

# Crystalline swelling of montmorillonites with divalent interlayer cations at high water to solid ratio – Indirect implications on bentonite chemical erosion?

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# BACKGROUND

This study have focused on the swelling properties of three montmorillonites with divalent interlayer cations with free access to water (Wyoming, Milos and Kutch).

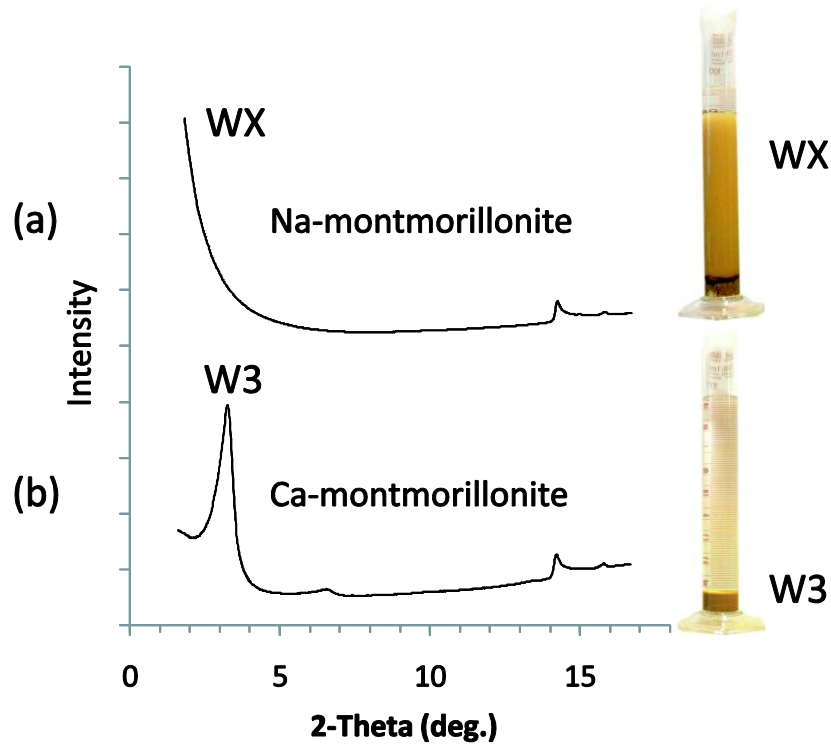
The swelling was studied using synchrotron XRD and SAXS.

The purpose was to investigate the effects from temperature, type of interlayer cation, salt concentration and type of montmorillonite on the basal spacing.

Some interesting observations were made that indirectly seem to link to important properties such as swelling pressure and osmotic swelling (chemical erosion)

The studies are documented in a number of publications and in a very recent PhD-thesis.



