Appendix 2

Chemical erosion

- An overview of chemical constraints on erosion rates (RA)
- Models of clay colloid formation/stability (HK)
- Consistency between experimental and modeling results (DB)

An overview of chemical constraints on erosion rates

Randy Arthur
November 4, 2009
Stockholm, Sweden

Historical context

- In SR-Can it was assumed that the buffer erosion rate [R_{buffer} (kg yr^{-1})] is given by:

  $$R_{buffer} = C_{max}Q_{eq}$$

  where,

  C_{max} – maximum bentonite concentration in a water suspension (kg m^{-3}),

  Q_{eq} – equivalent flow rate (m^{3} yr^{-1}).
- Q_{eq} was estimated based on hydrogeological modeling of the Forsmark and Laxemar sites.
- Citing unreferenced observations, SKB assumed C_{max} = 50 kg m^{-3}, while acknowledging significant uncertainty in this value.
- Is R_{buffer} better constrained by recent SKB studies[*]?

---

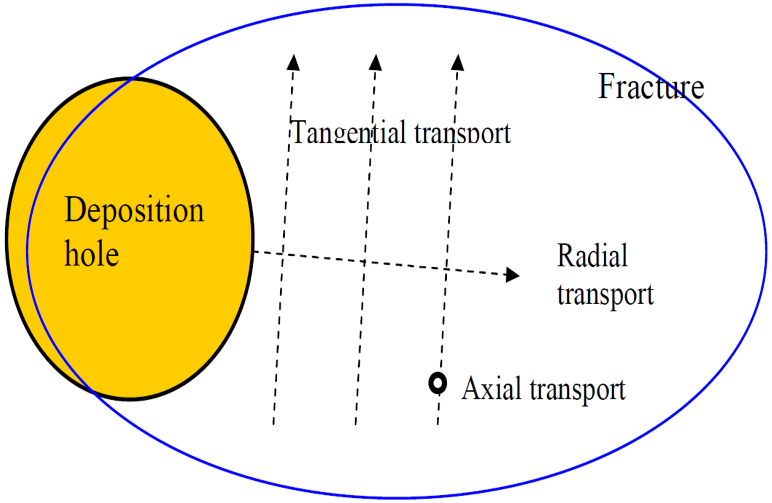
[*] Rheological constraints considered in "example"

Terminology

- **Colloidal system:** A dispersion of particles of colloidal size (between 1 nm and 1 μm in at least one dimension) in a continuous phase of different composition.
- **Sol:** A fluid or semi-fluid colloidal system.
- **Gel:** A non-fluid colloidal network having a finite yield stress.
  - **Repulsive gels-** result from electroviscous effects in systems having low salt concentrations and high colloid concentrations.
  - **Attractive (cohesive) gels-** form when attractive forces between particles outweigh repulsive forces in systems having relatively high salt concentrations and low colloid concentrations.
- **Gel point:** Point of incipient network formation characterizing the boundary between a gel and a sol.
- **Flocs:** Form when attractive forces between colloidal particles become strong enough to disrupt a gel's structure, causing the particles to aggregate and settle into a sediment.
- **Water ratio:** $w_r = m_w/m_s$
- **Colloid concentration:** w_r^{-1}

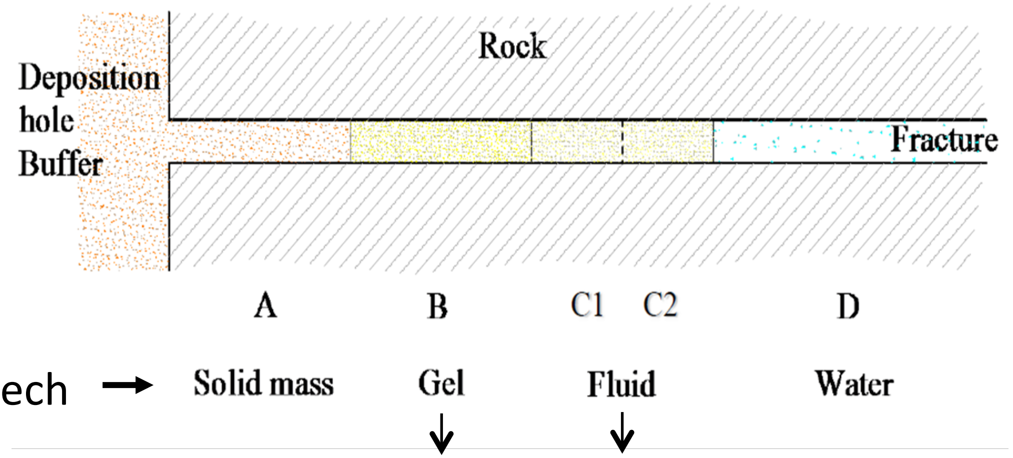
Source: IUPAC Compendium of Chemical Terminology (Gold Book); Lagaly (2006); Clay Tech 2009 draft final report.

Conceptual model



← Plan view

Cross section →



Clay Tech →

KTH group → Cohesive gel Expansive gel/sol

Two modeling approaches have been developed to estimate erosion rates

- KTH (Neretnieks et al., 2009): Comprehensive - based on physics, chemistry, surface chemistry, rheology, hydrology and transport phenomena.
- Clay Tech (Birgersson et al., 2009): bounding - based on rheology.
- KTH considered here.

