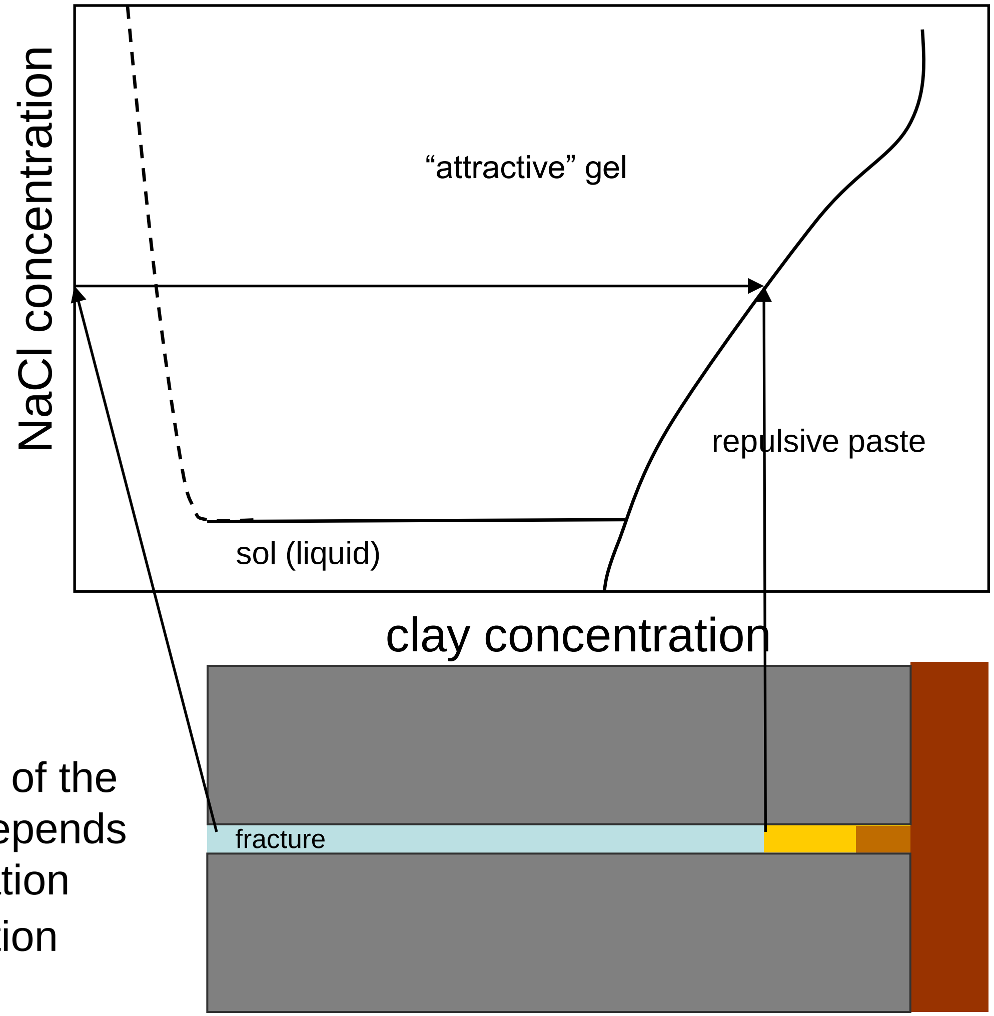
Update on erosion experiments

Magnus Hedström, Emelie Hansen

Clay Technology AB

BELBaR WP2 & WP4 meeting
Prague, 30-31 Oct 2014

Montmorillonite state/phase diagram



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

Deposition hole bentonite buffer

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Behaviour of montmorillonite at low ionic strength

decreasing salinity →

montmorillonite

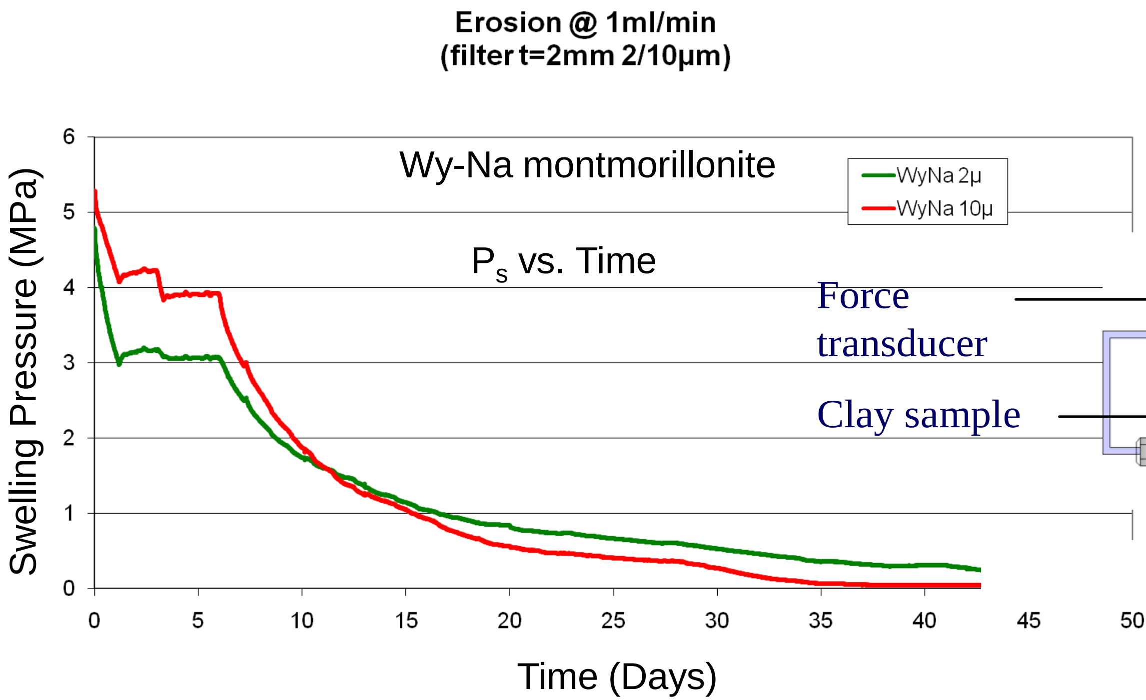
attractive gel — sol (liquid)

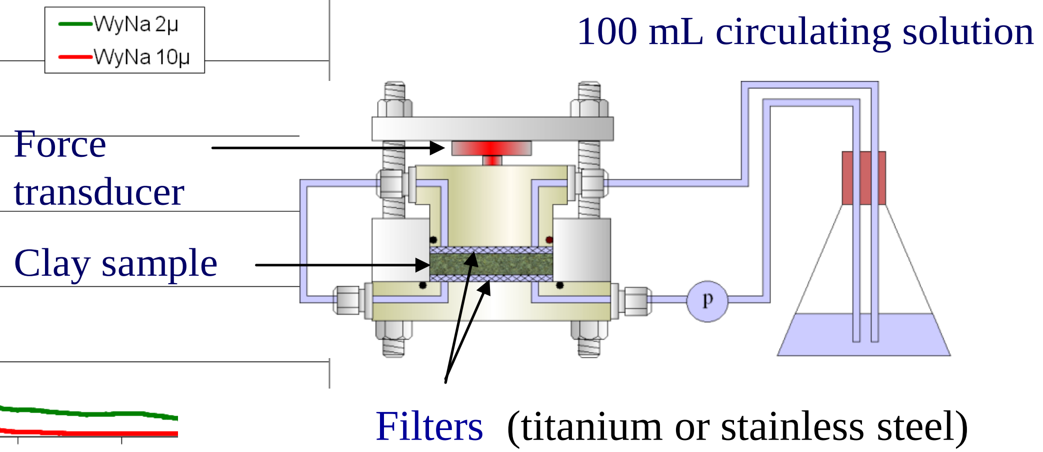
yield strength — viscosity

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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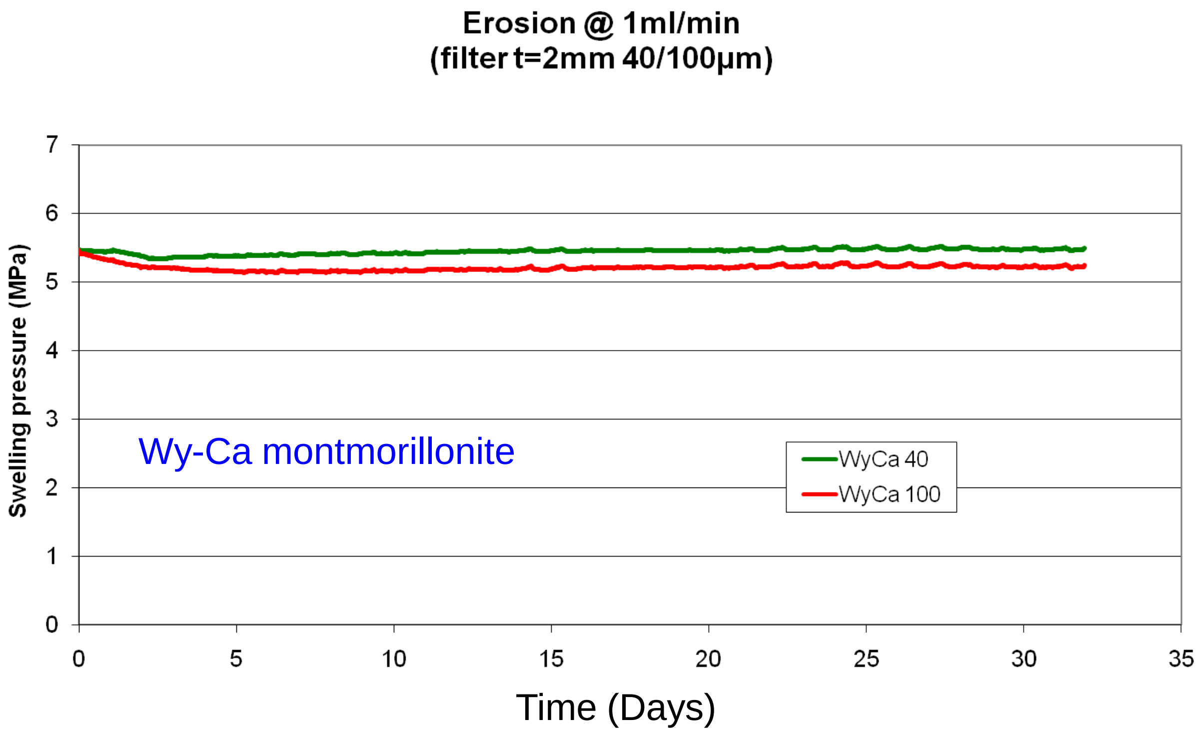
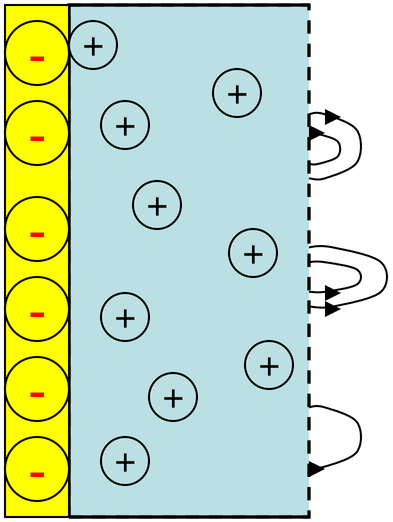
No erosion with Ca-montmorillonite



