Appendix 6

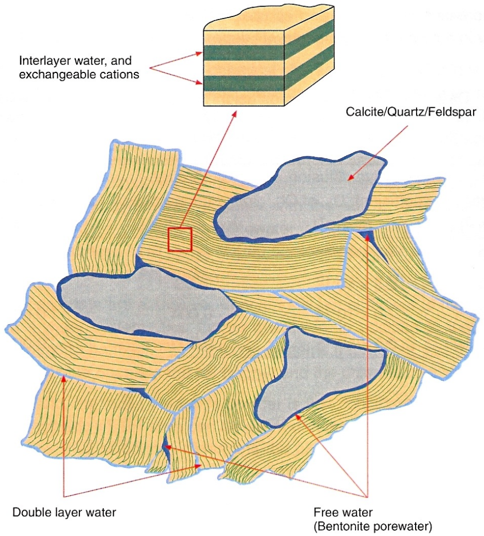
Buffer Erosion: Effects of Pore Fluid Chemistry

David Savage

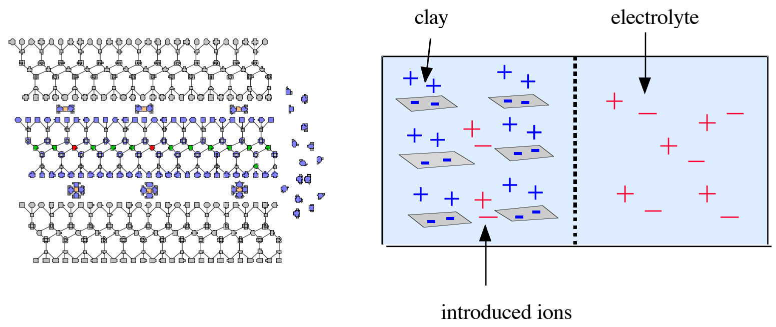
Pore fluid chemistry - issues

- Buffer erosion takes place in response to external events (infiltration of dilute groundwater), but bentonite pore fluid is chemically ‘conditioned’ within the bentonite by various processes.
- Moreover, there is considerable debate about the nature of porosity in compacted bentonite and the implications of this for transport of cations and anions:
  - do different types of porosity exist, or can solute transport behaviour be explained by a single porosity model?
- Any plausible model of erosion has to be consistent with these factors.

Bentonite - porosity models



Multiple porosity model



'polyelectrolyte' behaviour, single porosity model

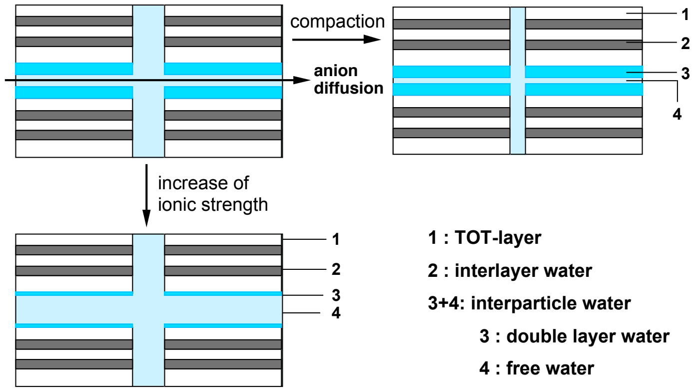
Bradbury & Baeyens Model
• 'different porosity types' = free water + double layer water + interlayer water
• Free water = 'mobile' (geochemical porosity)
• Double layer, interlayer waters = 'fixed'
• Implies transport of cations and anions in different types of pores
• Cations - through interlayer porosity
• Anions - through free porosity
• Charge balance? Semi-permeable membrane behaviour?

Birgersson & Karnland Model
• single porosity type = interlayer water
• geochemical properties governed by ion exchange and Donnan exclusion.
• no charge balance issues.
• transport of 'external' ions into clay can be accounted for.