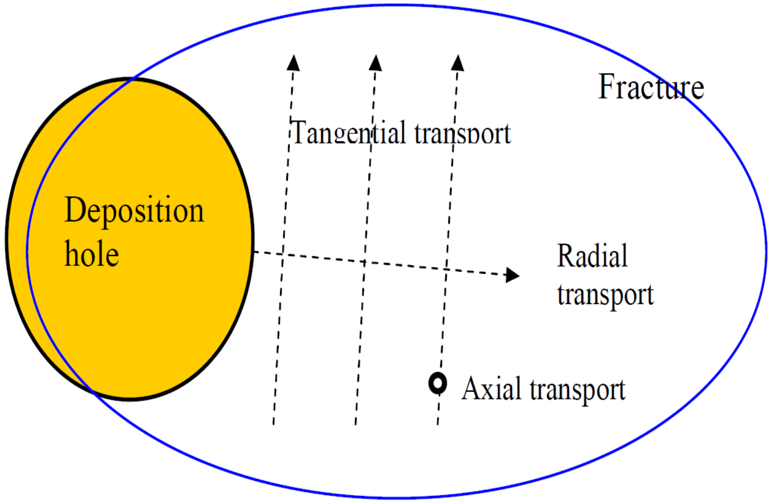
KTH model: Erosion modes

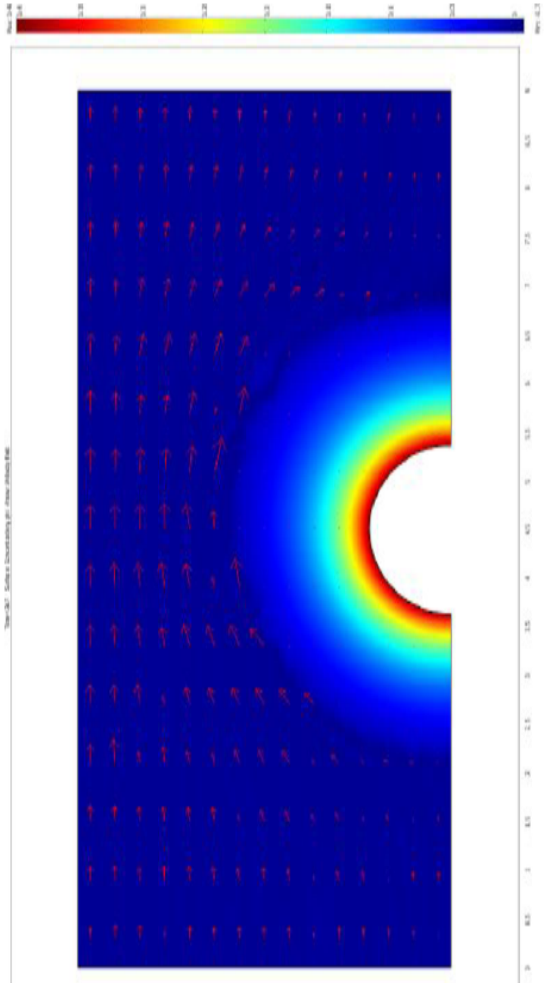
- Diffusive loss of “gel” (i.e., of clay particles)
- Advective loss of “gel” (i.e., advective flow of a viscous liquid)
- Particle Shearing by flowing groundwater
- Filtration

Erosion model: Advective & diffusive transport modes

- Two main model components.
  - Dynamic (force-balance) model:
    - gravity,
    - diffusion (solutes & colloidal particles),
    - van der Waals attractive forces between clay particles,
    - repulsive double-layer forces between particles, and
    - friction forces between particles and water.
  - Viscosity model – relates the viscosity of a non-Newtonian fluid to colloid volume fraction and water composition.
- Model evaluation entails finding simultaneous solutions to the Darcy flow equation, diffusion equations and force-balance equations governing the expansion of bentonite into a fracture of known aperture.
- Model output gives the rate of buffer mass loss.

Illustrative model results





Fracture transmissivity = 10^{-7} m^2 s^{-1}
Fracture aperture = 1 mm
Hydraulic gradient = 0.1

Estimated erosion rates*

Water velocity ($m\ yr^{-1}$)	Erosion rate ($g\ yr^{-1}$)	Penetration distance (m)
0.1	11	34.6
0.32	16	18.5
0.95	26	11.5
3.15	43	7.0
31.5	117	2.1
315	292	0.5

*Fracture aperture = 1 mm. Results at low water velocities may not be valid because the penetration distance may exceed the length of most fractures in the network.

Main conclusions

(Neretnieks et al., 2009)

- [The buffer] "…cannot be proved not to erode significantly with the flow rates and water compositions expected."
- Filtration by a filter cake of residual accessory minerals will likely hinder major loss of buffer.

Comments on the KTH model

- Applied only to highly idealized systems – WyNa in NaCl.
- Significant uncertainties in conceptual and mathematical models (e.g., applicability of DLVO/CCC).
- Significant uncertainties in parameter values.
- "A reliable and credible overall model will need considerable development work" (Neretnieks et al., 2009).
- Is this achievable in a timely manner?