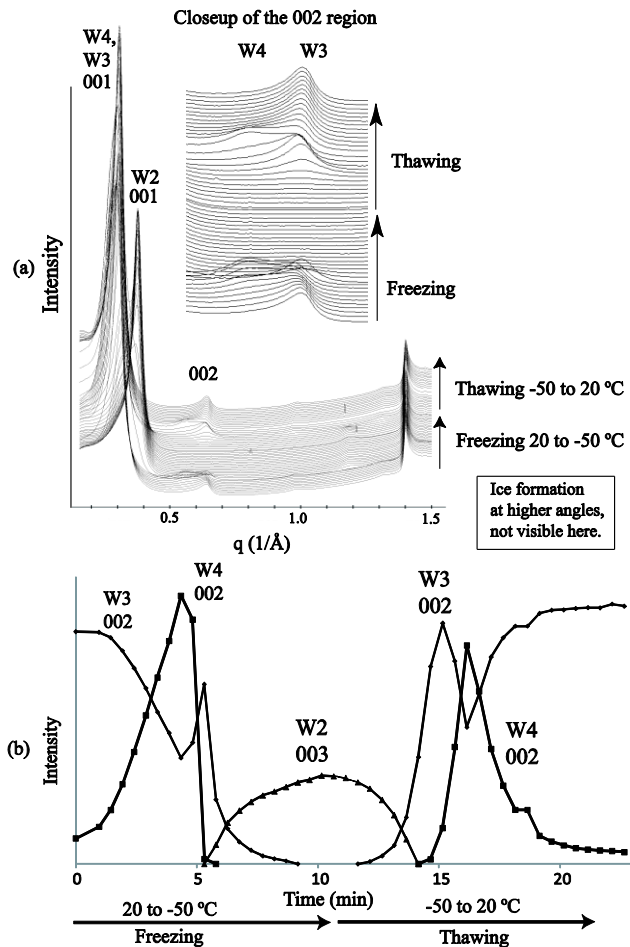


**Figure 14.** X-ray diffractograms of wet clays (left) and swelling tests (right). (a) Wyoming Na-montmorillonite in water showing osmotic swelling (WX). In the glass cylinder is a natural sodium-dominated bentonite (Asha 505) from the Kutch area, India. (b) Wyoming Ca-montmorillonite in water. In the glass cylinder is a natural calcium-dominated bentonite from Rokle, Czech Republic.

There are mainly two regions of swelling for smectites: (i) crystalline swelling with one to four layers of water and (ii) osmotic swelling caused by delamination of the tactoids into smaller tactoids or even into single platelets. The crystalline swelling is of relevance to the bentonite buffer saturation and the osmotic swelling is of relevance to chemical erosion.

Different forces are relevant for crystalline swelling and osmotic swelling, but in both cases (i) type of smectite, (ii) type of interlayer cation and (iii) salt content is relevant.

# TEMPERATURE



Upon cooling, Ca-Wyoming montmorillonite was found to expand from 19 Å to 21 Å prior to ice formation. After ice formation the clay mineral was dehydrated to 16 Å.

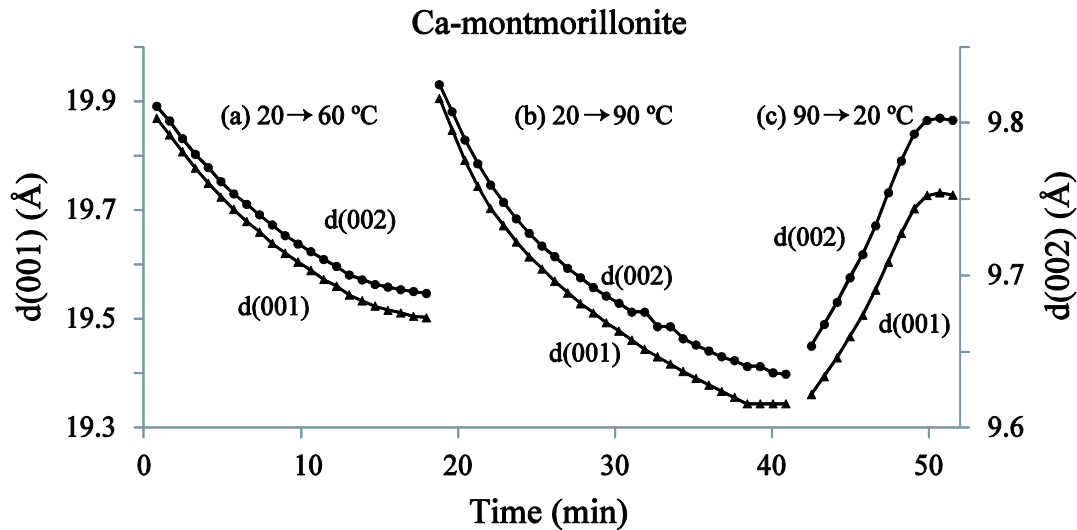
No earlier documentation of this expansion has been found.

Interestingly only parts of the montmorillonite showed this expansion behaviour, indicating potentially that two types of montmorillonite could be present in MX-80.