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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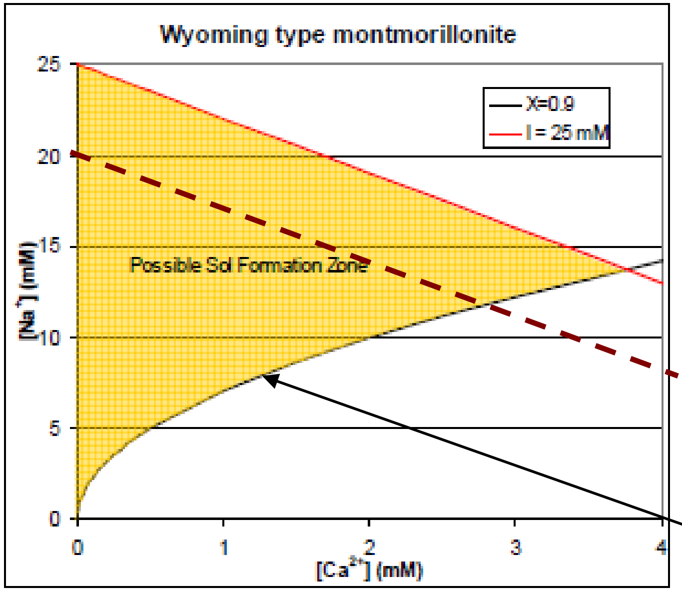
Mixed Ca/Na clays with excess ions

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

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

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

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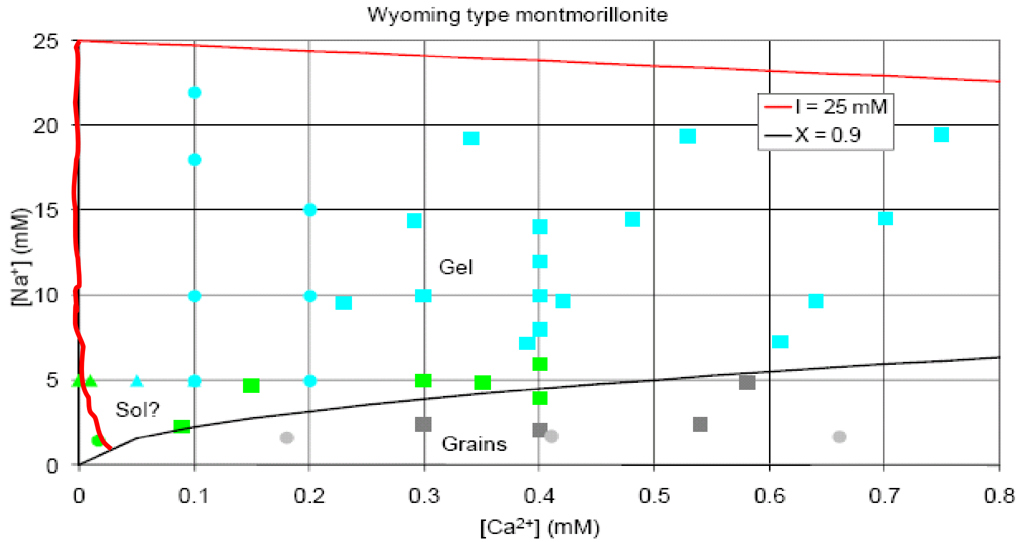
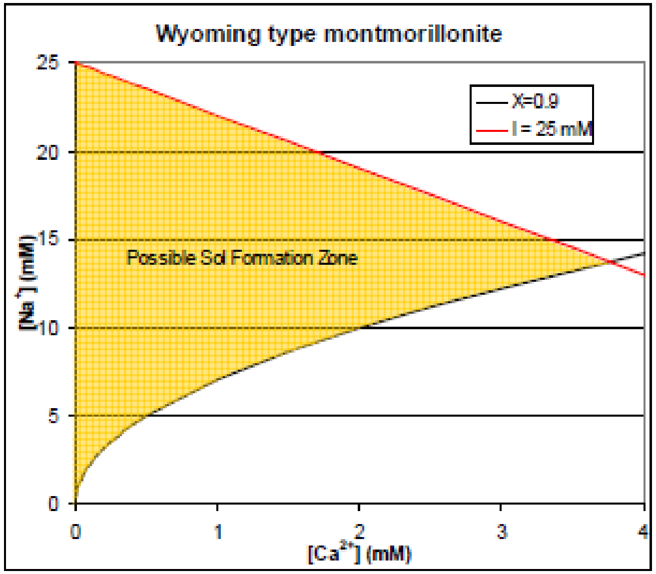
The experimental sol formation zone





Birgersson et al. SKB TR-09-34

- 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

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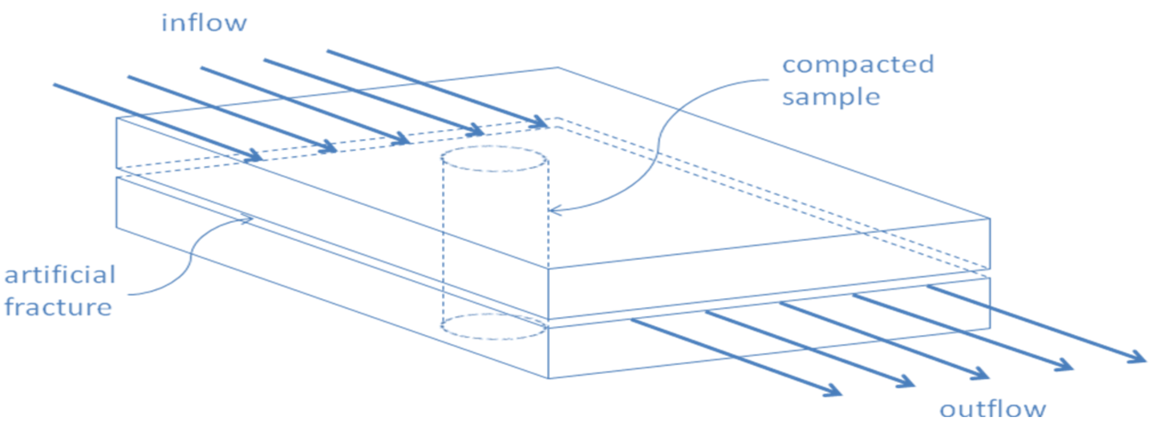
Focus on Na- or Ca/Na-montmorillonite

Montmorillonite from MX-80

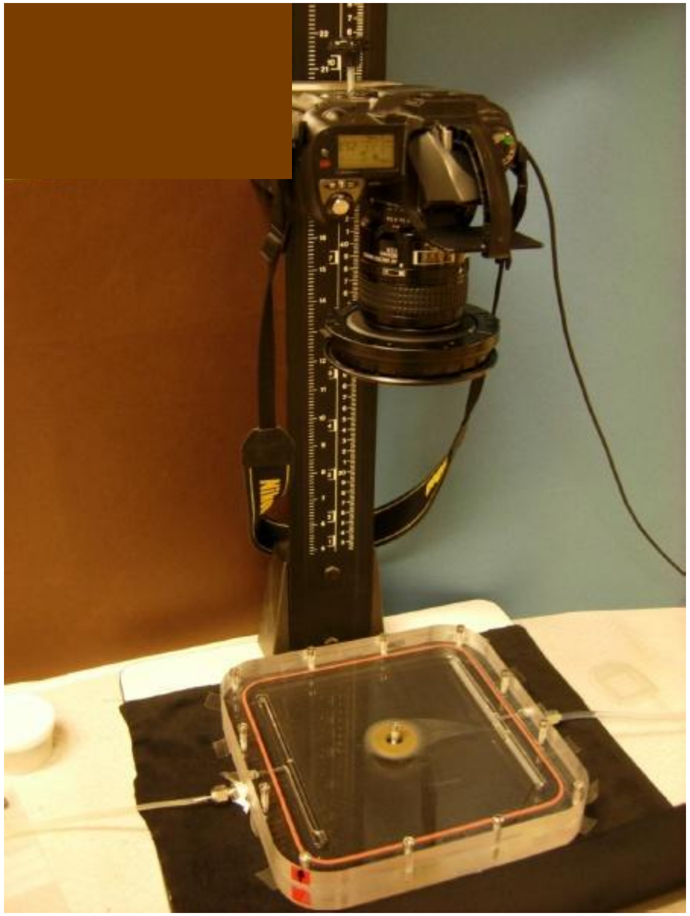
DI water, NaCl solution, NaCl + ~µM $CaCl_2$
Sometimes NaOH added to give pH 9-10
No effect of pH on erosion or formation of attractive gel

