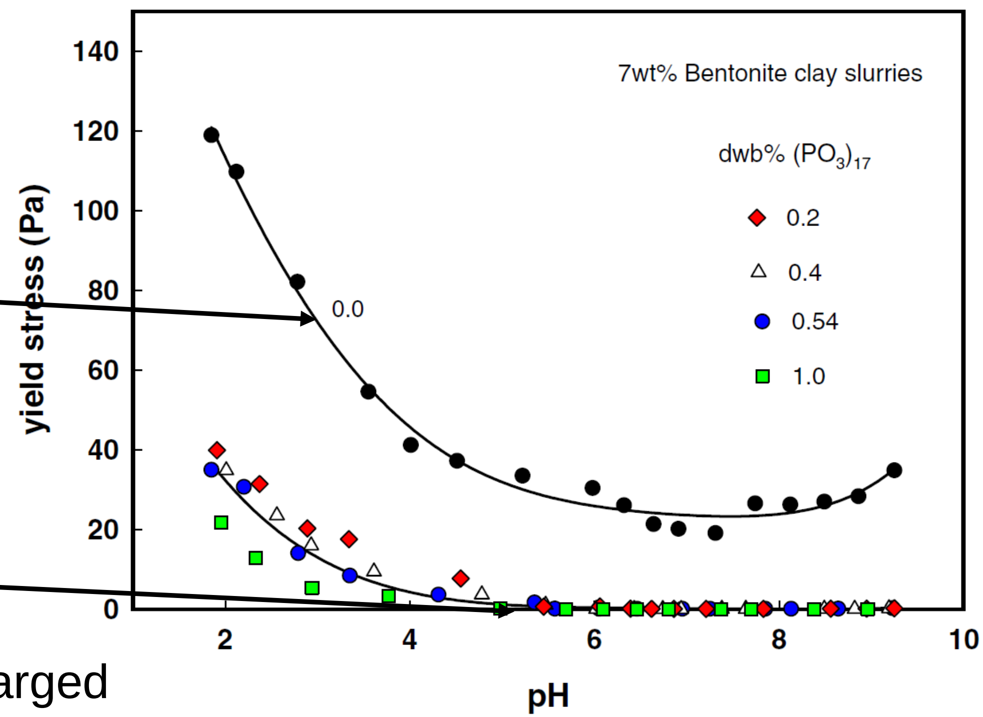
# Edge-face interaction gives attractive gel effect of pyrophosphate




Yield stress in 7 wt% bentonite slurry



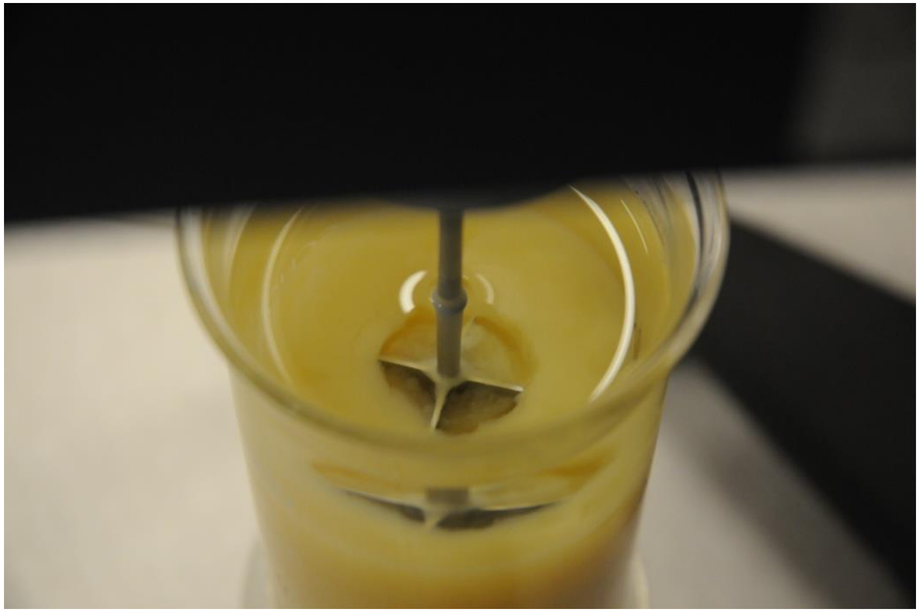

Both edge and face negatively charged
gel → sol

Goh *et al.* (2011).