**Figure 15.** Freezing and thawing of Wyoming Ca-montmorillonite (from MX-80; 30 wt% in water).

- (a) X-ray diffractograms of freezing and thawing, with a close-up of the 002 reflection region. Ice reflections are at higher angles and are not seen in this experiment.
- (b) (b) Integrated intensity of W4 and W3 002 reflections as a function of time (Svensson and Hansen, 2014).

# TEMPERATURE

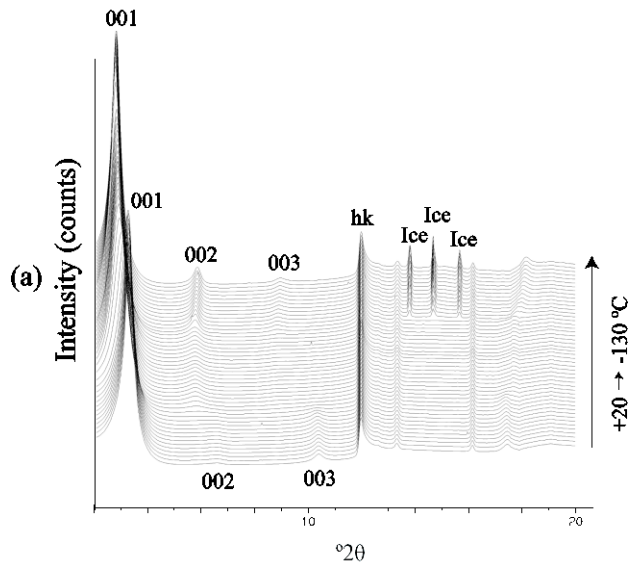


**Figure 18.** Ca-montmorillonite (30 wt% in water) basal spacing as a function of temperature given as d(001) (dots) and d(002) (triangles). Three consecutive series: (a) 20 → 60 °C, (b) 20 → 90 °C and (c) 90 → 20 °C (Svensson and Hansen, 2013a).

Expansion upon cooling indicate contraction upon heating, and this was also observed. Hence, the clay mineral released minor water at the elevated temperature even though it had unlimited access to free water. Upon cooling the clay mineral expanded again.

In contrast, osmotic swelling has been observed to increase at higher temperatures (Hansen et al. 2012) as increased osmotic swelling increase the entropy, while increased crystalline swelling decrease the entropy.

# SALT + TEMPERATURE



With the addition of salt the freezing point drops.

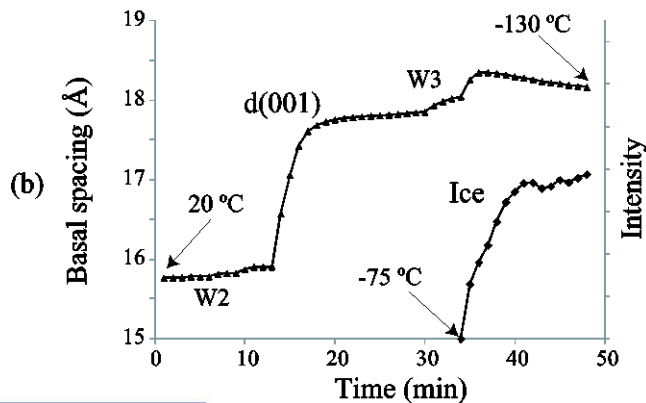
This allows the smectite to be cooled even further before the freezing process occur.

Adding salt to a smectite-water mixture dehydrate the smectite.

Freezing a smectite to -50 C also dehydrate the smectite.

However if you cool a smectite in salt solution from RT  $\rightarrow$  -50 C it will hydrate and expand.

In this extreme case from  $\sim 16 \text{ \AA}$  to  $\sim 18 \text{ \AA}$ .