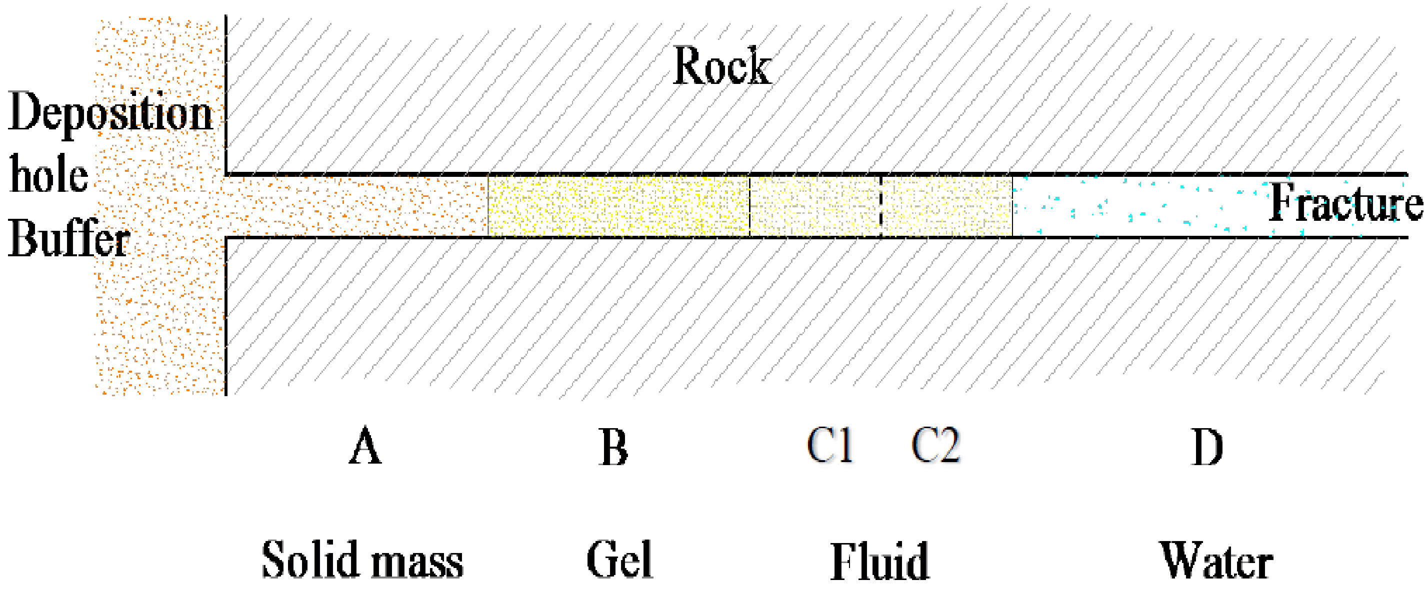
Example

Rheological constraints on C_{max}

Rationale

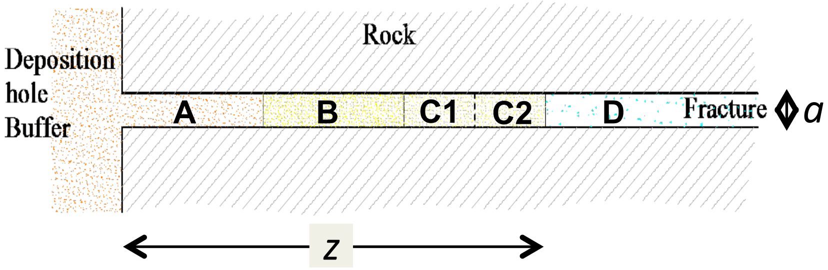
- Buffer erosion entails the loss of bentonite colloids by diffusion or advection in flowing groundwater.
- It seems reasonable to assume (as does SKB) that only bentonite sols are susceptible to erosion.
- In rheological terms, the gel point is defined by a threshold value for the shear strength, $S*$, above which only gels are stable (e.g., $S^* = 1$ Pa; Clay Tech 2009 draft final report).
- Because shear strength varies with water ratio, a specific value of w_r (w_r^*) can be related to S^*.
- For the case of bentonite extruded into a fracture, a sol can form only at locations in the fracture where $w_r \geq w_r^*$ (up to a limiting value of w_r at the sol-groundwater boundary).
- w_r^* thus constrains the location of the gel-sol boundary, and $1/w_r^*$ defines the corresponding upper bound on bentonite concentration in the sol.

Distribution of bentonite flocs, gels and sols in a fracture



Source: Börgesson & Nilsson presentation at the SKB Workshop on Buffer erosion - May 2008

