Rheology of montmorillonite/bentonite systems

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Non-Newtonian behaviour

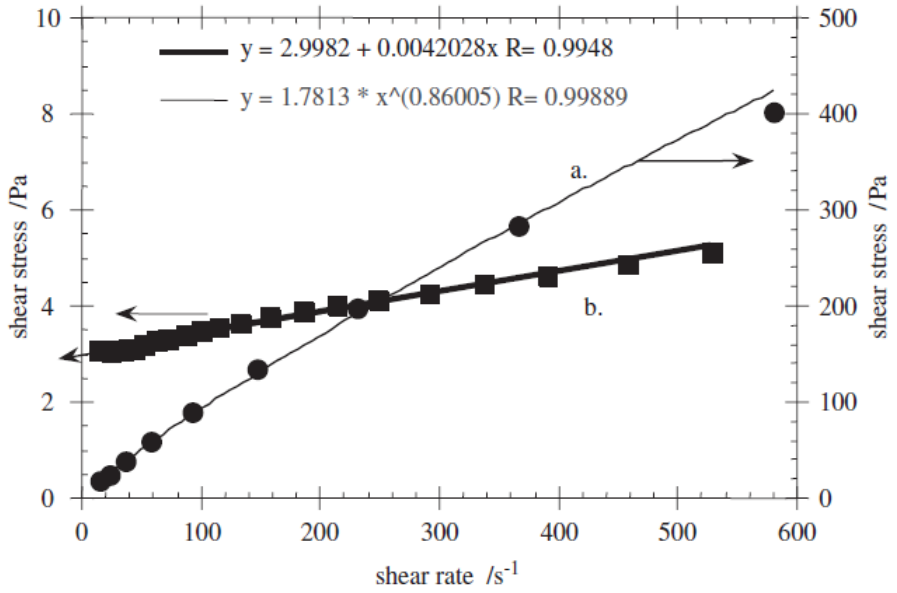


Figure 1.5 (a) Power-law behaviour from a 12% poly(vinylpyrolidone) solution; (b) Bingham plastic behaviour from a 14%w/v sodium kaolinite dispersion.

Power law
Shear thinning behaviour

$$\sigma = A\dot{\gamma}^n$$

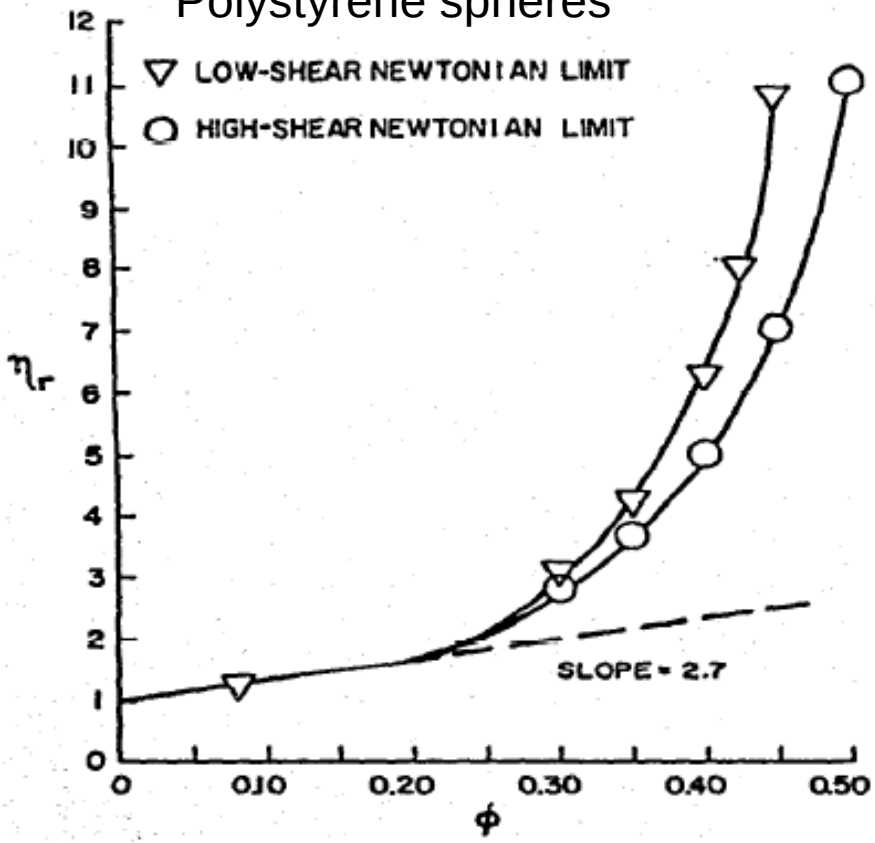
$$\eta(\dot{\gamma}) = A\dot{\gamma}^{n-1}$$

Bingham plastic

$$\sigma = \eta\dot{\gamma} + \sigma_B$$

Hard sphere viscosity

Polystyrene spheres



Dougherty-Krieger equation
concentrated dispersion

$$\eta(\phi) = \eta_0(1 + [\eta]\phi + O(\phi^2))$$

$$d\eta = \eta_0[\eta]d\phi$$

$$\frac{d\eta}{\eta_0} = [\eta]\frac{d\phi}{1-\phi/\phi_m}$$

$$\eta_r = [1-\phi/\phi_m]^{-[\eta]\phi_m}$$

Krieger; Adv. Colloid Interface Sci. **3** 111 (1972).