Phase diagrams Na-mmt, NaCl(aq)
MX-80 (Wy-Na)
Asha 505 (Ku-Na)

Erosion in artificial fractures

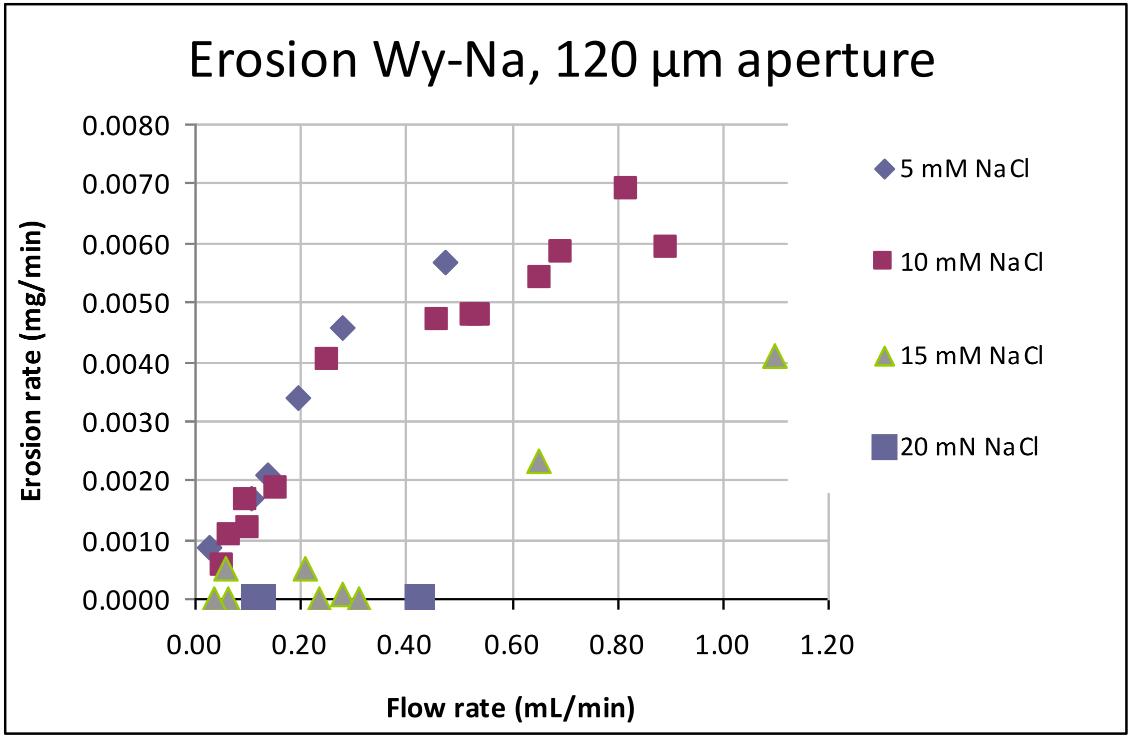


Schatz et al. POSIVA 2012-44.



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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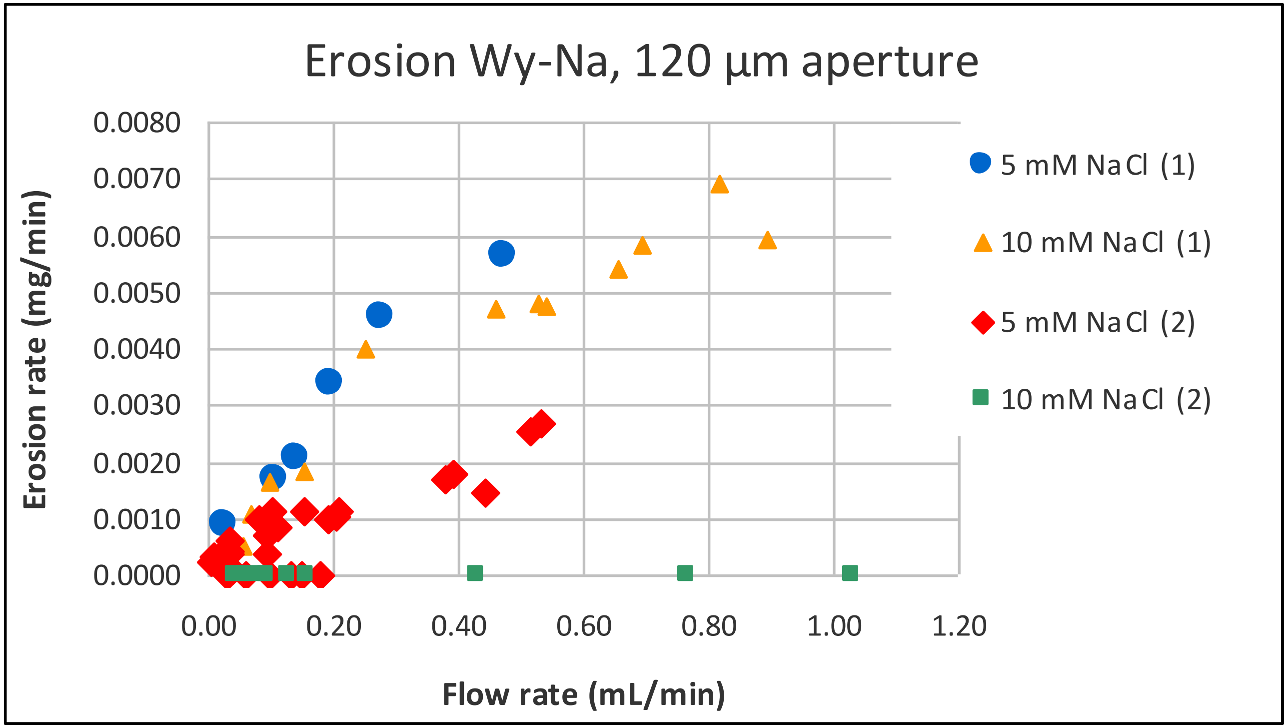
Comparison of erosion rates



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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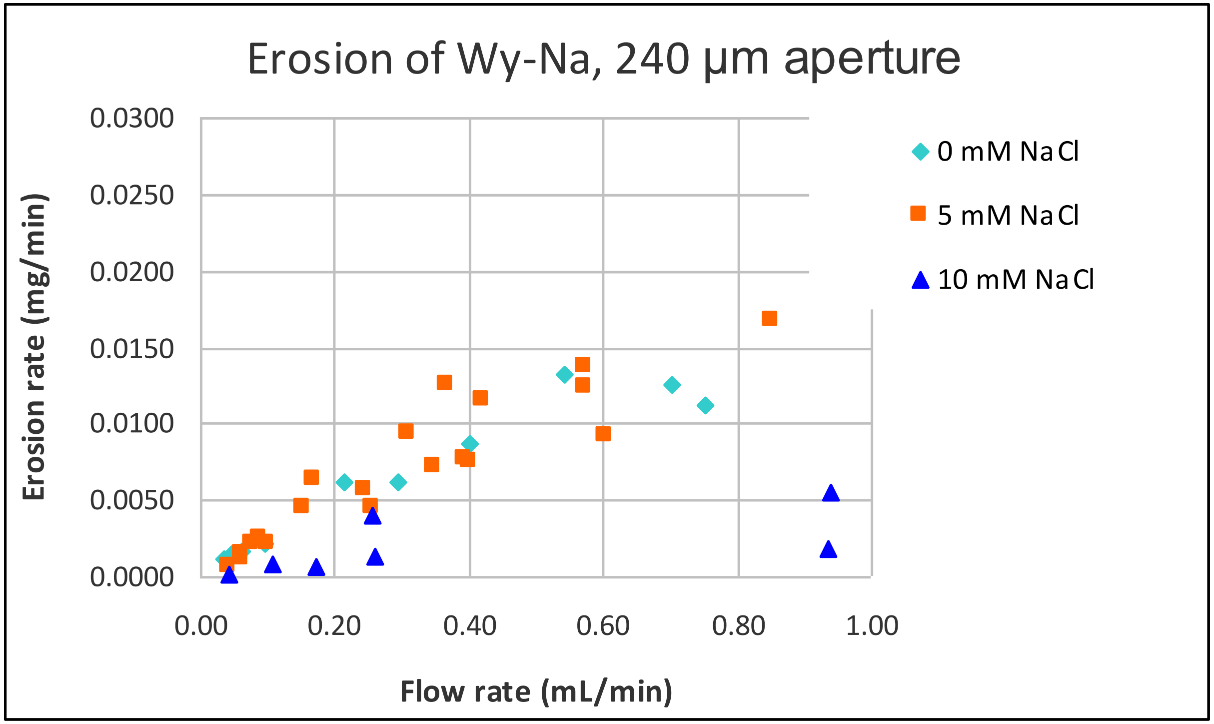
Results 240µm aperture