Distribution of swelling pressures in extruded bentonite

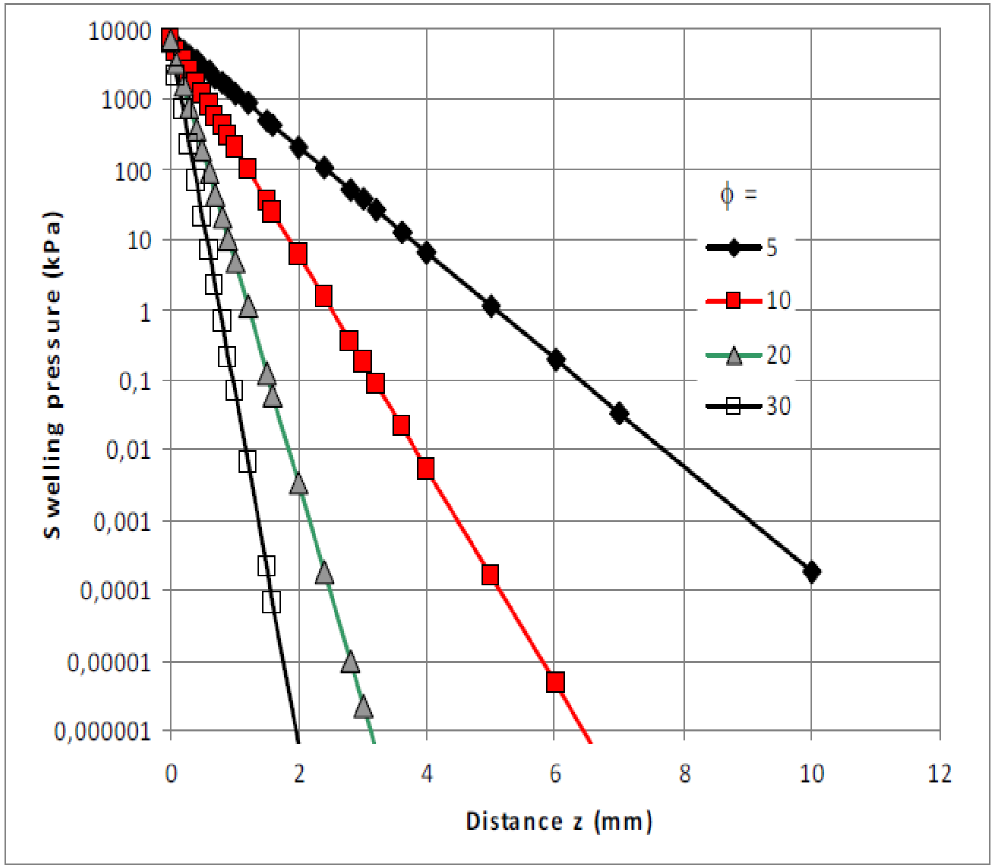


$$\sigma = \sigma_0 e^{-2\tan\phi(\frac{z}{a})}$$

σ - swelling pressure at z

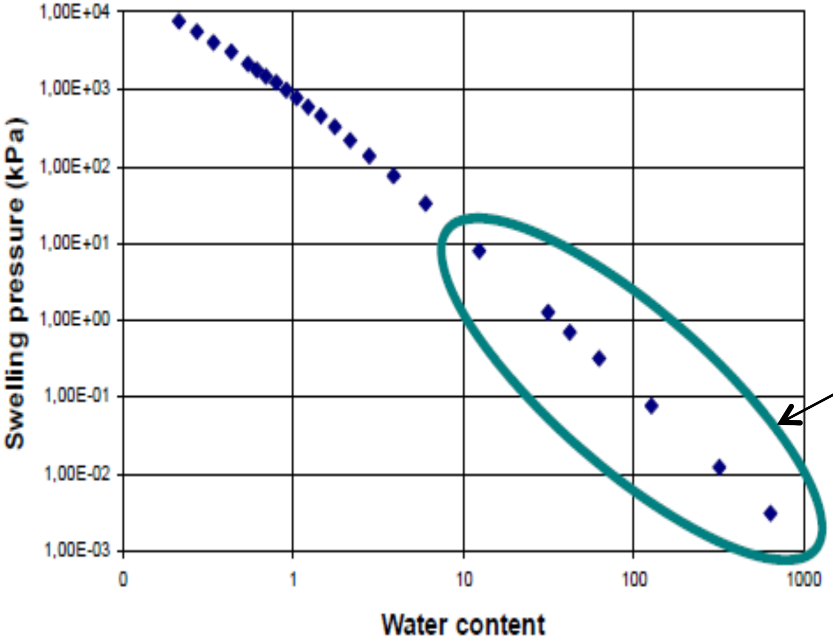
σ_0 - swelling pressure at the deposition hole-fracture boundary (z = 0)

ϕ - friction angle



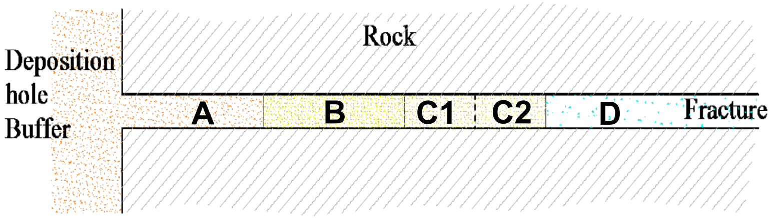
(Source: Clay Tech 2009 draft final report)