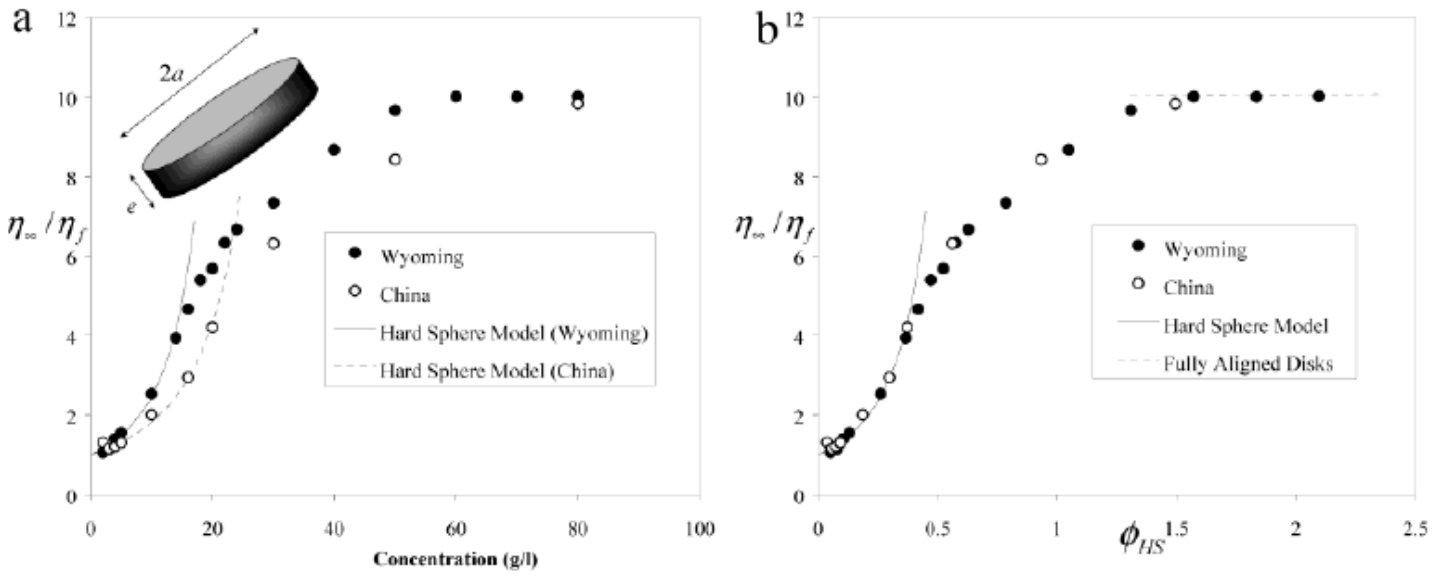
Viscosity of clay suspensions

$$\eta_r = \left[1 - \phi_{HS} / \phi_m\right]^{-2}$$

Berli & Quemada; Langmuir **16** 7968 (2000).

$$\phi_{HS} = C\frac{4a}{3e}$$

Baravian, Vantelon & Thomas; Langmuir **19** 8109 (2003).



Viscosity of clay suspensions

$$\eta_r = \frac{\eta_\infty}{\eta_f}\left(\frac{1+P_e}{\chi+P_e}\right)^2$$

$$\chi = \frac{1-\frac{\alpha\phi_{HS}}{\phi_0^*}}{1-\frac{\alpha\phi_{HS}}{\phi_\infty^*}}$$

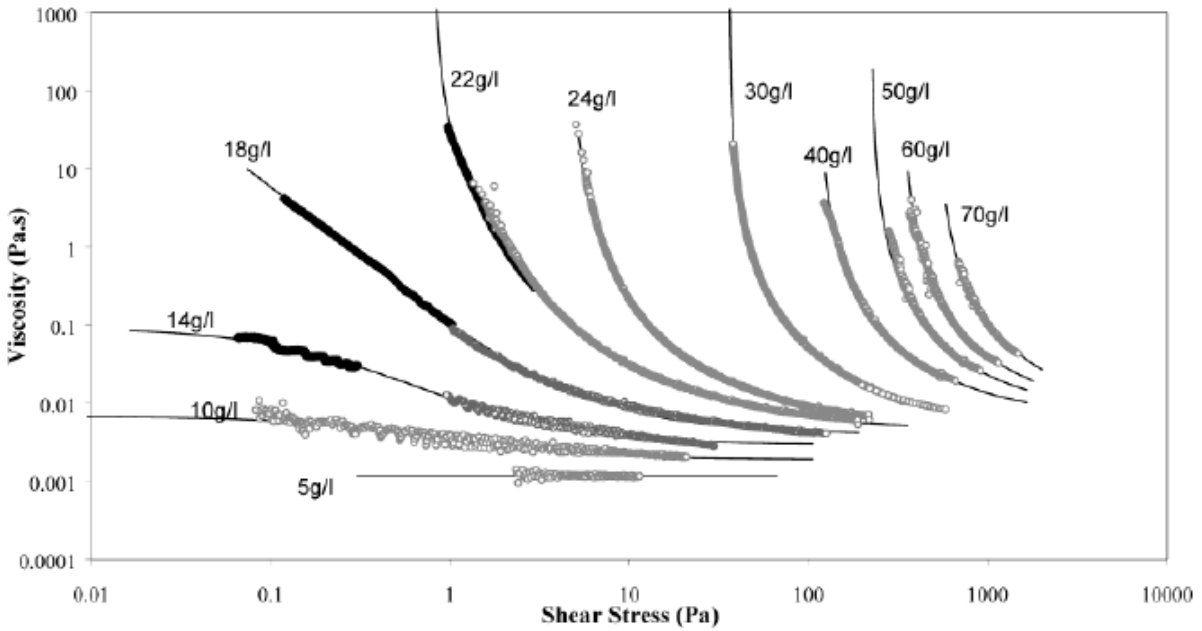
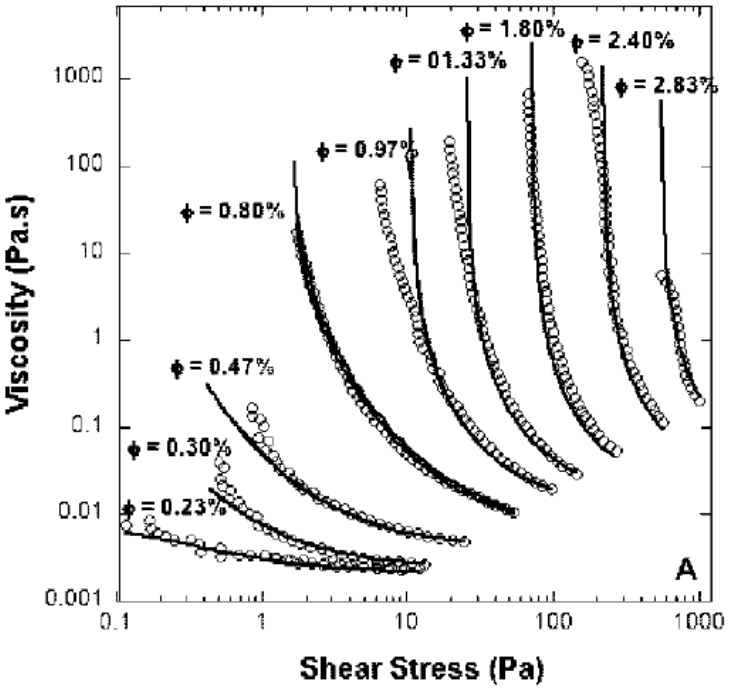