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

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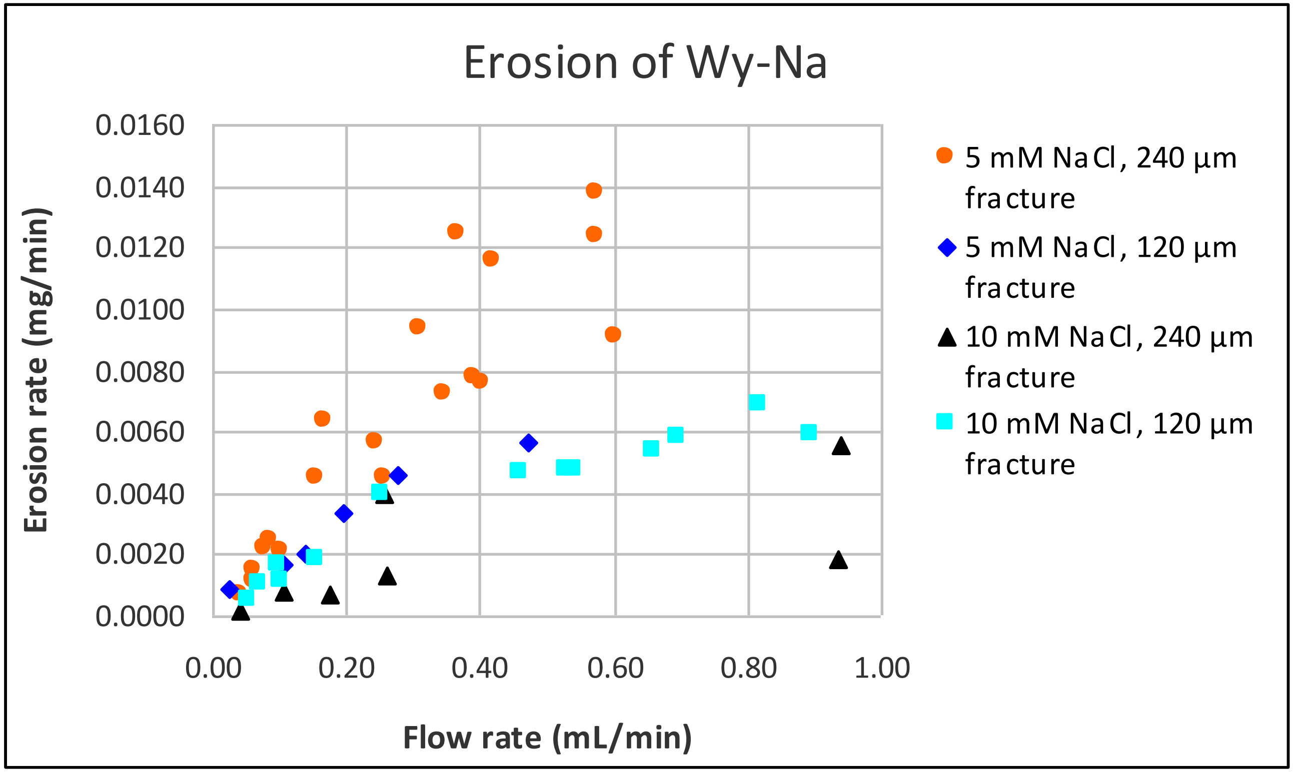
Comparison: 120 and 240μm aperture



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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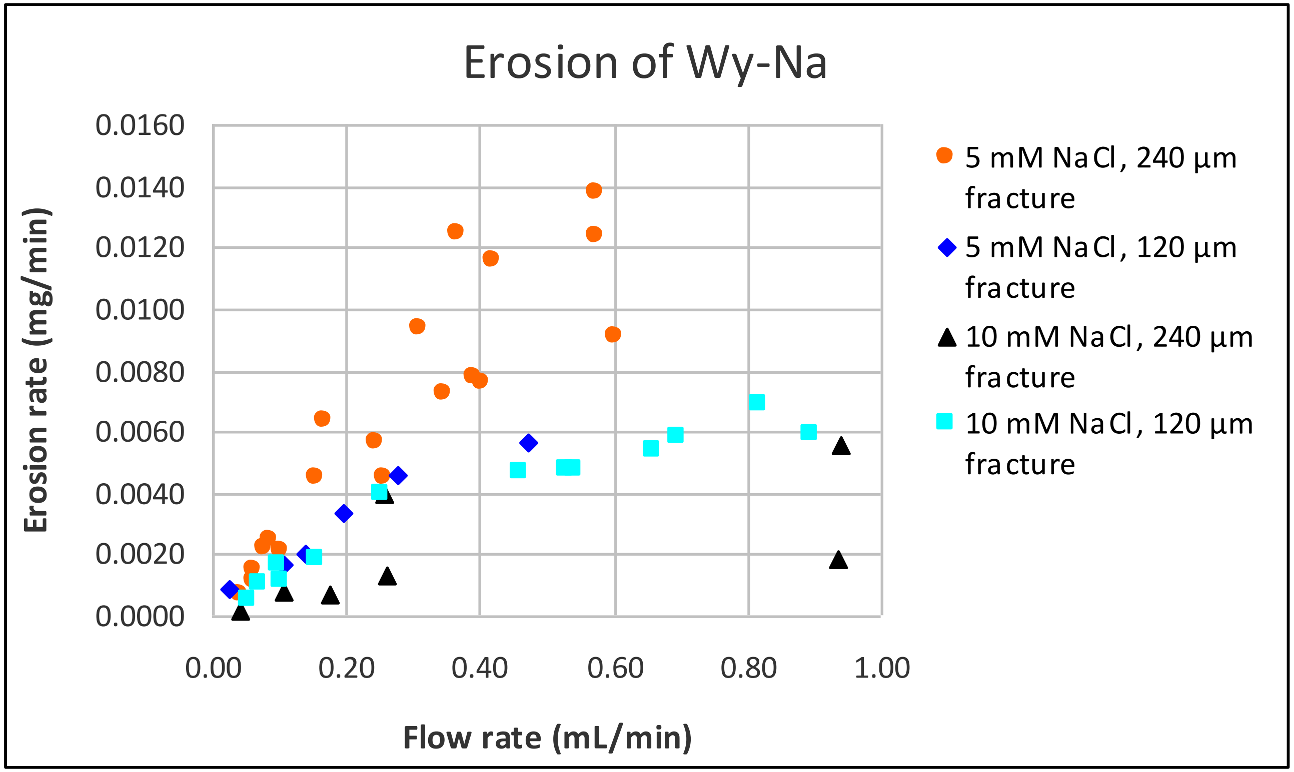
Comparison: 120 and 240µm aperture



Unit erosion rate (normalized to area) for the lowest flow rate at 5 mM
120 µm:23 kg/m²/yr
240 µm: 4-6 kg/m²/yr

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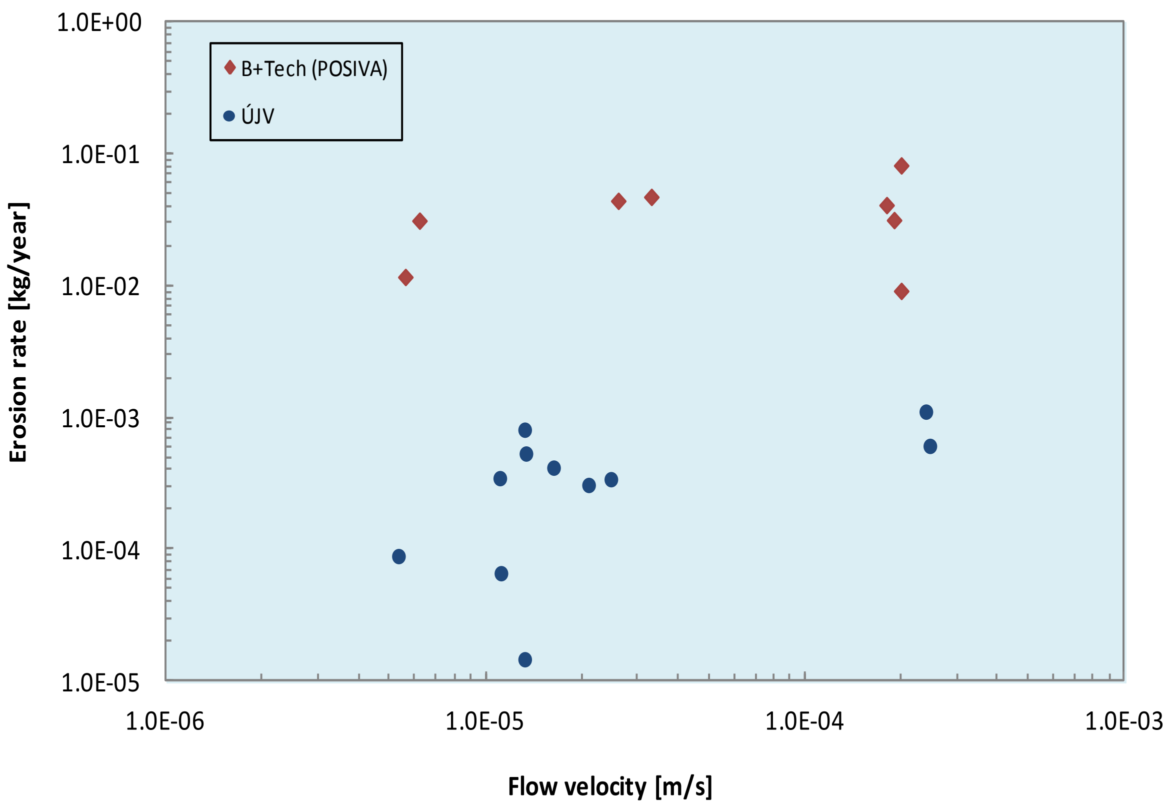
Unit erosion rates: CT;B+Tech; ÚJV Řež

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/yr, 0.15-2 mm (D2.5)