Swelling pressure is related to w_r

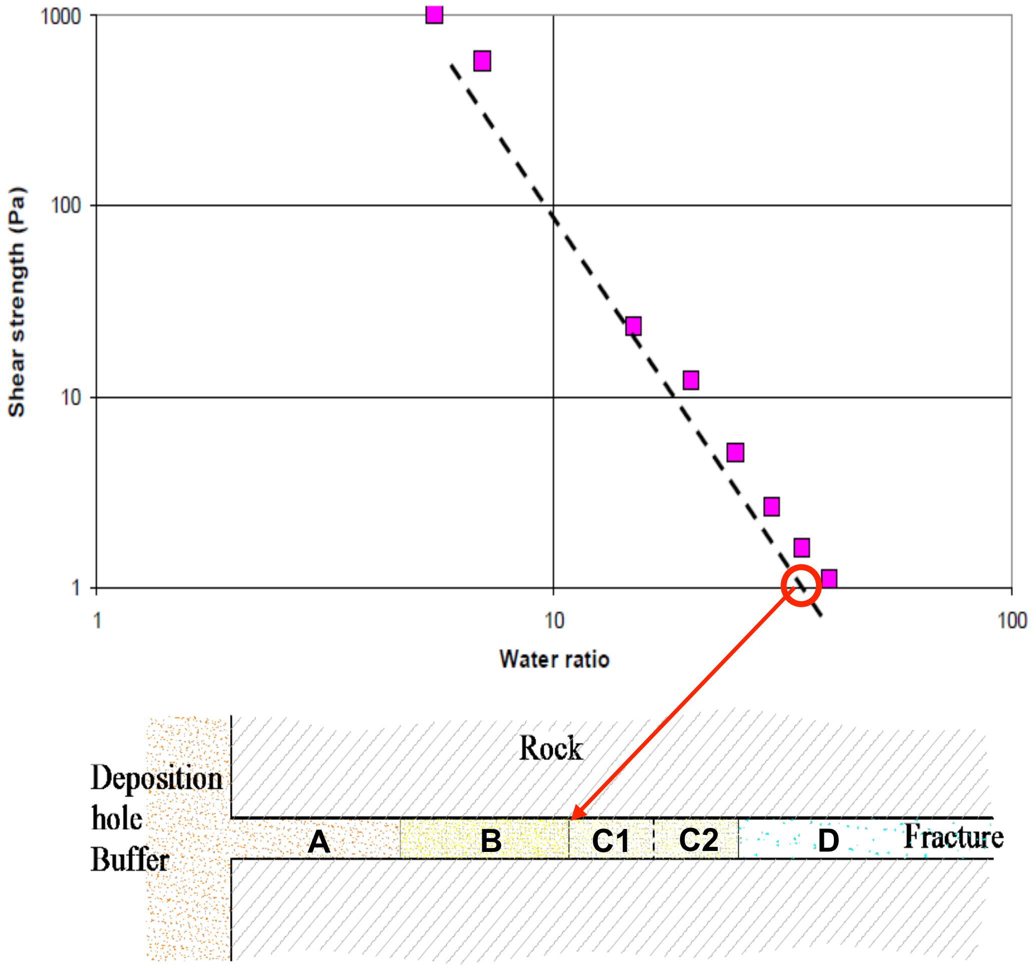


WyNa in distilled water (from Börgesson and Nilsson, Dec. 2008 SKB workshop on buffer erosion)

Range of estimated values based on DLVO theory



w_r is related to shear strength



MX80 in distilled water after one day resting time (Clay Tech 2009 draft final report). Square symbols refer to measured values in vane tests. The dashed line represents a "good fit" to the measured values. The circle indicates the water ratio at the gel point, where $S^* = 1$ Pa.

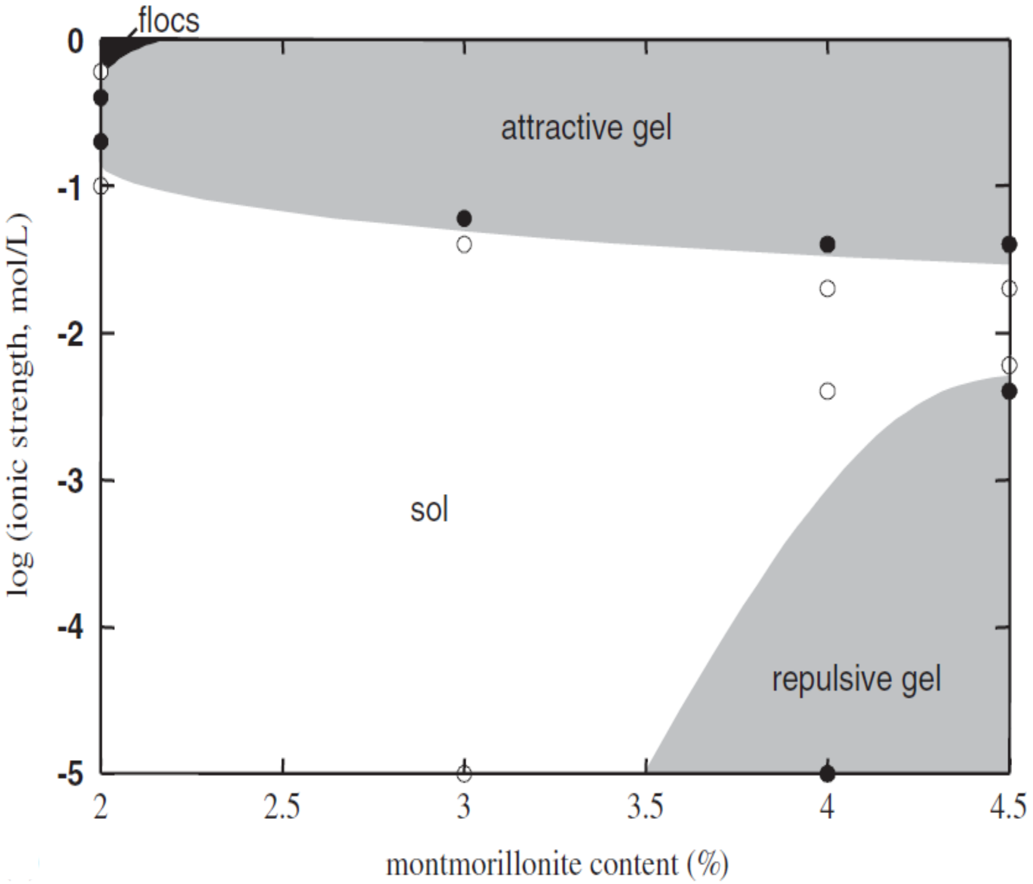
Results and conclusions

- The results of a limited number of vane tests involving MX80 in distilled water suggest $w_r^* = 35$ at $S^* = 1$ Pa (Clay Tech 2009 draft final report).
- Taking this value as being representative of the minimum water ratio that could exist in a bentonite sol gives a corresponding value of C_{max} **= 29 kg m^{-3}**.
- This is similar to the SR-Can value, $C_{max} = 50$ kg m^{-3}.
- Rheological constraints on C_{max} are robust in the sense that they do not require a detailed understanding of colloid behavior, and can be determined experimentally.
- SKB's studies indicate, however, that experimental results can be quite sensitive to sample preparation methodology, sample history, bentonite type and water chemistry.