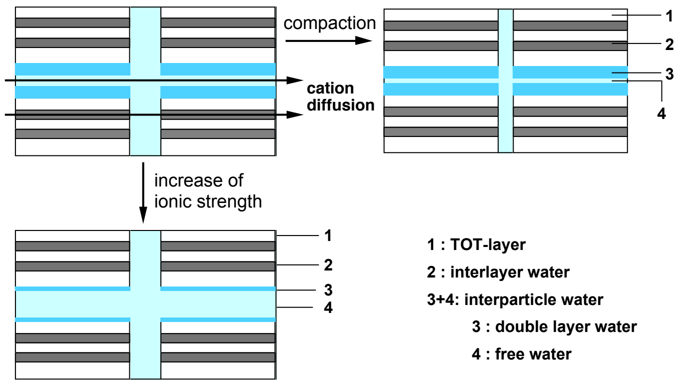
Implications for transport

‘Multiple Porosity Model’

Anions

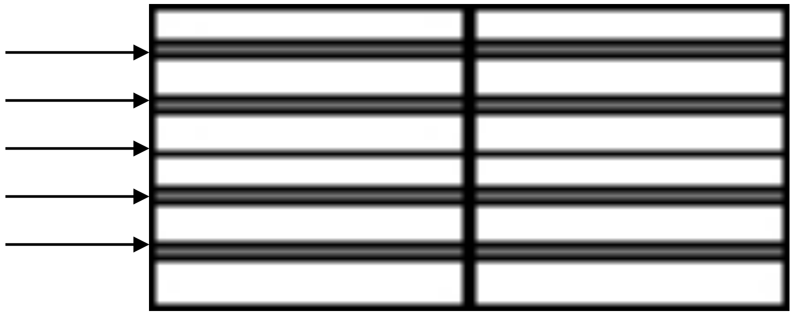


Cations

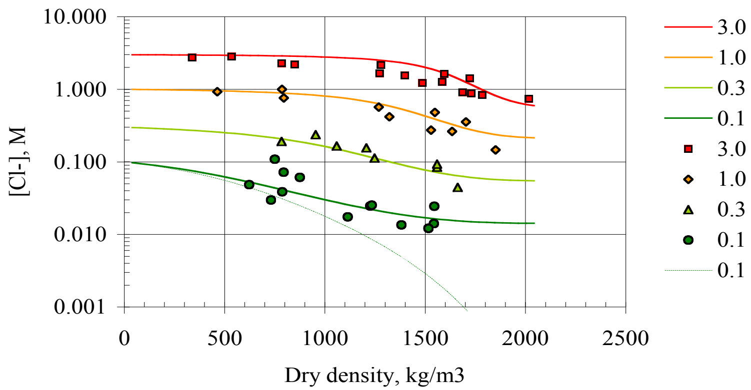


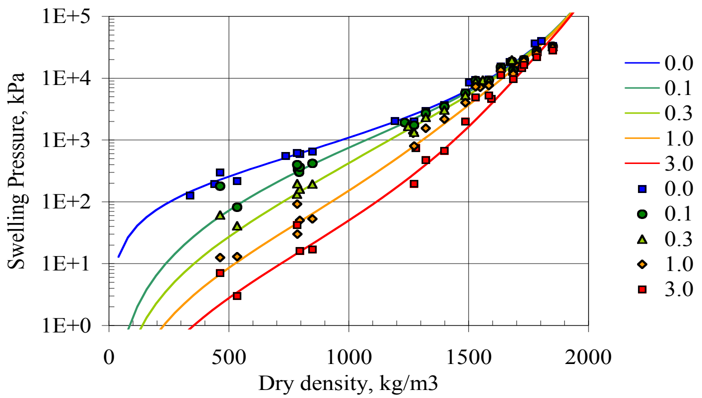
‘Single Porosity Model’