Figure 1. Viscosity–shear stress variation for montmorillonite Na^+ suspension at various concentrations: solid curve, adjustment of the viscosity model (eqs 7 and 4); black symbols, cone and plate experiments; grey symbols, parallel plate experiments.

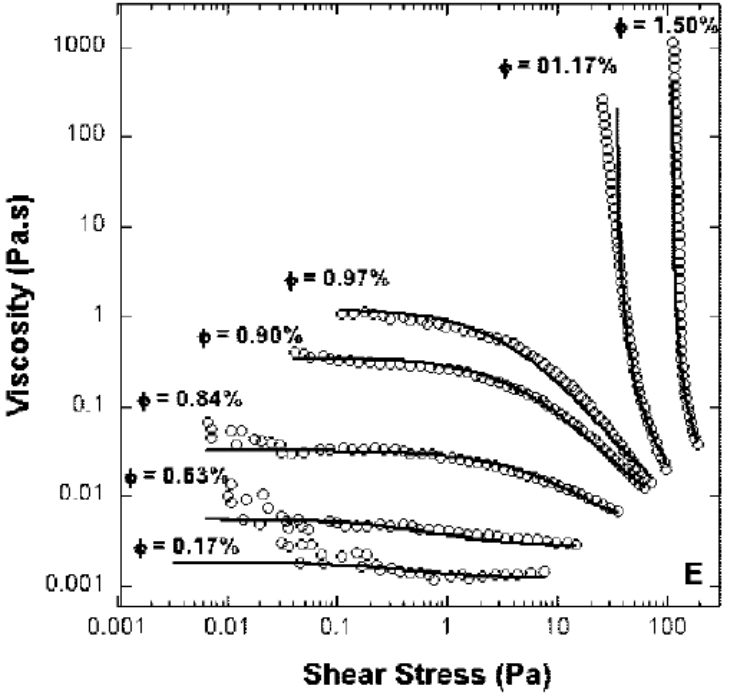
Baravian, Vantelon & Thomas; Langmuir **19** 8109 (2003).