Indirect “proof” of positive edge charge

# Rheology of “attractive” gels

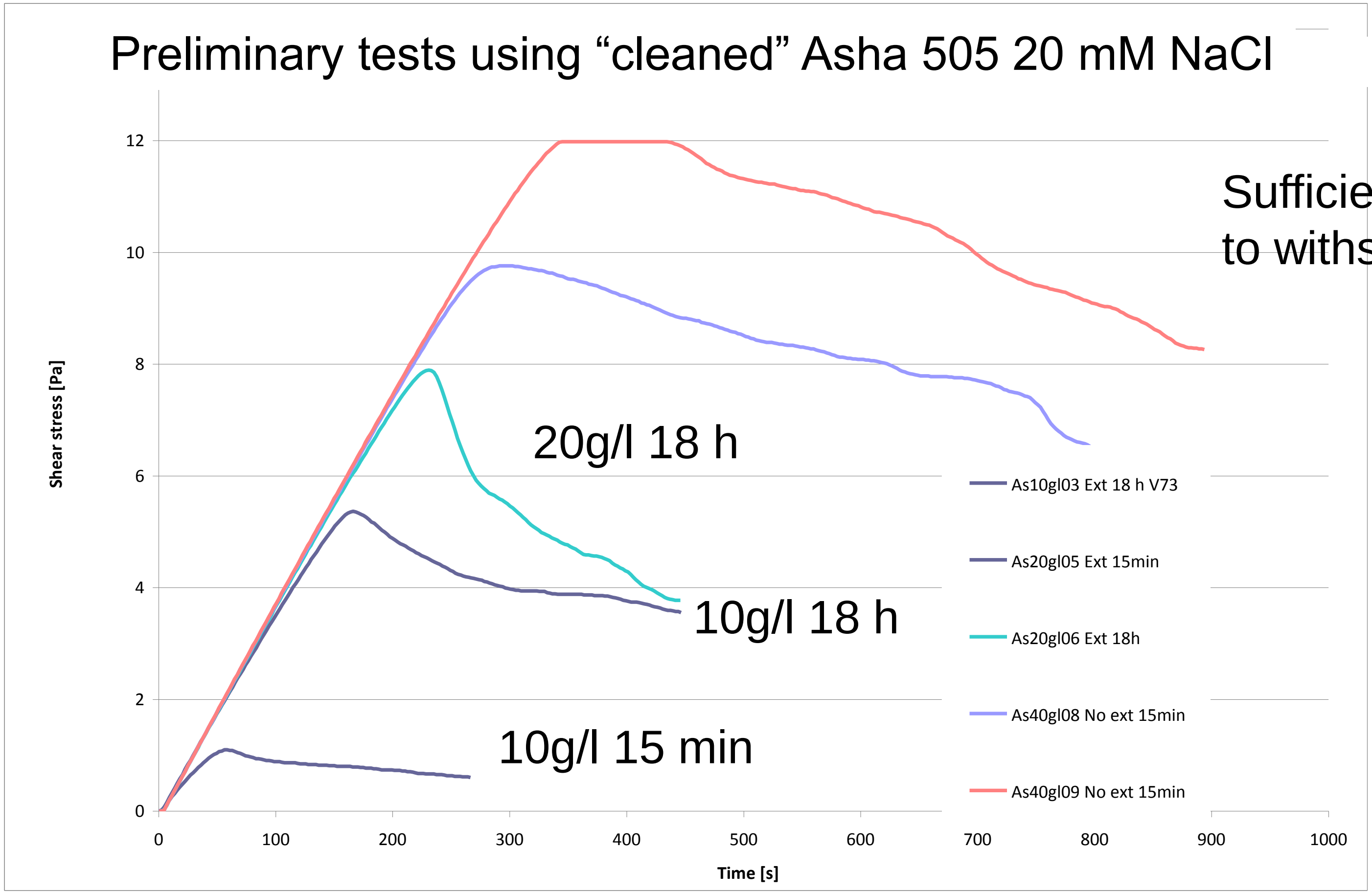
Preliminary tests using “cleaned” Asha 505 20g/l in 20 mM NaCl



Data from these types of experiments

- Need to be communicated
- Theory should explain this behaviour

# Rheology at relevant boundary conditions




Sufficient yield strength
to withstand expected shear

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# Observations in the context of gel/sol properties

- Mechanical properties
  - Attractive gel – yield strength – no erosion
  - Sol – viscosity – erosion
- Without the formation of gel erosion rates may be high
  - 4-20 kg/m$^2$/yr Wy-Na, 0.4-55 kg/m$^2$/yr B75 (Divalent ions)
- Role of gravity (B+Tech) 1000 kg/m$^2$/yr!
  - What would be the effect of structured fracture?
- Hysteresis – coming from higher to lower salinity gives lower erosion rates

# Observations

- Including edge-face forces crucial for
  - attractive gel
  - hysteresis effect (most likely)
- Na-montmorillonite still difficult to understand
- Mixed Ca/Na system – CCC is not a defined quantity
  - Caused too optimistic view on the erosion problem
  - "CCC" becomes at least 2-dimensional "sol-formation zone"
    - SKB-TR 09-34

- Looking forward to have in-depth discussion with the other groups doing experiments!