Anions, cations



Implications for swelling pressure



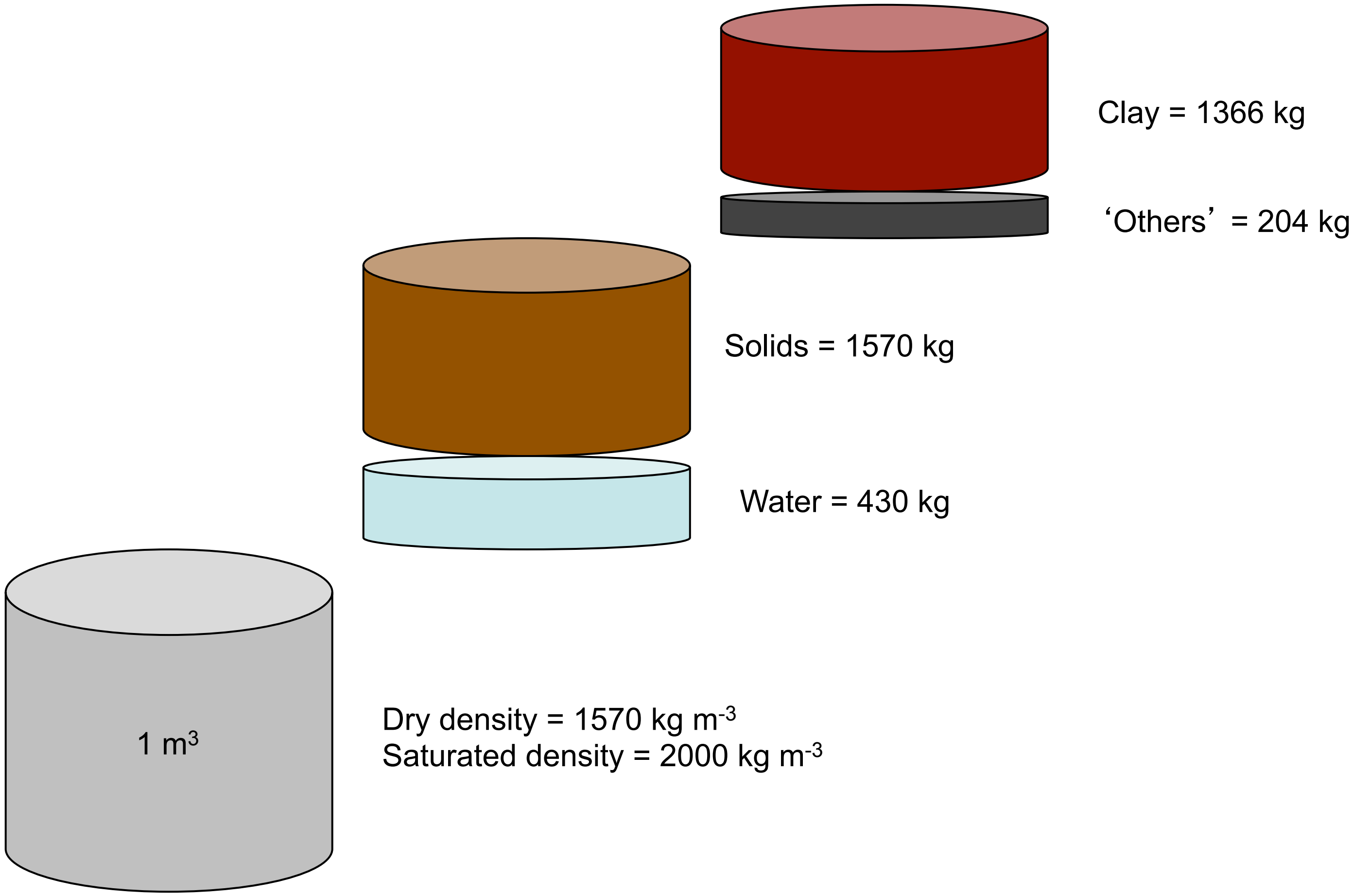


- Single porosity model is also consistent with interpretation of swelling pressure results (osmotic effects governed by Donnan exclusion):
  - "*reduction in concentration of mobile ions within an ion exchange membrane due to the presence of fixed ions of the same sign as the mobile ions*"
- Important to have consistent geochemical models.
- Which model has SKB chosen to interpret and model buffer erosion?