Viscosity for different size fractions

large



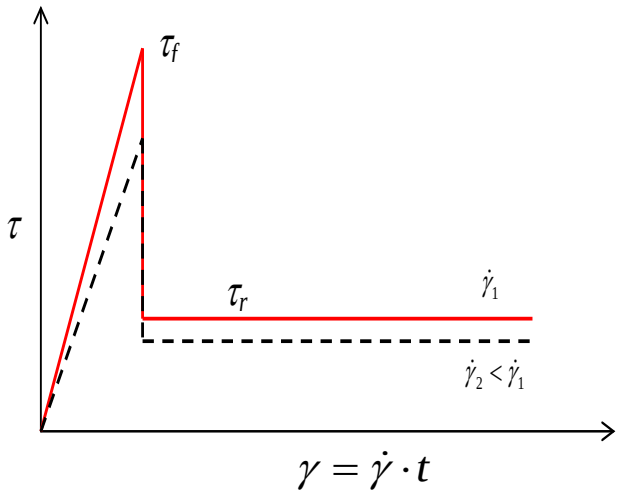
small



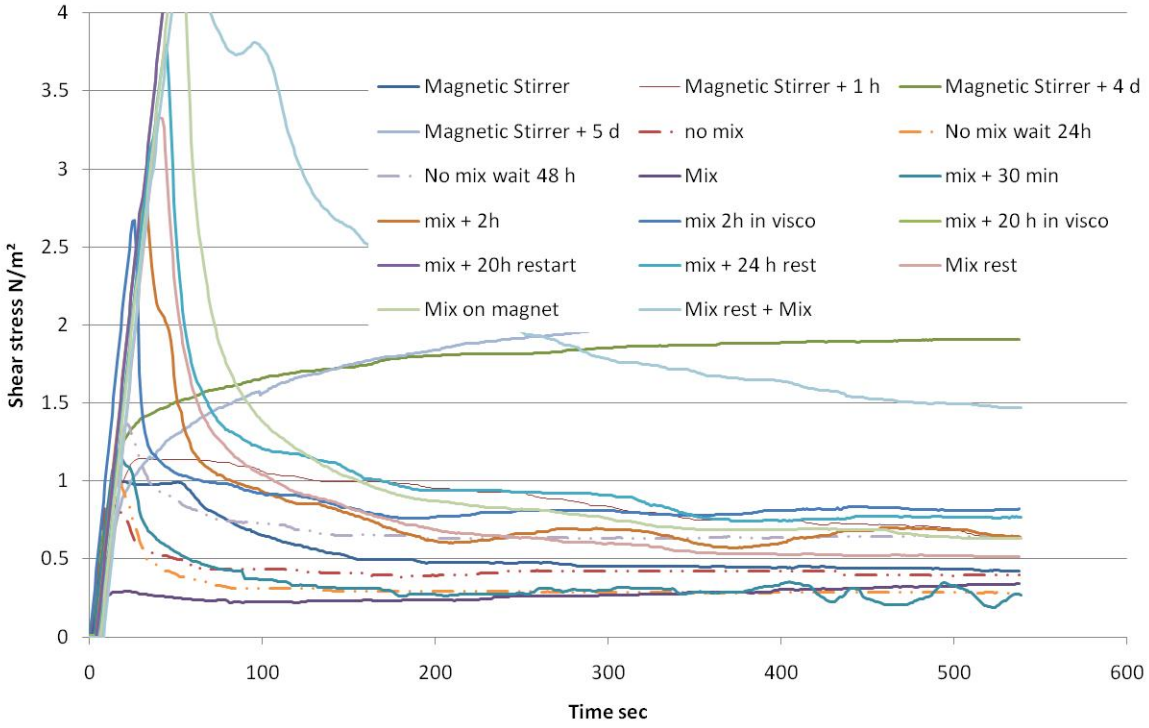
Michot et ; Langmuir **25** 127 (2009).

Result depends on history

Idealized stress-strain behaviour



MX-80 50 g/l (0.01 M NaCl)

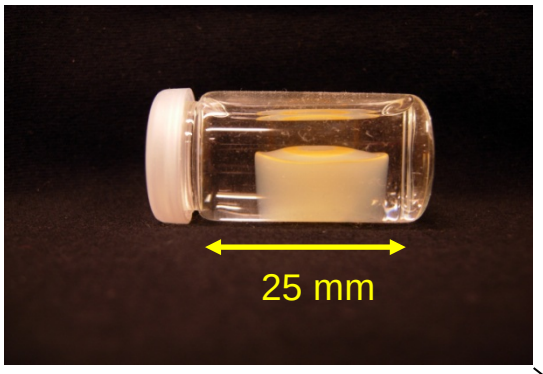


Birgersson et al. SKB TR-09-34 (2009).

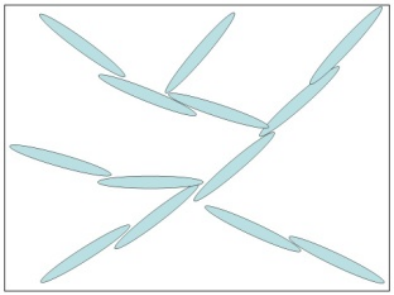