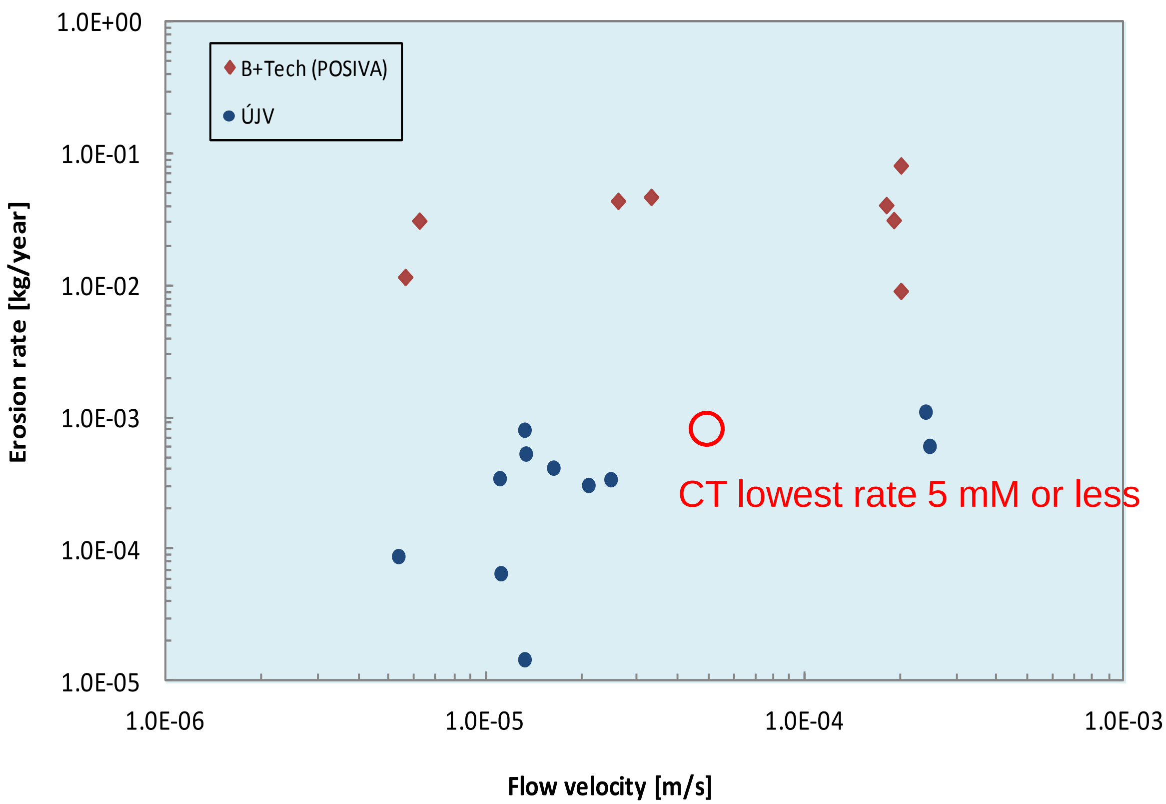
Comparison:B+Tech; ÚJV Řež (D2.5)



Wy-Na, WyNa/Ca 1 mm

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

Comparison:B+Tech; ÚJV Řež (D2.5)



Wy-Na, WyNa/Ca 1 mm

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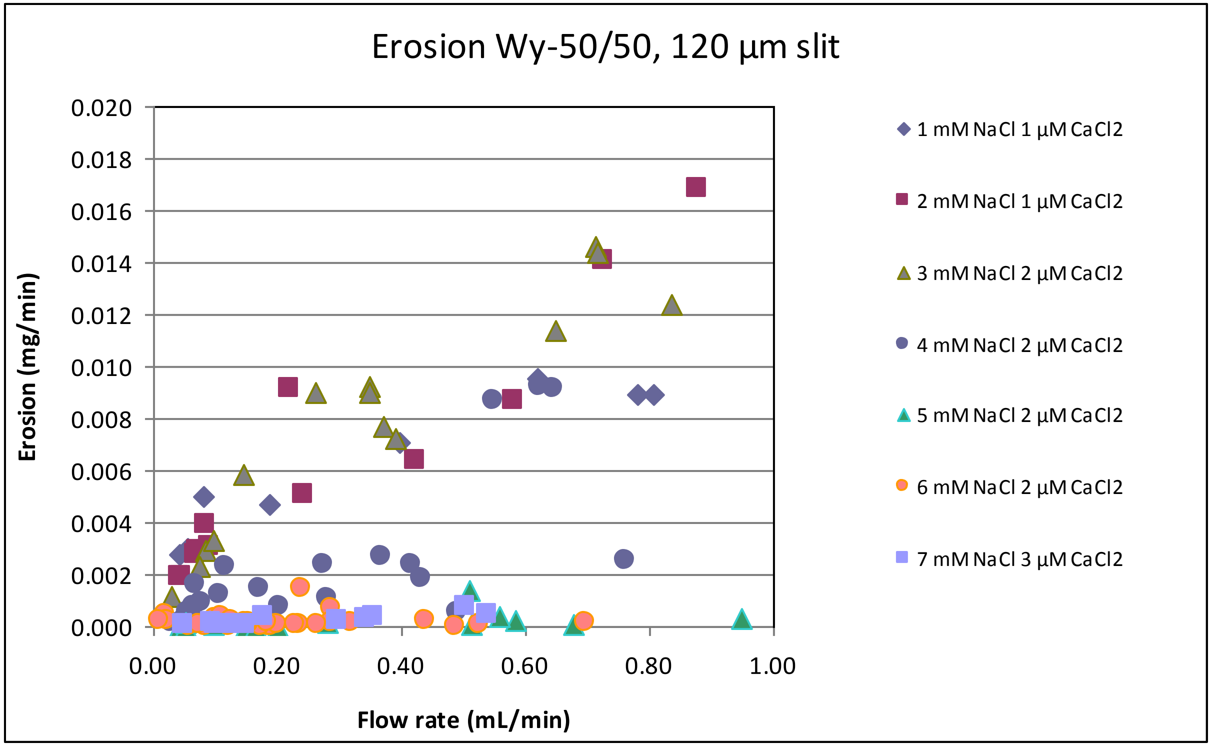
Wy-Ca/Na (50/50) 120 aperture



Increasing ionic strength: NaCl (mM) + $CaCl_2$ (µM)

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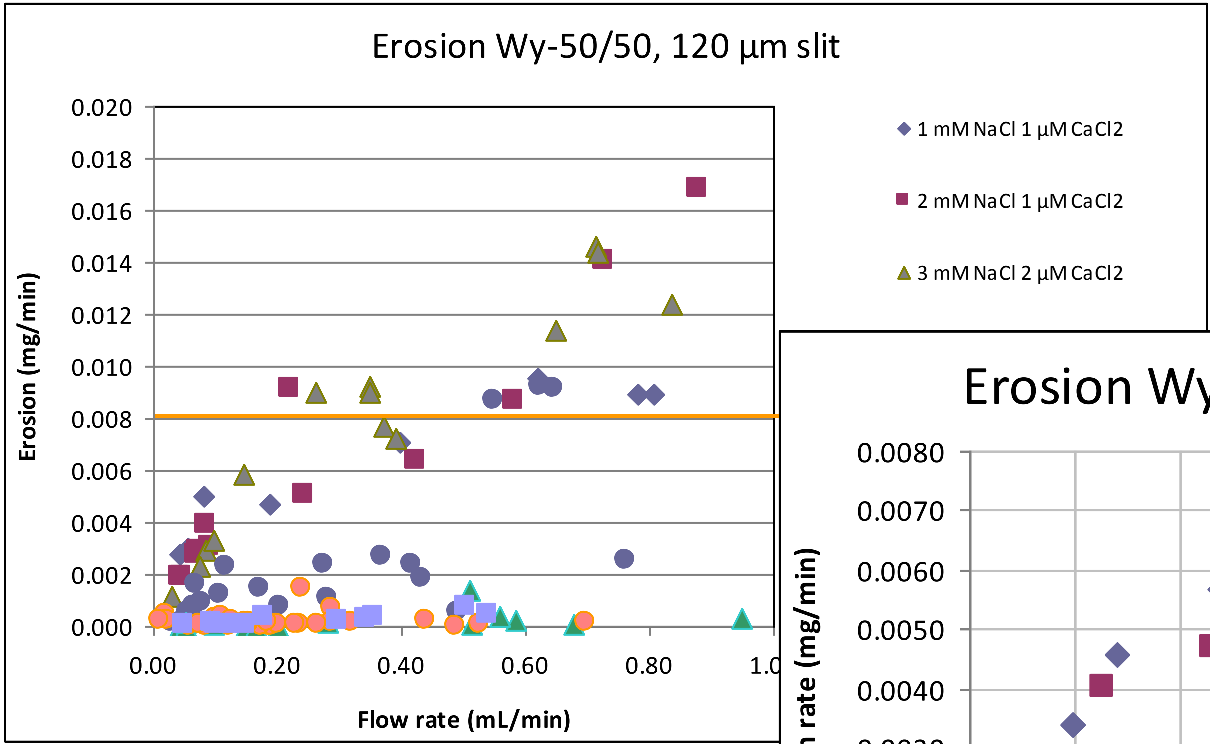
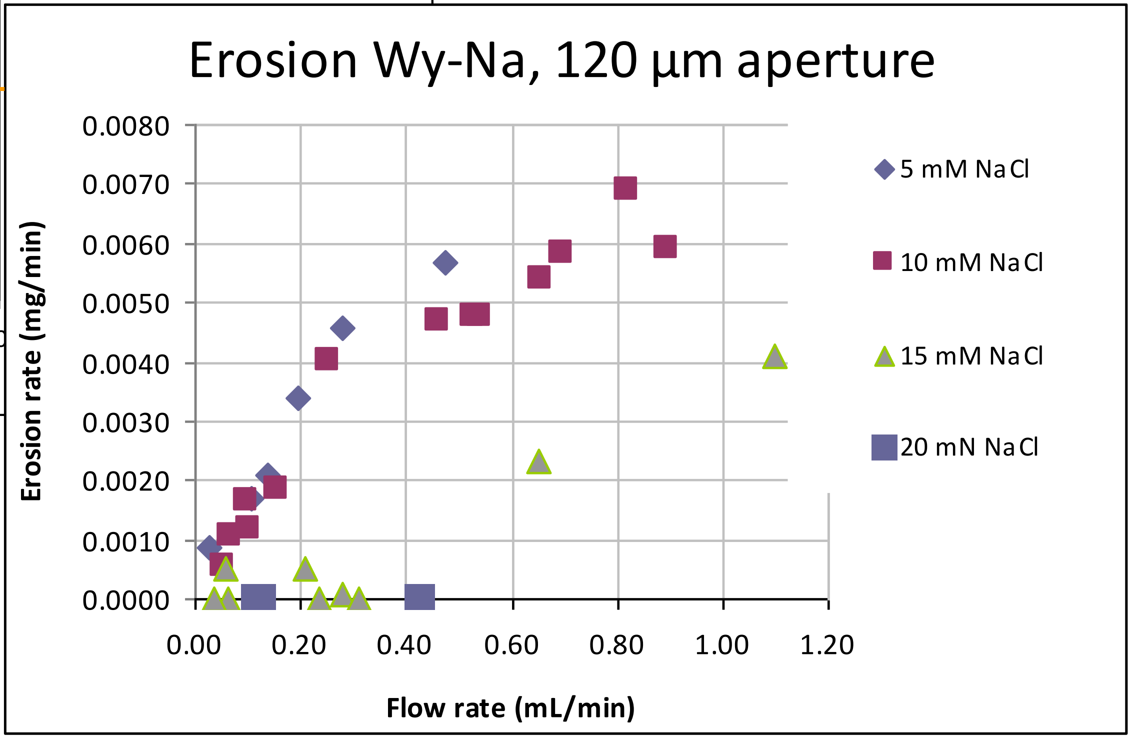
Wy-Ca/Na (50/50) and Wy-Na; 120 aperture