Mass balances and processes

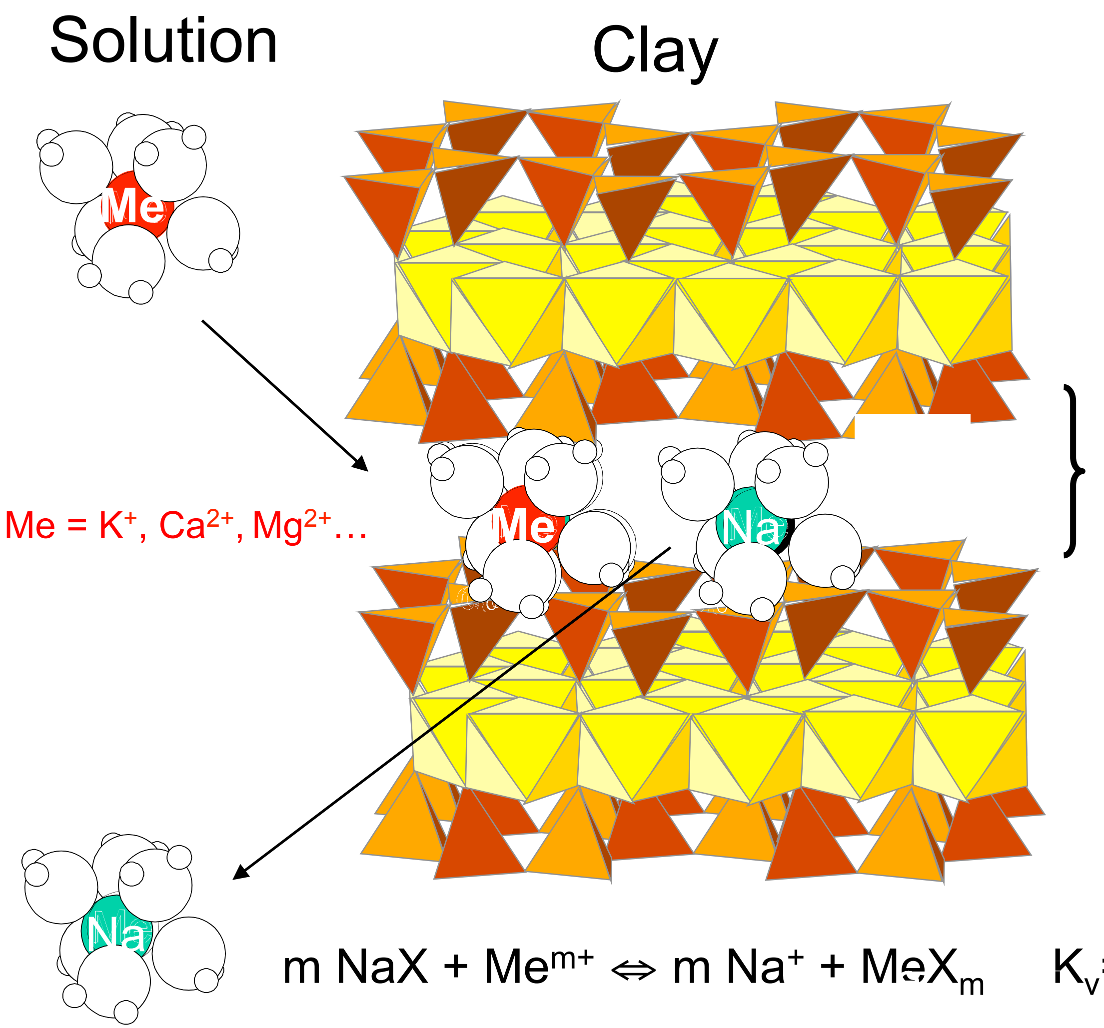
- Bentonite properties and pore fluid composition will depend upon constituent minerals and compaction density:
  - proportion and type of montmorillonite;
  - types and amounts of trace minerals;
  - 'external factors' such as salinity of saturating groundwater.
- Pore fluid is chemically 'conditioned' within the bentonite by various processes:
  - clay ion exchange (rapid);
  - clay edge site protonation-deprotonation (rapid);
  - dissolution of trace gypsum (rapid to slow);
  - hydrolysis of clay and trace silicates (slow).