Protocol used by ClayTech in TR-09-34

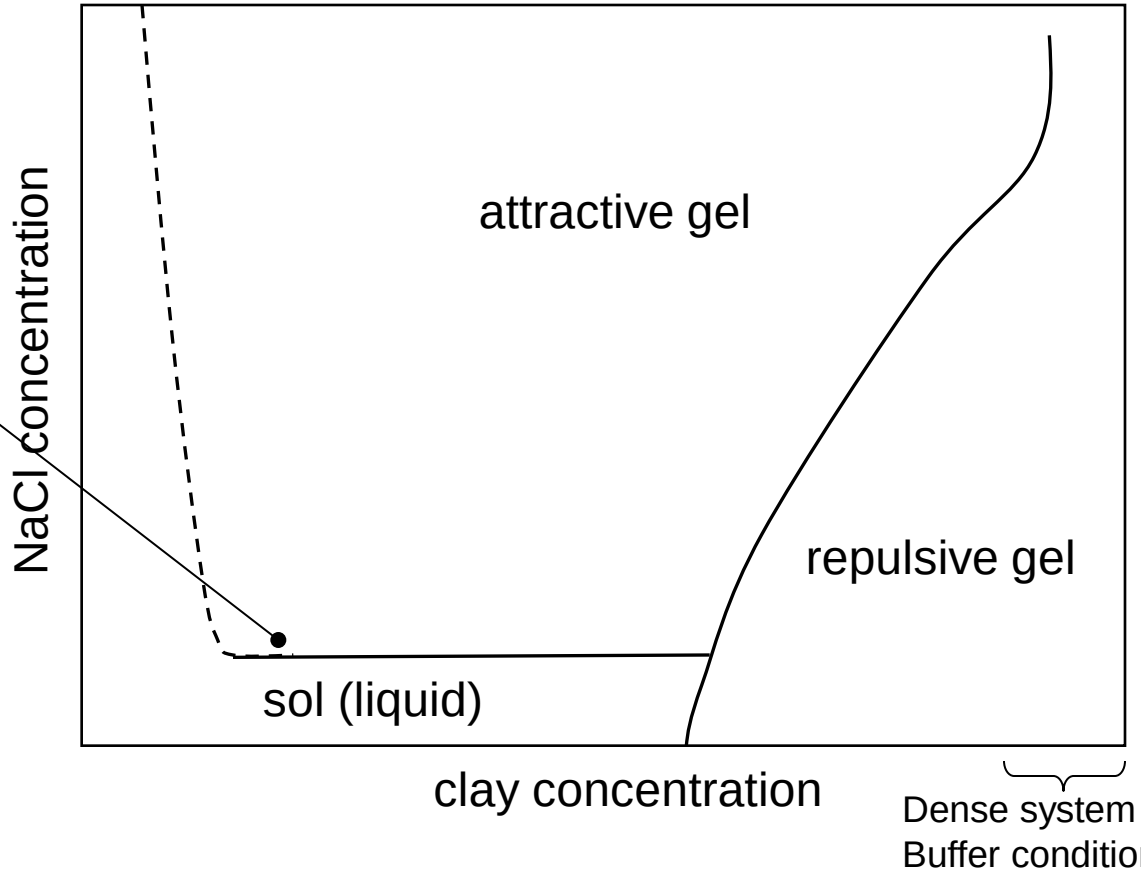
- Dry clay powder is poured into water and left to rest for 24 hours
- Before testing, the bentonite sample is shaken in order to obtain a fairly homogeneous mixture
- The required amount of bentonite slurry is sucked up with a graded syringe and injected into the test cup
- The cup and spindle is mounted in the viscometer and the test starts