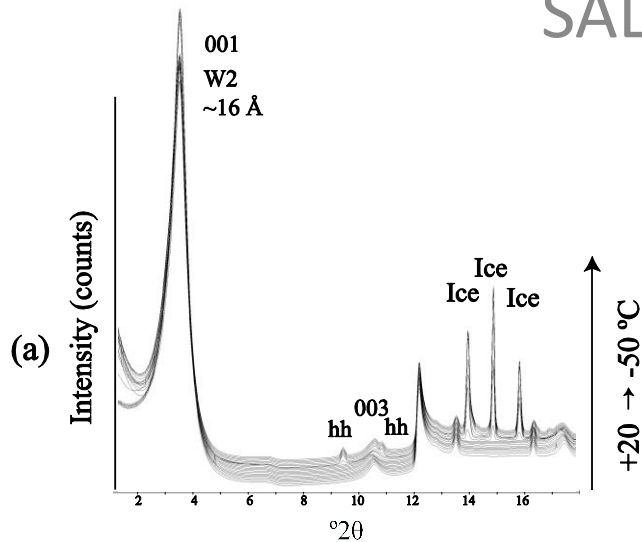


**Figure 16. Freezing of Ca-montmorillonite (30 wt%) in 3M CaCl<sub>2</sub> from +20 to -130 °C resolved in time.**

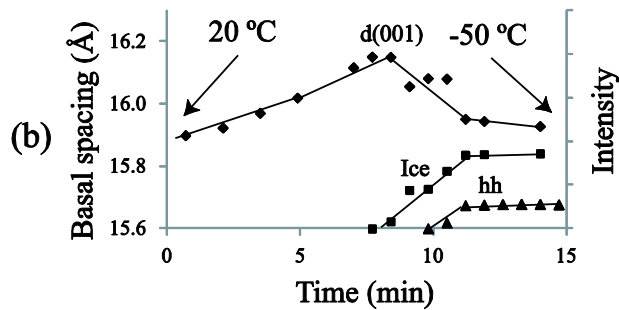
(a) Consecutively recorded diffractograms and (b) basal spacing and ice intensity as a function of time (temperature).  $\lambda = 0.955 \text{ \AA}$  (Svensson and Hansen, 2013a).



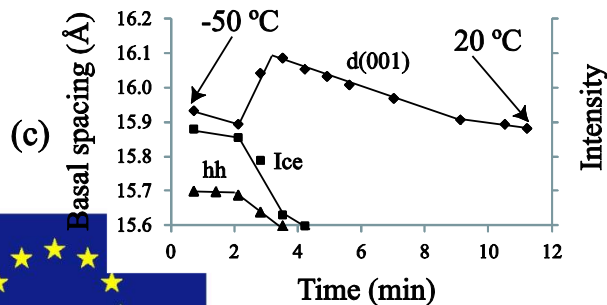
# SALT + TEMPERATURE



Similar behaviour is seen in Na-montmorillonite with NaCl, but the expansion is much smaller, and at low enough temperatures hydrated Na<sup>+</sup> and Cl<sup>-</sup> ions leave the interlayer space causing the smectite to contract and crystalline hydrohalite (hh) and ice form instead.

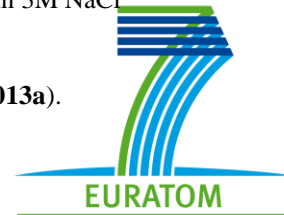
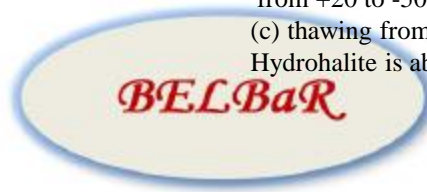


Hence in the Ca-case, Ca<sup>2+</sup> and Cl<sup>-</sup> was found to stay within the interlayer space resulting in an expanded clay mineral, while in the Na-case the ions instead formed an crystalline external phases.