Bentonite - constituents



Cation exchange (fast)

Cation exchange	meq/100 g clay	Eq m^{-3} bentonite
$X^- + Na^+ = NaX$	54.0	738
$X^- + K^+ = KX$	1.5	20
$2X^- + Ca^+ = CaX_2$	13.5	184
$2X^- + Mg^+ = MgX_2$	6.0	82
TOTAL	75.0	1024



Interlayer Space

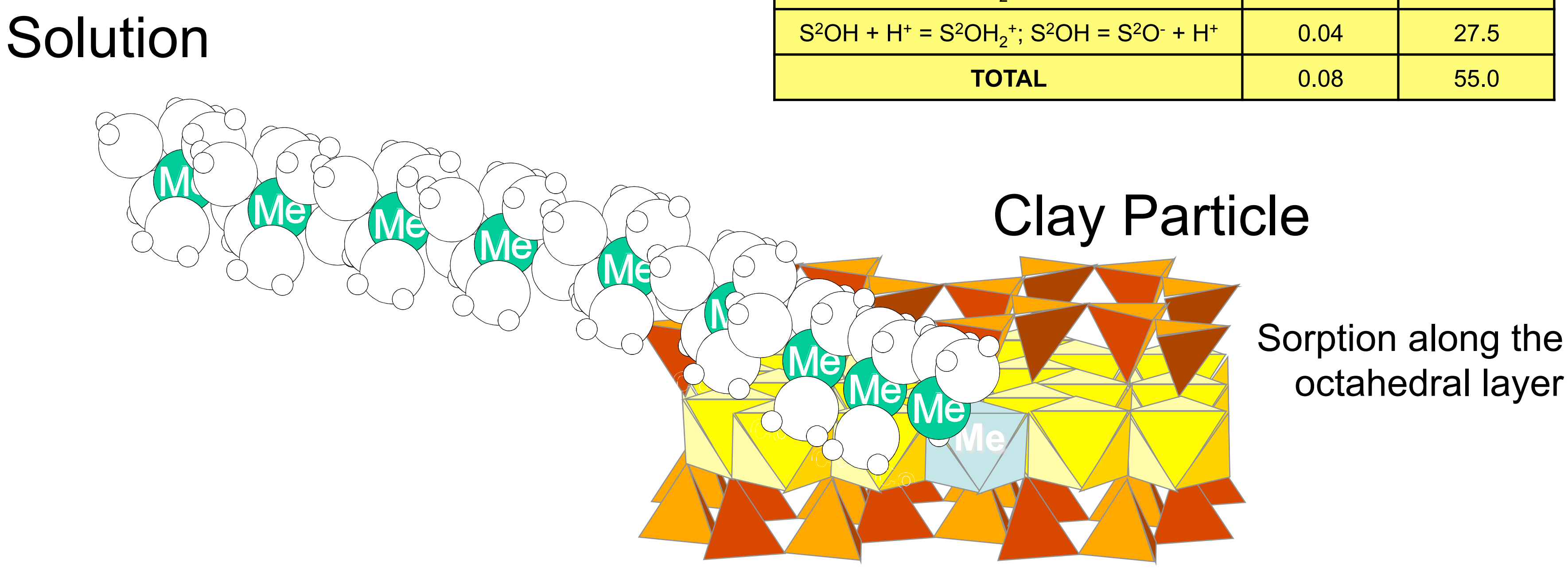
(limited to 2-3 water molecule layers in compacted bentonite)

$$m\,NaX + Me^{m+} \Leftrightarrow m\,Na^+ + MeX_m \qquad K_v = \frac{X_{Me}\left(Na^+\right)^m}{X_{Na}^m\left(Me^{m+}\right)}$$

with X^- = one mole of exchanger, X_{Me} = Me mole fraction in exchanger

Edge site adsorption (fast)