Montmorillonite state/phase diagram

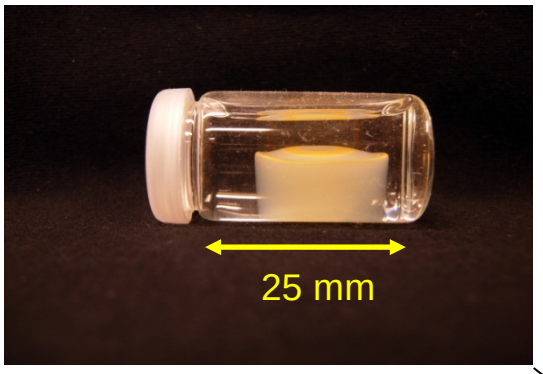


~1400 nm of water between clay layers
Diameter of typical clay platelet 100-500 nm





Montmorillonite state/phase diagram



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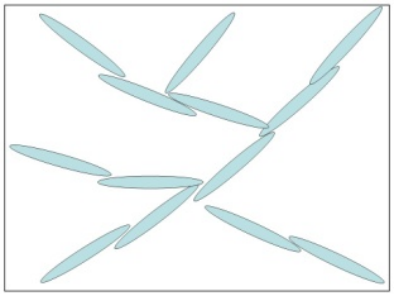
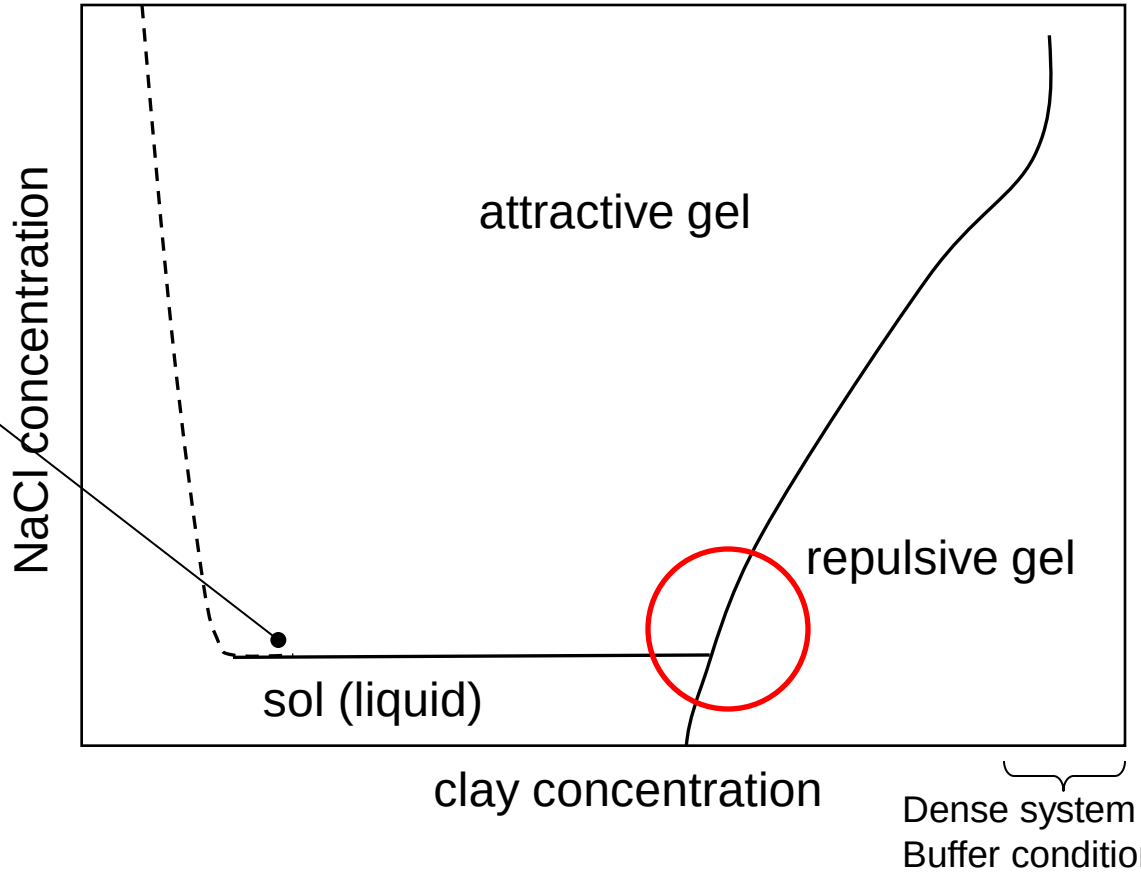
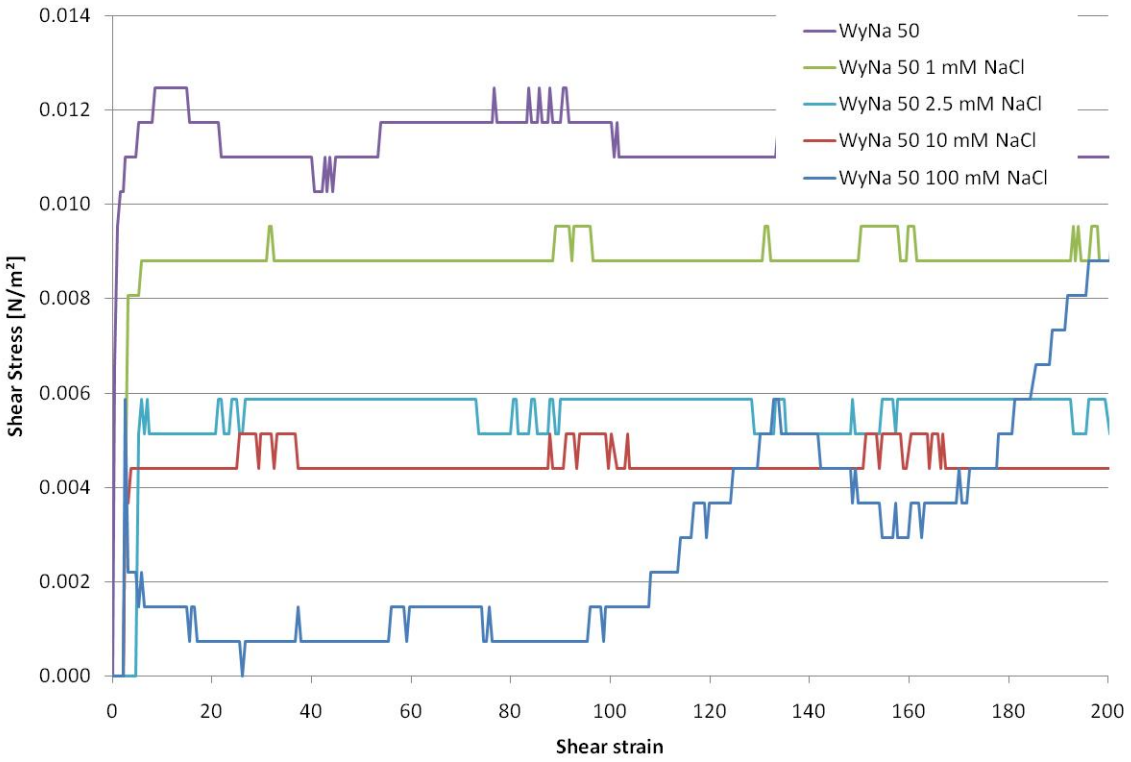