Ion exchange & ionic strength constraints on the stability of clay flocs, gels and sols

Randy Arthur
November 4, 2009
Stockholm, Sweden

Phase/state diagrams



Wy-Na in NaCl (Abend & Lagaly, 2000; Appl. Clay Sci., 16, 201-227). Note that montmorillonite content (%) x 10 = w_r^{-1} (g l^{-1})

But…glacial meltwaters are not simple electrolyte solutions

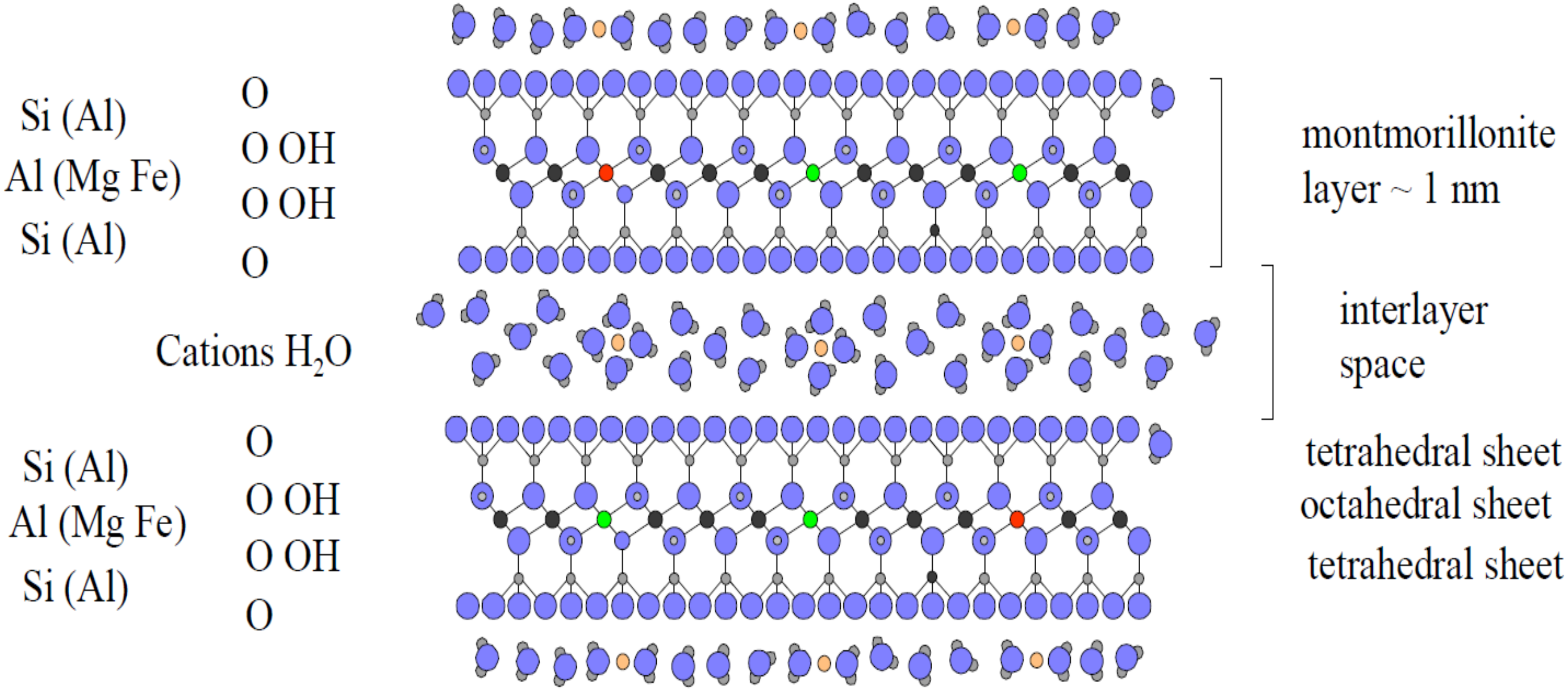
[Analytical data* from Brown (2002; Appl. Geochem., 17, 855-883)]

Glacier	**Ca^{2+}**	**Mg^{2+}**	**Na^{+}**	**K^{+}**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**NO_3^-**
Bench	550	36	25	61	427	2	262	-
Haut Glacier d' Arolla	160-470	15-49	5.1-36	5.4-18	180-360	0.85-92	30-240	0.0-30
Nigardsbreen	8.8-38	1.6-7.8	8.3-2.5	1.0-4.4	1.4-8.5	9.8-25	7.0-41	1.9-11
Gornergletscher	130-334	16-190	8.7-43	2.6-33	-	-	-	-
Walcott	226-1292	16-188	17-97	2.3-33	206-1030	9.5-87	42-678	-
Koettlitz	72-92	5.8-6.6	11-34	0.8-6.9	91-132	0.55-1.2	3.4-7.6	-
Howchin	1072-1342	122-194	364-610	44-68	1360-1560	119-257	342-1165	-
Ward	722-828	288-336	879-1436	90-109	1080-1450	667-1020	218-230	-
Berendon	90-763	1.6-19	0.87-7.8	0.38-5.1	230-785	25-27	-	-
Tsanfleuron	638	92	4.9	6.3	627	5.5	118	11
Chhota-Shigri	75-260	6.6-41	25-65	22-51	-	-	-	-
Scott Turnerbreen	120-300	99-290	110-740	5.1-19	110-260	-	96-200	-
Fjallsjökull	208-274	32-60	30-120	2.8-7.2	190-300	-	26-66	-
Chamberlain	75-304	8.2-123	4.3-8.7	0.0-5.1	150-200	5.6-20	29-310	-
Engabreen	82-623	4-65	11-212	0-27	51-675	10-191	0-142	0-15
Grimsvotn	359	115	482	12	573	87	132	-
Austre Okstindbreen	281-411	8.2-41	15-137	4.3-29	-	-	-	-
Argentière	20-480	6-66	10-89	5.2-6	110-400	-	10-60	-

---

* Concentrations in $\mu eq\ l^{-1}$

And…montmorillonites have variable concentrations of exchangeable cations (mainly Na^+ and Ca^{2+})



Can phase/state diagrams be constructed for more relevant systems?