Edge protonation-deprotonation	Mol kg^{-1} clay	Mol m^{-3} bentonite
$S^1OH + H^+ = S^1OH_2^+$; $S^1OH = S^1O^- + H^+$	0.04	27.5
$S^2OH + H^+ = S^2OH_2^+$; $S^2OH = S^2O^- + H^+$	0.04	27.5
TOTAL	0.08	55.0

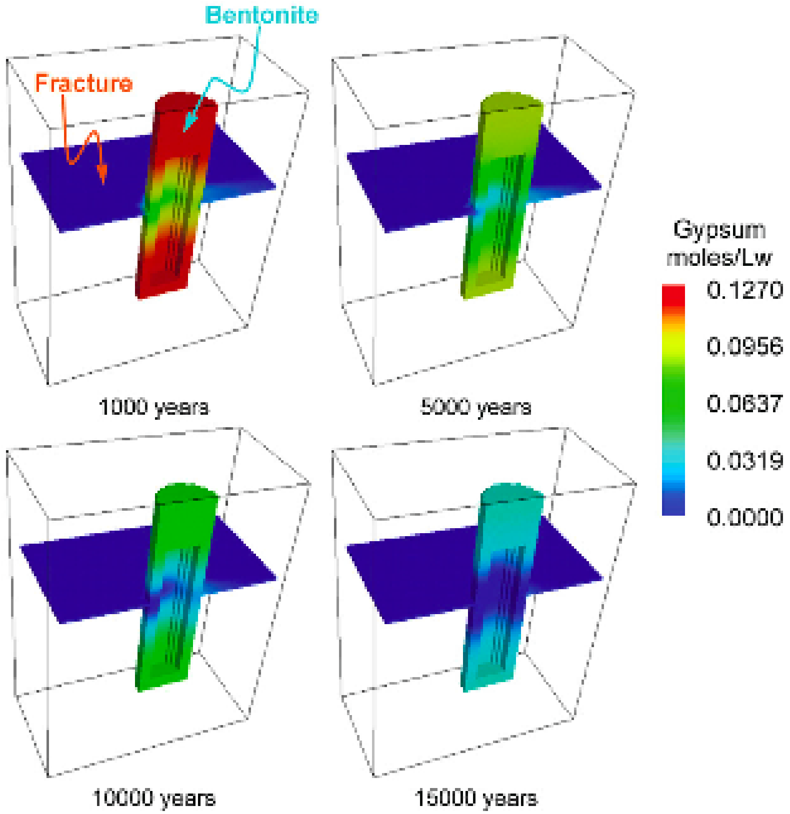


e.g. protonation-deprotonation:

$$\equiv SOH + H^+ \Leftrightarrow \equiv SOH_2^+$$

$$\equiv SOH \Leftrightarrow \equiv SO^- + H^+$$

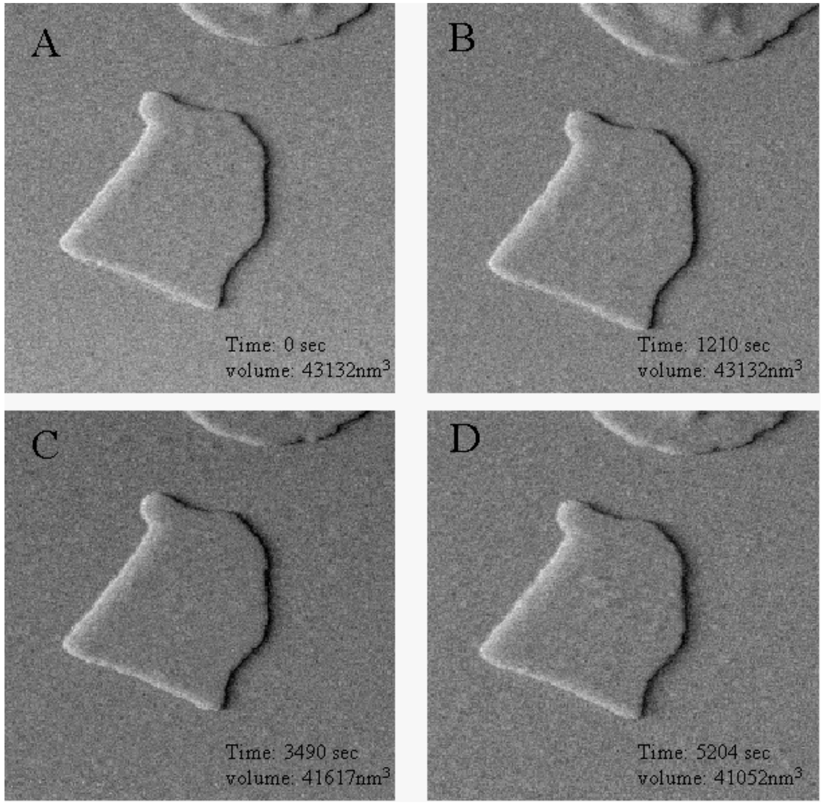
Bentonite: trace minerals

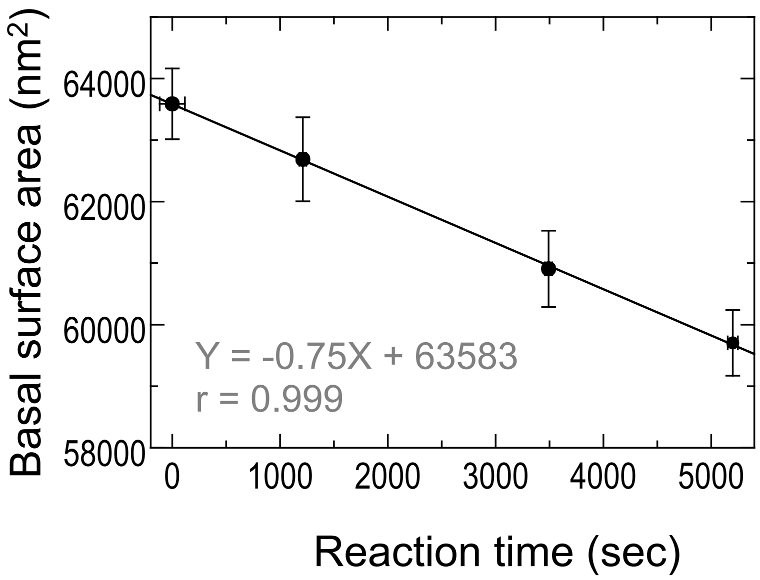


- SKB's near-field simulations for SR-Can show that (equilibrium) gypsum dissolution in granite groundwater removes 50 % after 1 000 years with complete removal after 20 000 years.
- How would incorporation of kinetics affect this situation?

Mineral	Kg m^{-3}	Reaction	Log K 25 °C	Log *k* (25 °C) mol m^{-2} s^{-1}	Mol s^{-1} m^{-3} bentonite
Quartz	82	$SiO_2 = SiO_{2(aq)}$	-3.99	-14.0	3.0E-10
Feldspar	110	$NaAlSi_3O_8 + 4H^+ = Na^+ + Al^{3+} + SiO_{2(aq)} + 2H_2O$	2.76	-12.0	2.0E-08
Pyrite	1.6	$FeS_2 + H_2O = Fe^{2+} + 2H^+ + 1.75HS^- + .25SO_4^{2-}$	-24.65	-4.55	0.3
Gypsum	11	$CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.85	-2.79	27