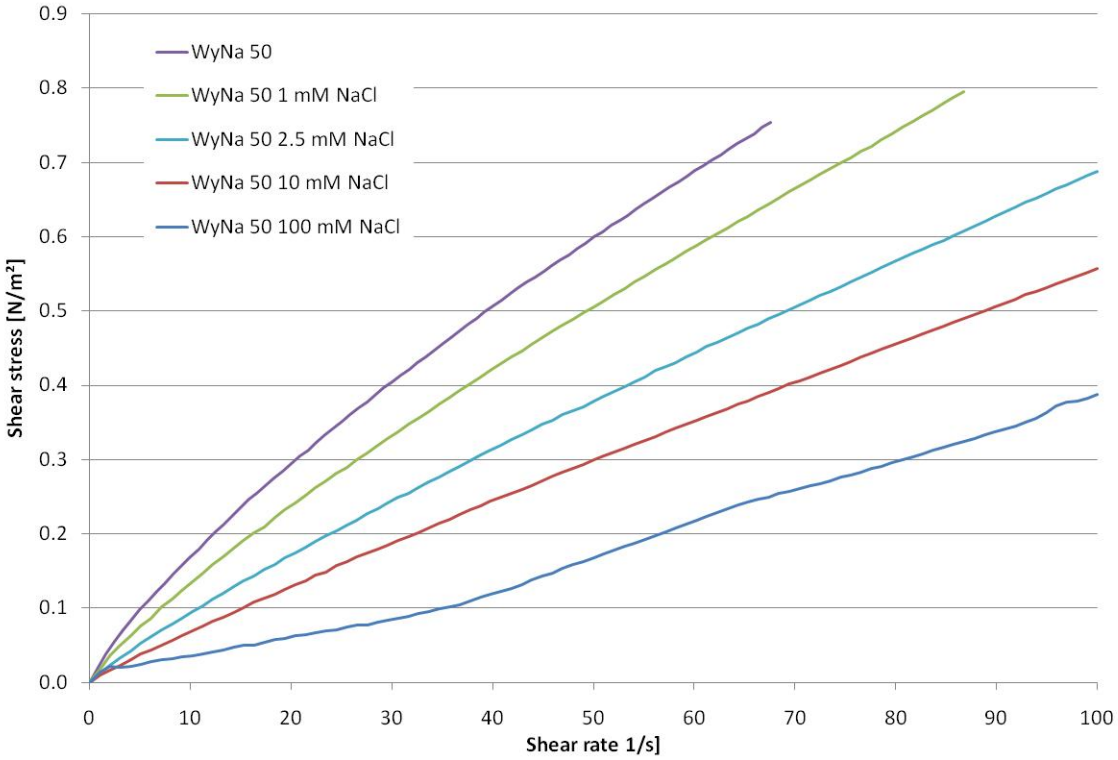
Stress-strain for Wy-Na 20g/l



Shear rate 0.5 1/s

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

Viscosity Wy-Na 20g/l

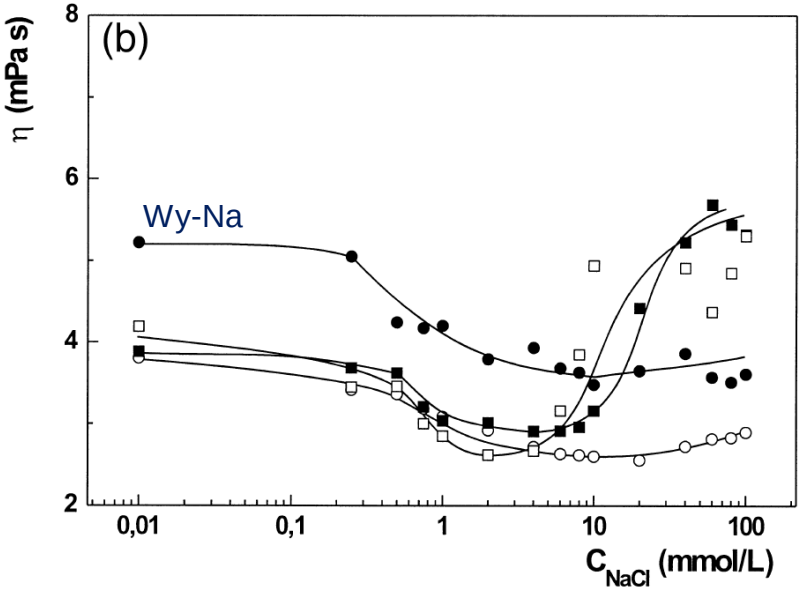


Seemingly viscosity gets lowered when salinity is increased

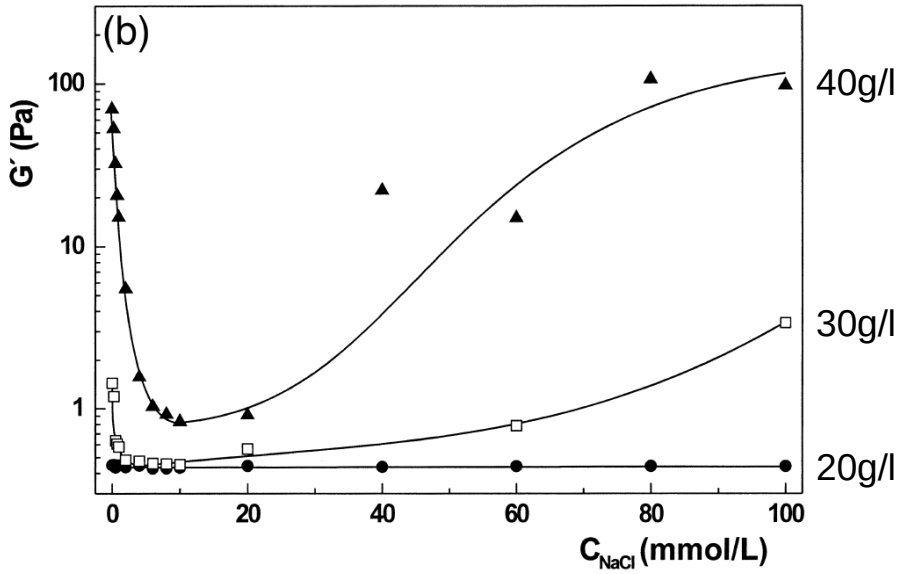
Birgersson et al. SKB TR-09-34 (2009).