Unit erosion rates

23 kg/m²/yr Wy-Na 5 mM
500 m/yr

6 kg/m²/yr Wy 50/50 4 mM
600 m/yr

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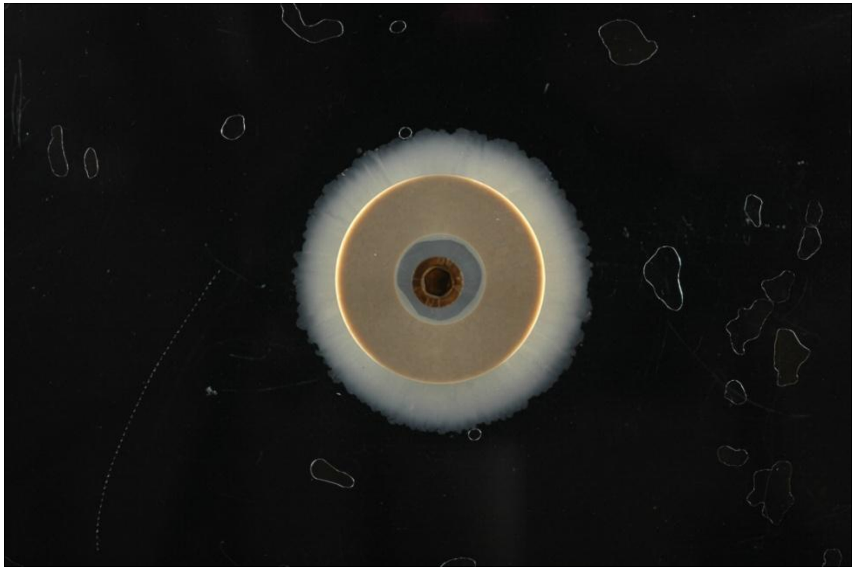
Hysteresis effects

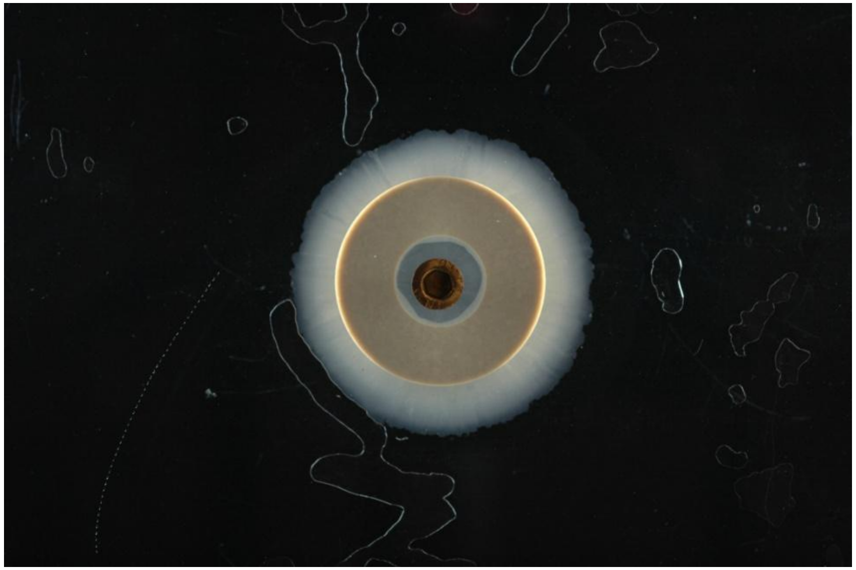
Increasing NaCl conc.

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

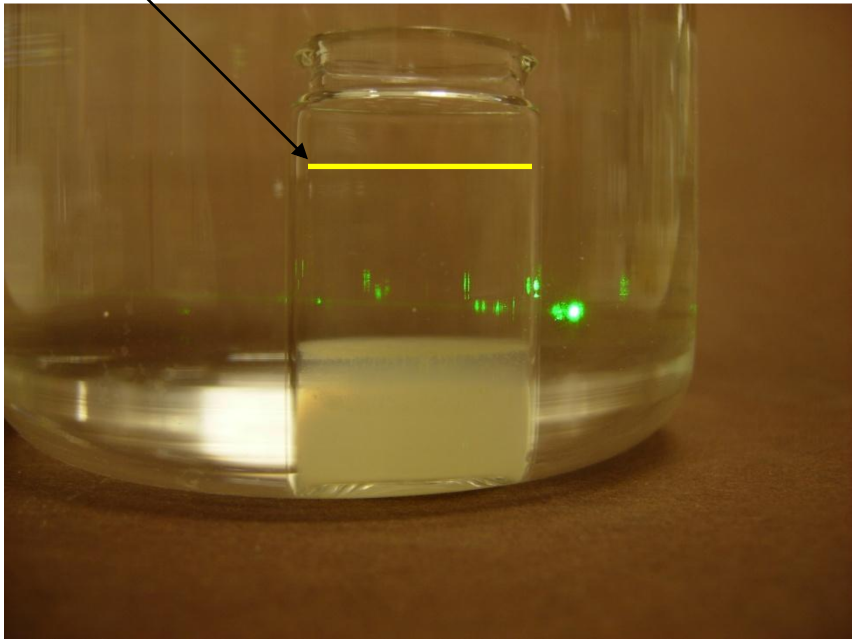
0.05 g Wy-Na in 10 ml 100 mM NaCl

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



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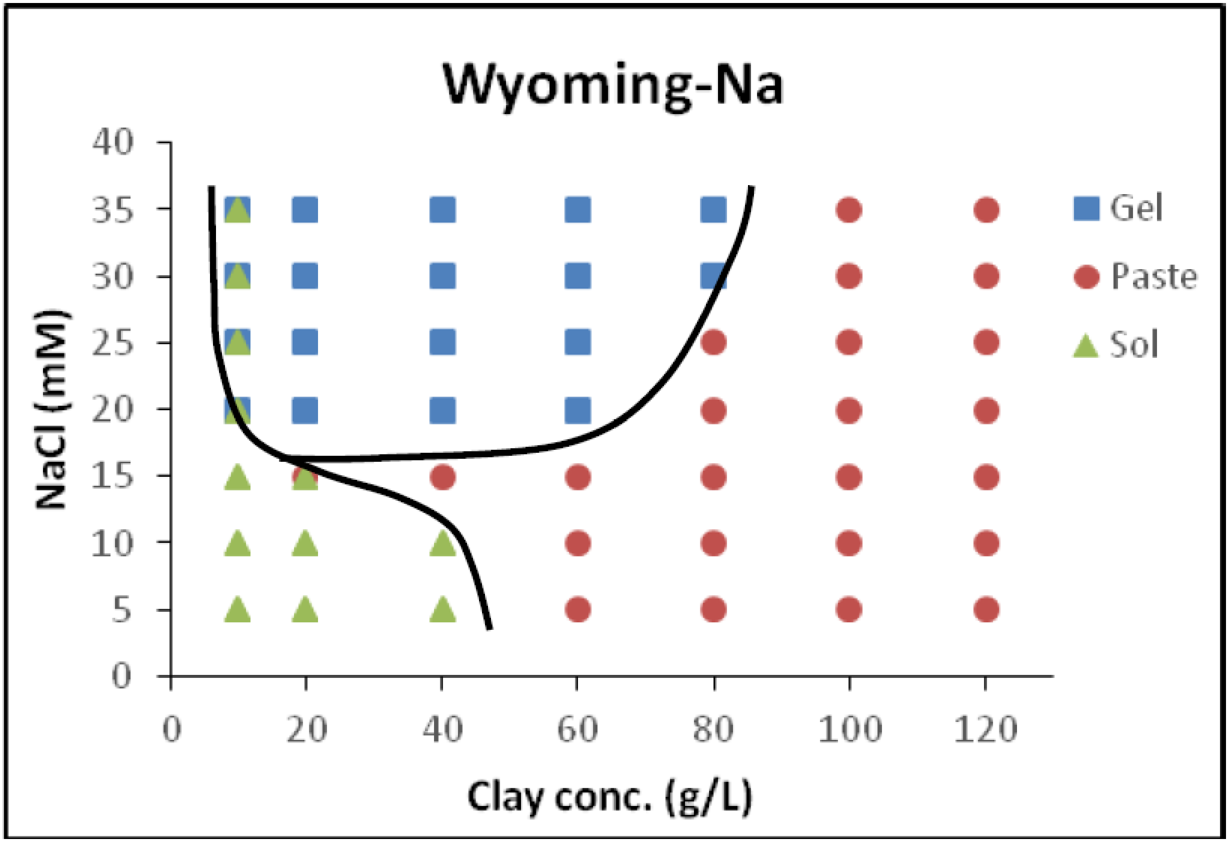
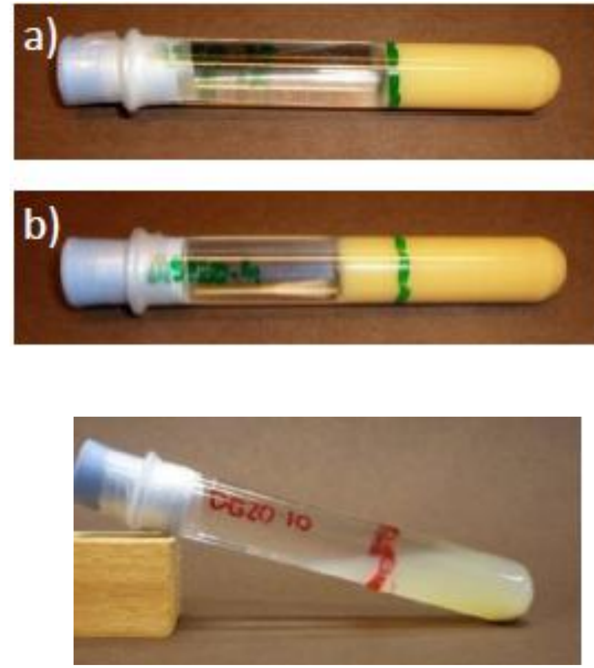
Wy-Na phase diagram