Bentonite: 'slow' hydrolysis reactions

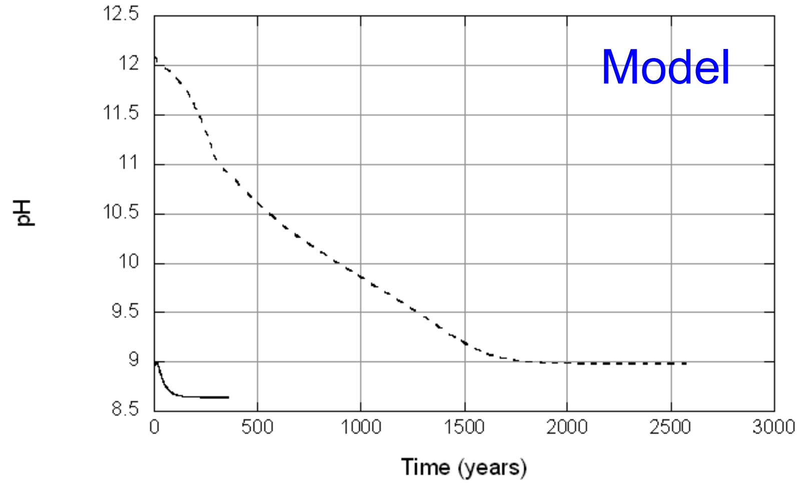


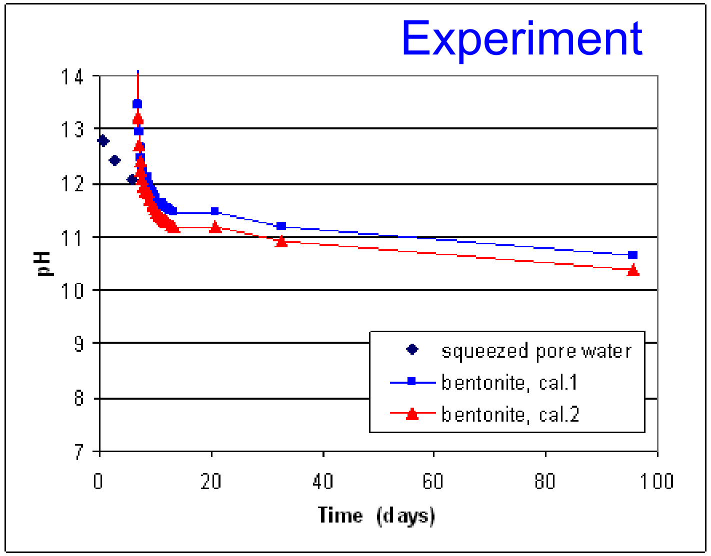


From Sato et al. (2005)

Mineral	Reaction	Log K 25 °C	Log *k* (25 °C) mol m^{-2} s^{-1}	Mol s^{-1} m^{-3} bentonite
Na-mont	$Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 6H^+ = .33Na^+ + .33Mg^{2+} + 1.67Al^{3+} + 4SiO_{2(aq)} + 4H_2O$	2.48	-14.0	4.0E-07

Bentonite: clay hydrolysis





- Calculations for SSM show that although slow, clay hydrolysis reactions can impact upon pH buffering in bentonite in the long-term.
- Should such reactions be considered in erosion modelling?

Pore fluid chemistry - summary

- There is considerable debate about the nature of porosity in compacted bentonite and the implications of this for transport of cations and anions:
  - do different types of porosity exist, or can solute transport behaviour be explained by a single porosity model?
  - a single porosity model is also consistent with swelling pressure data.
  - which model will SKB use in SR-Site?
- Bentonite pore fluid is chemically ‘conditioned’ within the bentonite by various processes and relevant mass balances:
  - clay ion exchange (rapid);
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- Any plausible model of erosion has to be consistent with these factors.