Ion-exchange constraints

(Clay Tech 2009 draft final report)

- For the reaction $Ca^{2+} + 2Na(clay) = 2Na^{+} + Ca(clay)$:

$$K_{GT} = \frac{X_{\text{Ca-clay}} a^{2}_{\text{Na}^{+}}}{X^{2}_{Na-clay} a_{\text{Ca}^{2+}}}$$

- For electrolytes containing no other exchangeable cations than Na^{+} & Ca^{2+}, and assuming activity = concentration ([ ]):

$$K_{GT} = \frac{X_{\text{Ca(clay)}}[\text{Na}^{+}]^{2}}{(1 - X_{\text{Ca(clay)}})^{2}[\text{Ca}^{2+}]}$$

- $[Na^{+}]$ can thus be calculated as a function of $[Ca^{2+}]$ if $X_{\text{Ca(clay)}}$ and K_{GT} are known.
- Strongly attractive ion-ion correlation forces prevent the formation of montmorillonite sols & gels when $X_{\text{Ca(clay)}} \geq 0.9$.
- Solution conditions favoring sol formation (and thus potential buffer erosion) can thus be represented in terms of a range of Na^{+} and Ca^{2+} concentrations that are compatible with $X_{\text{Ca(clay)}} \leq 0.9$.

Aside: A possible erosion-inhibiting process

- Rearranging the first equation from the preceding viewgraph, and assuming only exchangeable Na and Ca:

$$2 + \frac{a^2_{\mathrm{Na^+}}}{K_{GT}a_{Ca^{2+}}} = X_{\mathrm{Ca(clay)}} + \frac{1}{X_{\mathrm{Ca(clay)}}}$$

- For $X_{\mathrm{Ca(clay)}} \geq 0.9$, $(a^2_{\mathrm{Na}}{}^+/a_{\mathrm{Ca}}{}^{2+})$ must therefore be ≤ 0.05 [$K_{GT} = 4.5$ (Clay Tech 2009 draft final report)].
- Aqueous-speciation calculations indicate:
  - for glacial meltwaters (Brown 2002) and Grimsel meltwater: $(a^2_{\mathrm{Na}}{}^+/a_{\mathrm{Ca}}{}^{2+}) < 0.01$,
  - for a representative groundwater (Forsmark, KFM02A at 512m): $(a^2_{\mathrm{Na}}{}^+/a_{\mathrm{Ca}}{}^{2+}) = 0.7$,
  - For a saline groundwater (Laxemar "most saline"): $(a^2_{\mathrm{Na}}{}^+/a_{\mathrm{Ca}}{}^{2+}) = 1.1$.
- This suggests that although meltwaters are generally assumed to have $M_{\mathrm{ca2+}} <$ CCC, thus stimulating buffer erosion, $(a^2_{\mathrm{Na}}{}^+/a_{\mathrm{Ca}}{}^{2+})$ would also be small enough in these solutions to promote alteration of montmorillonites to $X \geq 0.9$, thus inhibiting buffer erosion.
- Promising, but further evaluation is needed.

Ionic-strength constraints

(Clay Tech 2009 draft final report)

- Ionic strength:

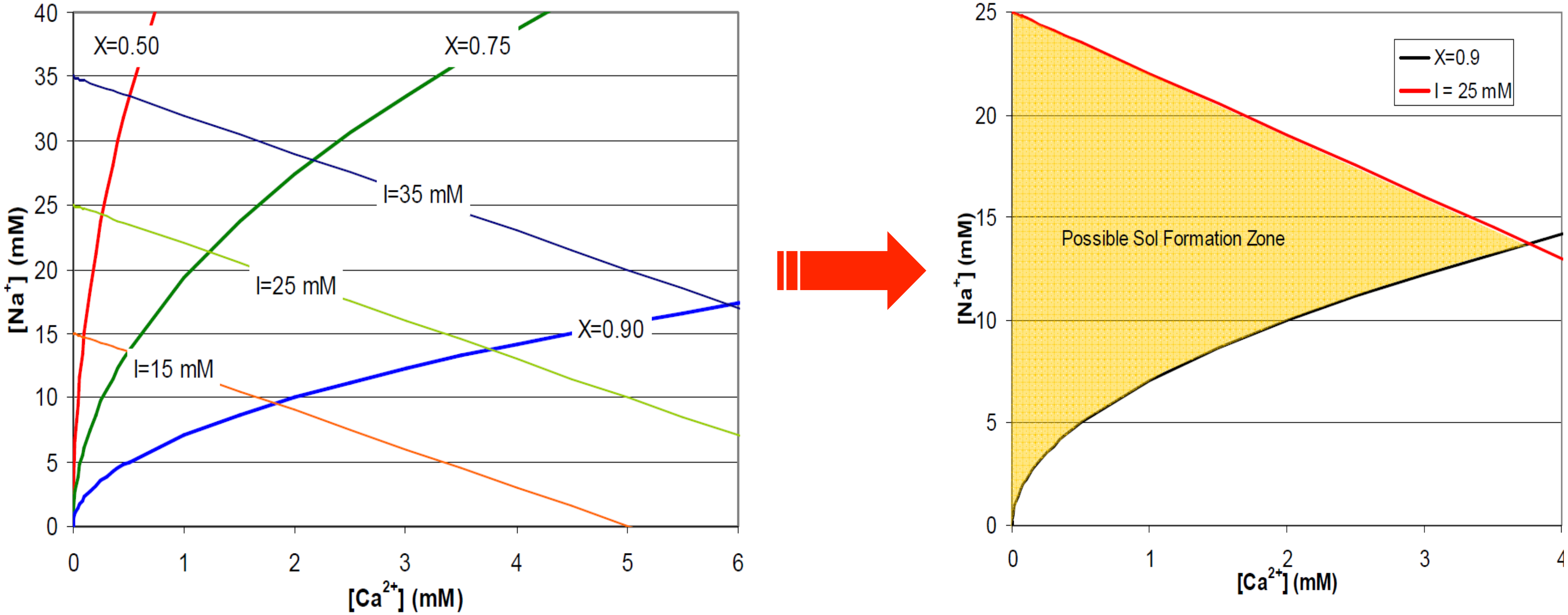
$$I = \frac{1}{2}\sum (m_i z_i^2)$$

- If the solution consists of a Na-Ca electrolyte with only monovalent anions:

$$I = [\mathrm{Na}^+] + 3[\mathrm{Ca}^{2+}]$$

- For a given value of *I*, $[\mathrm{Na}^+]$ can be calculated as a function of $[\mathrm{Ca}^{2+}]$.
- Turbidity measurements made in swelling and sedimentation experiments indicate that Wy-Na sols can form in pure NaCl solutions only if $I \le 25$ mM.
- This value is assumed to be conservatively bounding for mixed Na/Ca electrolytes with Wy-Na/Ca.