Hansen, Hedström 2014 to be submitted

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

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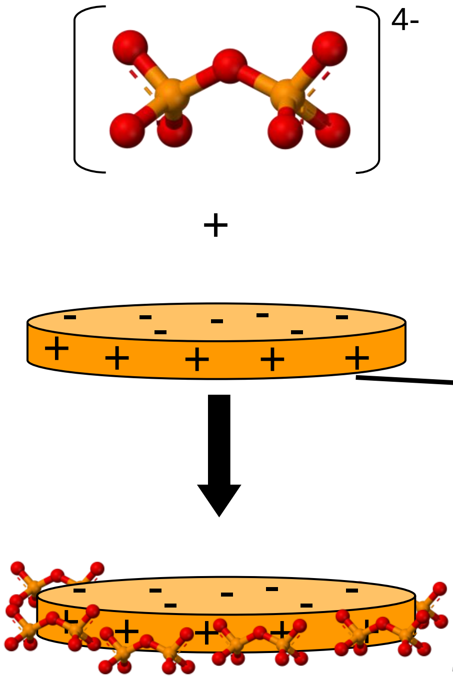
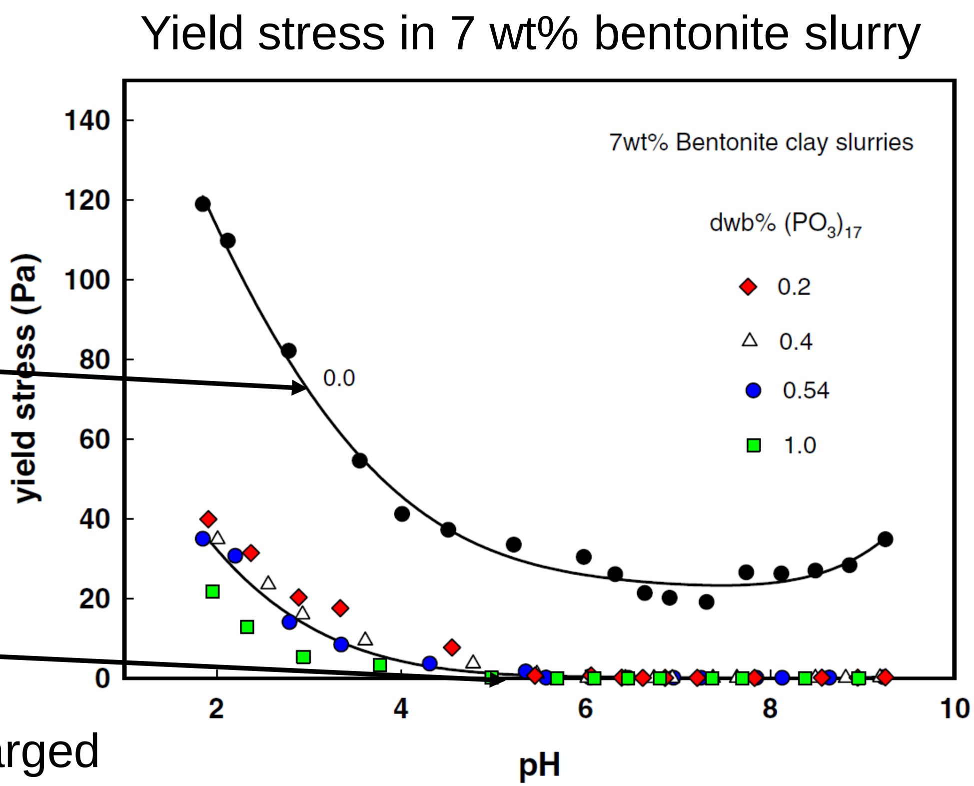
Edge-face interaction gives attractive gel effect of pyrophosphate





Both edge and face negatively charged
gel → sol

Goh *et al.* (2011).

Indirect "proof" of positive edge charge

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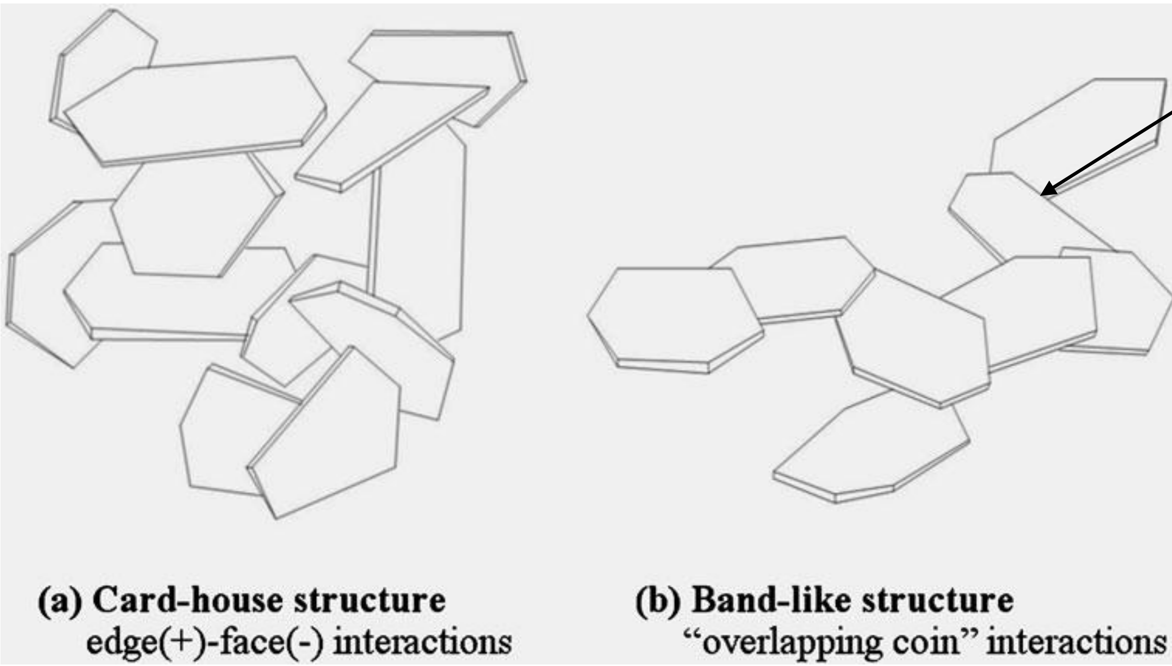
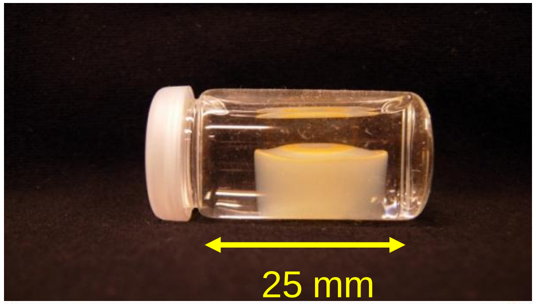
House of cards or overlapping coin?

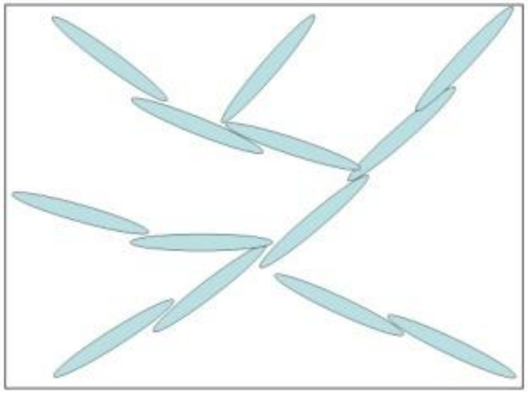
Hypothetical gel structures



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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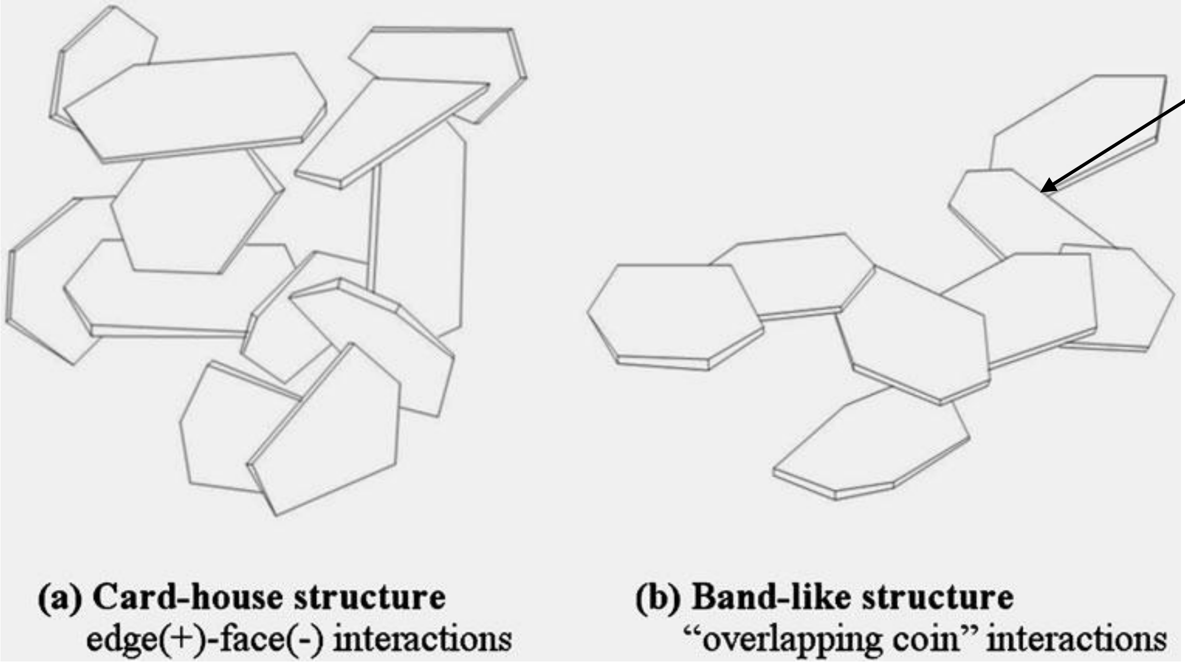
House of cards or overlapping coin?