Wy-Na 20g/l

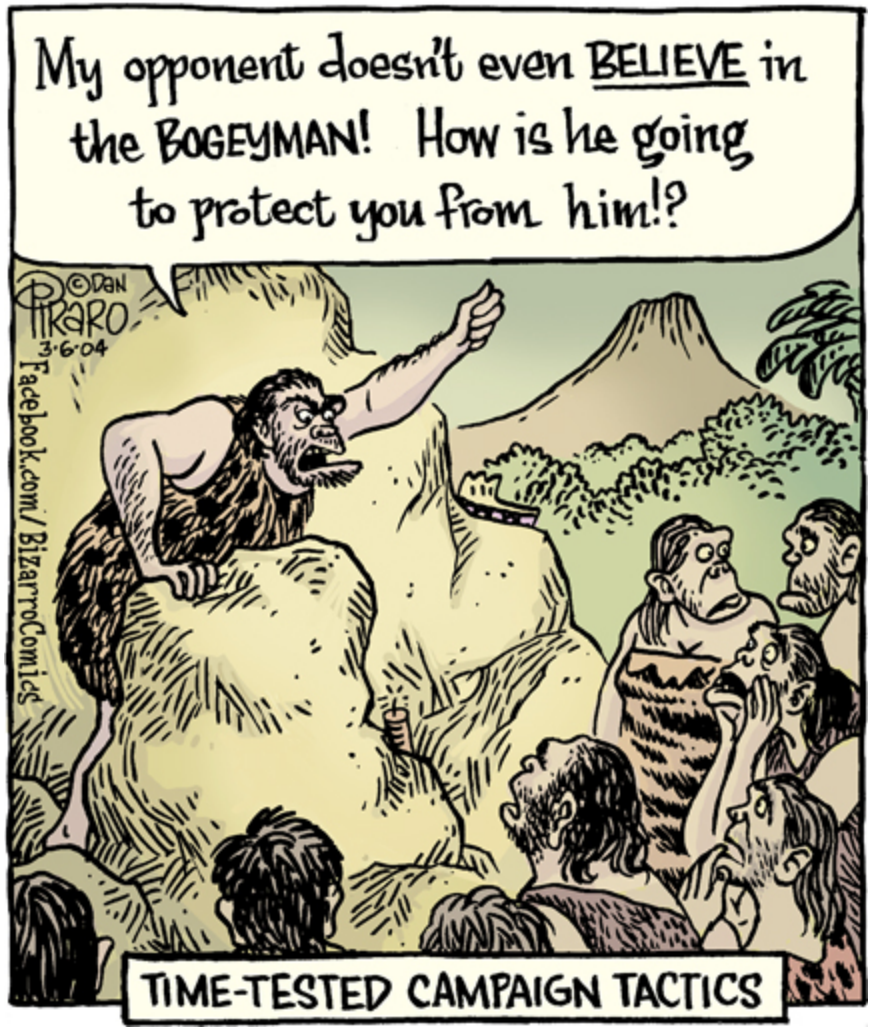
Plastic viscosity



Storage modulus



Abend & Lagaly; App. Clay Sci. **16** 201 (2000).


My opponent doesn't even BELIEVE in the BOGEYMAN! How is he going to protect you from him!?
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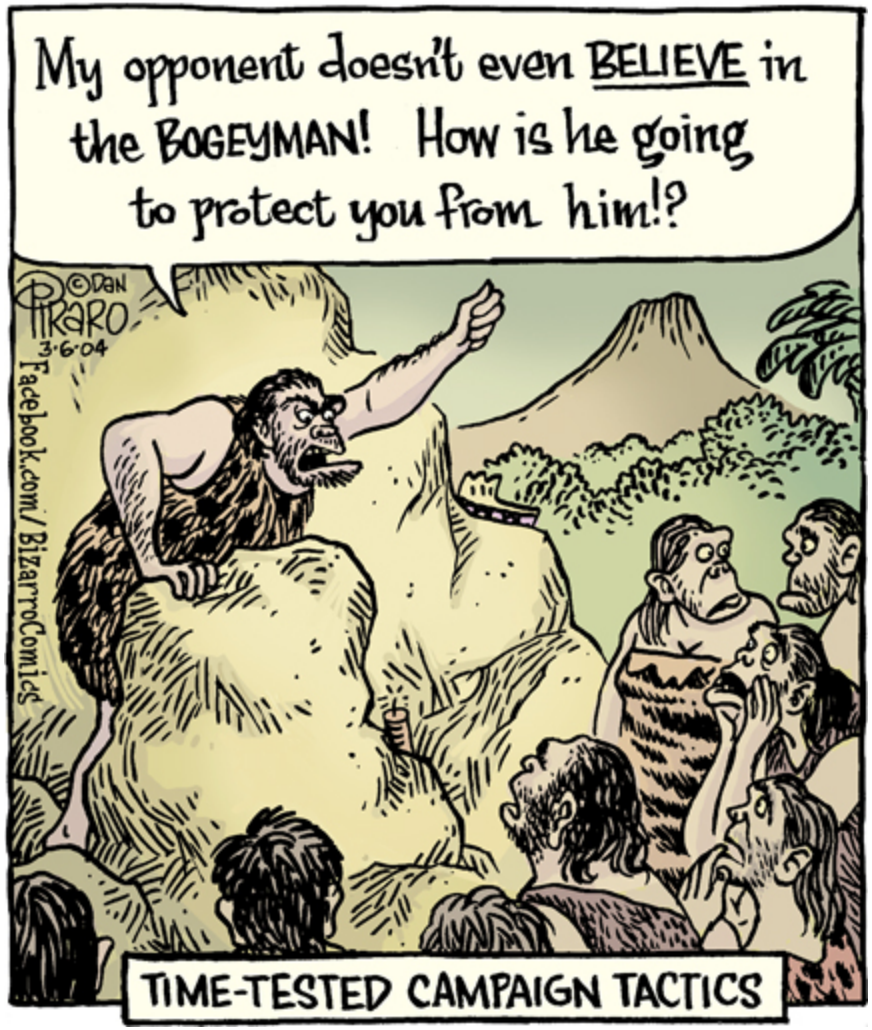
TIME-TESTED CAMPAIGN TACTICS



What about rheology of attractive montmorillonite gels?

Some comments on mixed Ca/Na-clay

- Never done in a controlled way (to our knowledge)
  - Bentonite natural mix of different counter-ions
  - Some experiments on Na-mmt with CaCl
- Produce a gel or sol by mixing known amounts of Ca and Na clay
  - 25/75 50/50 and 75/25 is a reasonable test matrix
- Similar concerns regarding test preparation as for Na-montmorillonite
- Additional complication with added salt due to ion exchange
  - Equilibration using dialysis membrane

Conclusions

- Describe the system carefully
  - composition
  - preparation
  - resting time
  - boundary condition
- Explain why it is of importance for the erosion problem

Conclusions

- Hard to deduce particle forces from rheology
  - many different models seem to fit data
  - do not interpret parameters literally

- Empirical relations satisfactory enough