Construction of “beak” diagrams

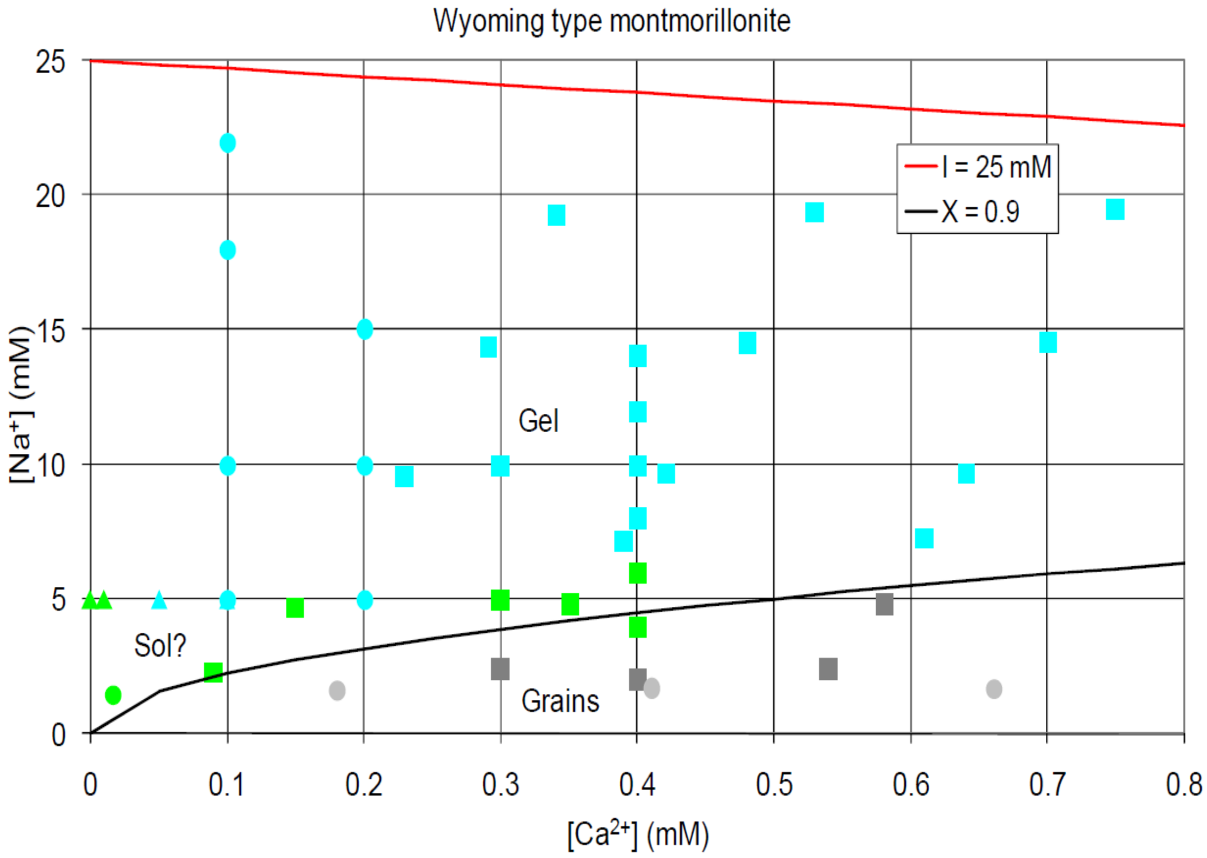


Theoretical

Bounding

Source: Clay Tech 2009 draft final report

Experimental evaluation → conditions favoring sol formation are much more limited than expected based on the bounding model



<u>Colors</u>

Turquoise - gel

Gray – floc

Green – possible sol

<u>Symbols</u>

Square - Sed. Tests, initial Ca-mont.

Circle – Sed. Tests, initial Na-mont.

Triangle - Swell. Tests, initial Na-mont.

Source: Clay Tech 2009 draft final report

Conclusions: Comments on the Clay Tech model

- Useful framework for thinking about sol-gel stability.
- Theory is unclear:
  - Poorly defined terms and questionable assumptions (e.g., activities, free-ion concentrations, total analytical concentrations, stoichiometric versus effective ionic strength).
- Theory is incomplete:
  - Apparently does not consider effects of sol concentration on critical ionic strength.
- Experimental results are unconvincing:
  - Na^+ & Ca^{2+} concentrations are calculated, not measured, values - pH not determined.
  - Gels defined by turbidimetric measurements have the water ratios of sols based on rheological measurements.
  - Gel-formation is attributed to face (-)/edge (+) interactions, but there is conflicting evidence as to whether edges have positive charges at pH > 6.5.
- Approach has still only been applied to relatively simple Na/Ca systems.
- Uncertain whether this approach can be made sufficiently robust for use in a safety case.
- Equilibrium constraints on $X_{Ca(clay)} \geq 0.9$ for montmorillonites in contact with glacial meltwaters should be further evaluated.