Hypothetical gel structures



Possible interactions
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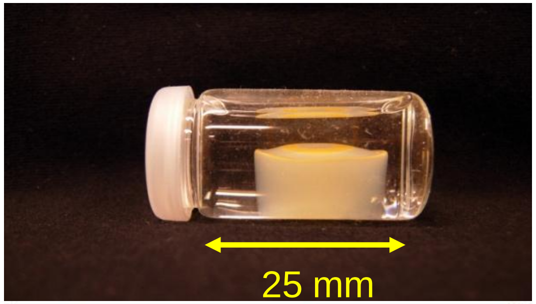

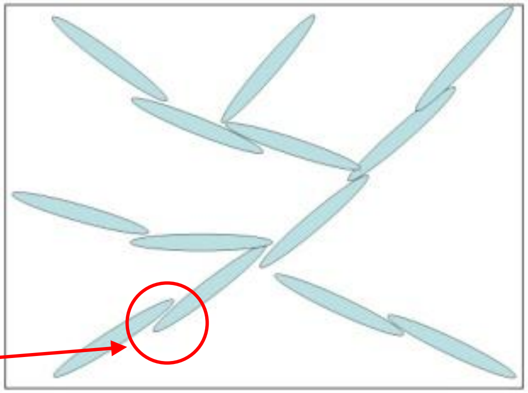

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Update: ΔH ~4-5k_BT

Branched band-like structure

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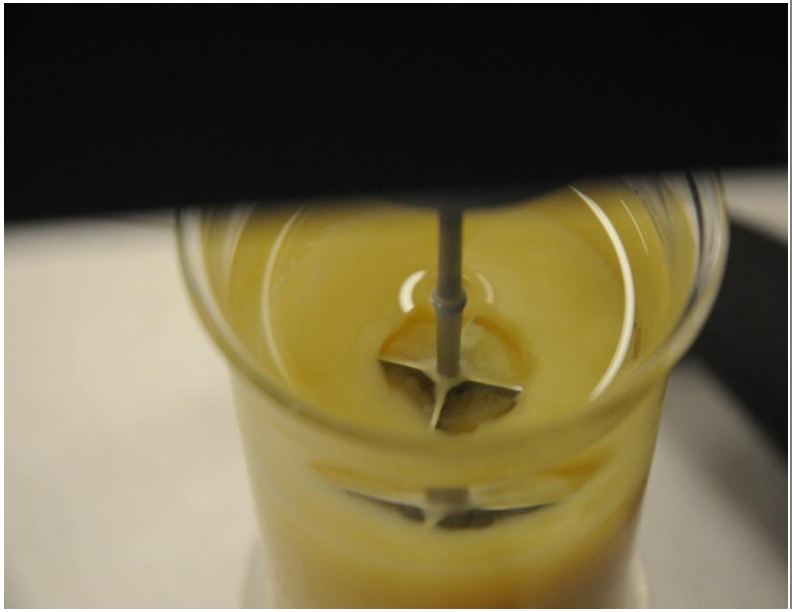
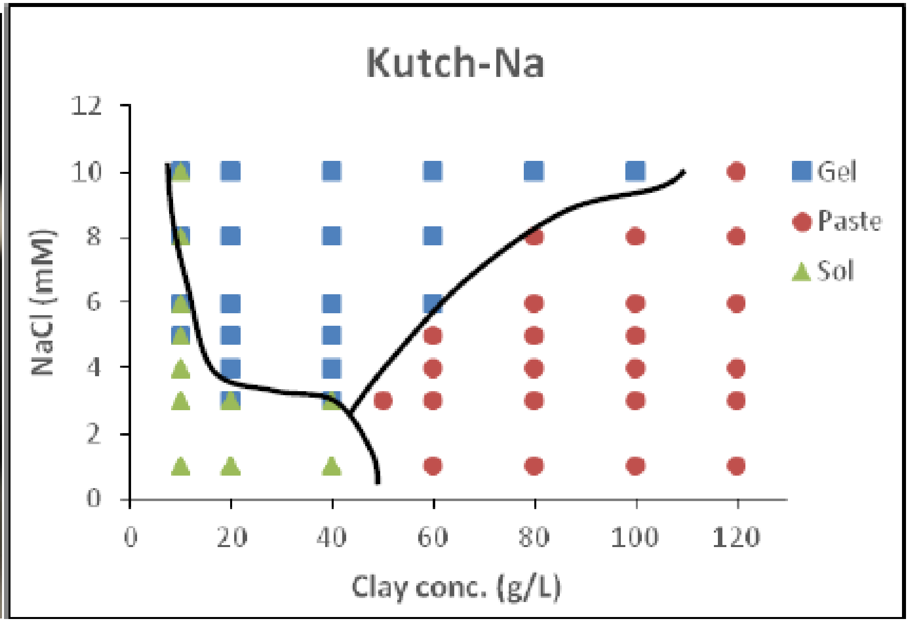
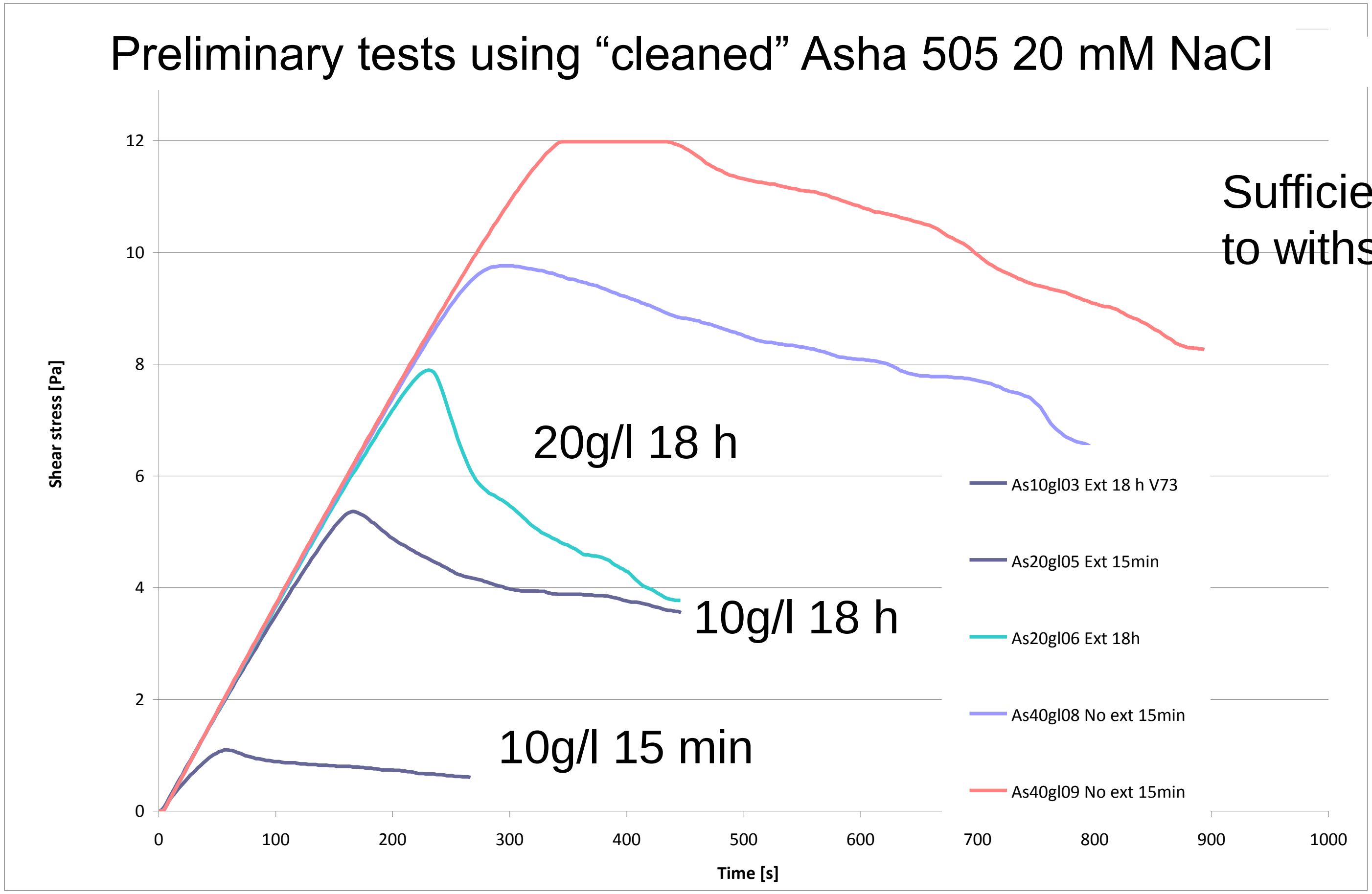
Rheology of "attractive" gels

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





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)
  - 6 kg kg/m^2/yr Wy-Ca/Na (50-50) I = 4 mM
- Role of gravity (B+Tech) 1000 kg/m^2/yr!
- Hysteresis – coming from higher to lower salinity gives lower erosion rates

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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

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.