# 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 no 295487, the BELBaR project.

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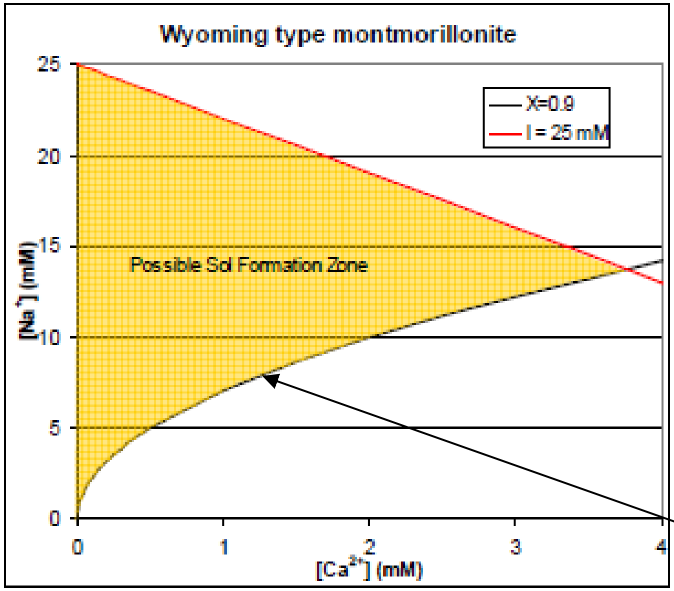
# Mixed Ca/Na clays with excess ions

Ionic strength 25 mM




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

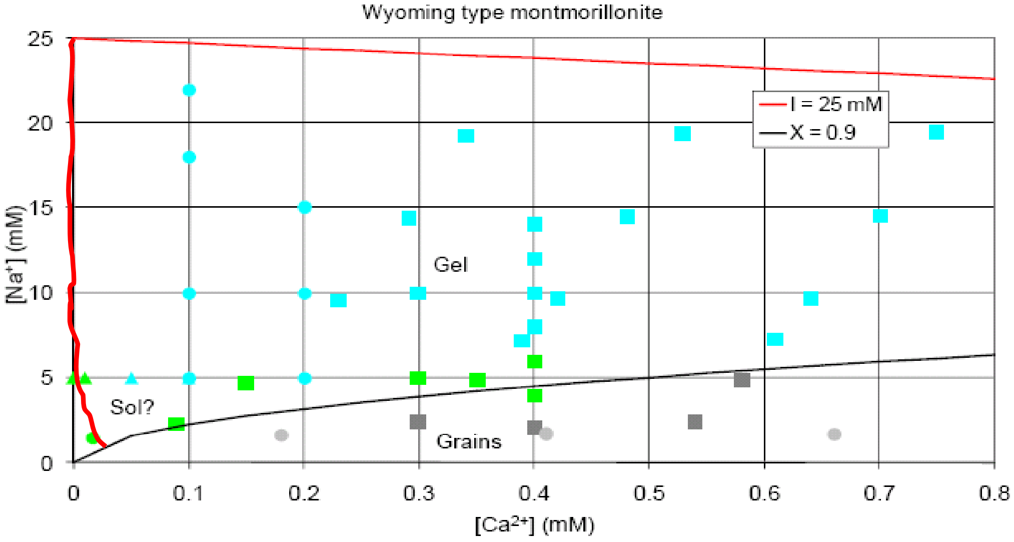
Ion-exchange equilibrium key concept

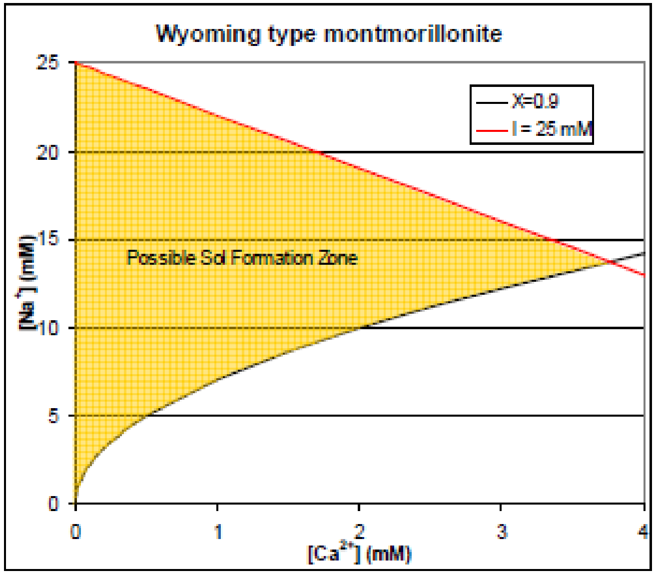
Note that chloride is the anion

$$\left[Na^{+}\right] = \sqrt{\frac{K_{GT}(1-x)^{2}\left[Ca^{2+}\right]}{x}}$$

90% calcium in exchange position
assuming $K_{GT}$=4.5

# The experimental sol formation zone




- 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
- Small SFZ →Possible to control ionic strength using 1:1 salt e.g. NaCl
- Questionable if this is the usual correlation effect seen in parallel clay layer configuration and divalent cations. More tests needed!