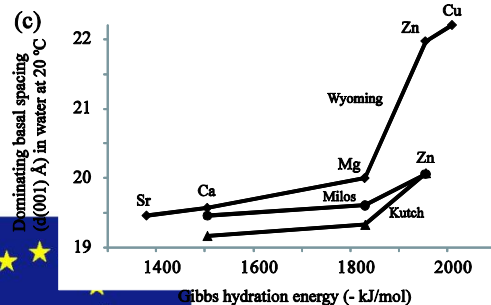
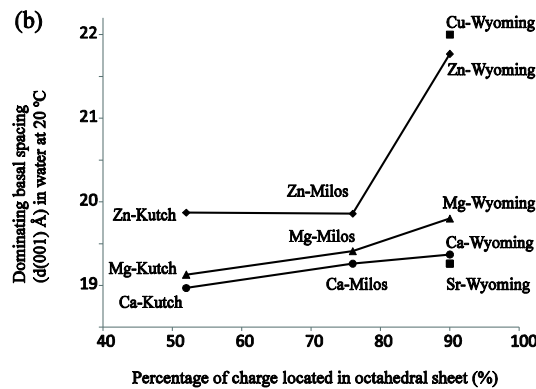
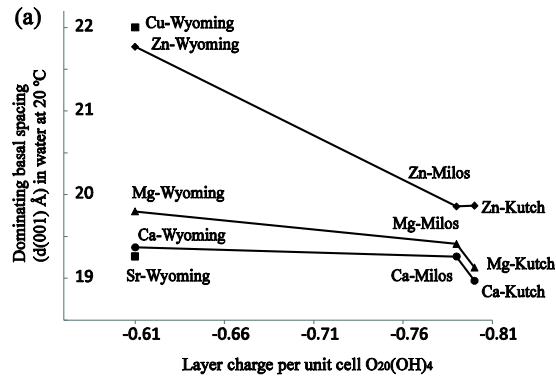


Hence at low temperatures, a little bit of salt decreased the dehydration of the smectite by lowering the water potential inside the interlayer.

**Figure 17.** (a,b) Freezing of Na-montmorillonite (30 wt%) in 3M NaCl from +20 to -50 °C resolved in time (c) thawing from -50 to 20 °C ( $\lambda = 0.955 \text{ \AA}$ ). Hydrohalite is abbreviated as hh (Svensson and Hansen, 2013a).



# INTERLAYER CATION and LAYER CHARGE

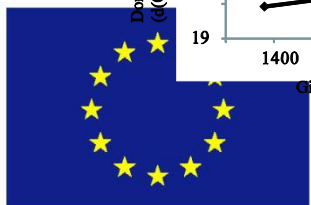


-Expansion upon cooling was seen also in the Milos and Kutch smectites, however not to the same extent. Only fractions of the Wyoming montmorillonite formed the 21 Å hydrate.

-By increasing the Gibbs hydration energy of the interlayer cation 21 Å was seen also in room temperature, and in the case of Cu- and Zn- Wyoming the 21 Å hydrate was more present than 19 Å hydrate.

-With the same interlayer cation the Wyoming expanded more than Milos, that expanded more than the Kutch smectite.

**Figure 19.** Dominating basal spacing of smectites in liquid water (30 wt% smectite) with divalent interlayer cations as a function of (a) total layer charge, (b) layer charge distribution and (c) Gibbs hydration energy of the interlayer cation (Svensson and Hansen, 2014).





# EXPLANATION



The Gibbs free energy equation describes the conditions for a spontaneous chemical reaction to occur ( $\Delta G < 0$ ), and is a balance between the enthalpy and the entropy of the reaction:

$$\Delta G = \Delta H - T\Delta S$$

At reduced temperatures the entropic term ( $T\Delta S$ ) is also reduced and the enthalpy ( $\Delta H$ ) of the reaction becomes more dominant, and the somewhat incompletely hydrated interlayer cations may hence hydrate further (exothermic process with  $\Delta H < 0$ ).

So decreasing the temperature decrease the impact from entropy and allow further swelling. Alternatively one may increase the overall Gibbs energy of hydration of the interlayer cation, this may also expand the montmorillonite.

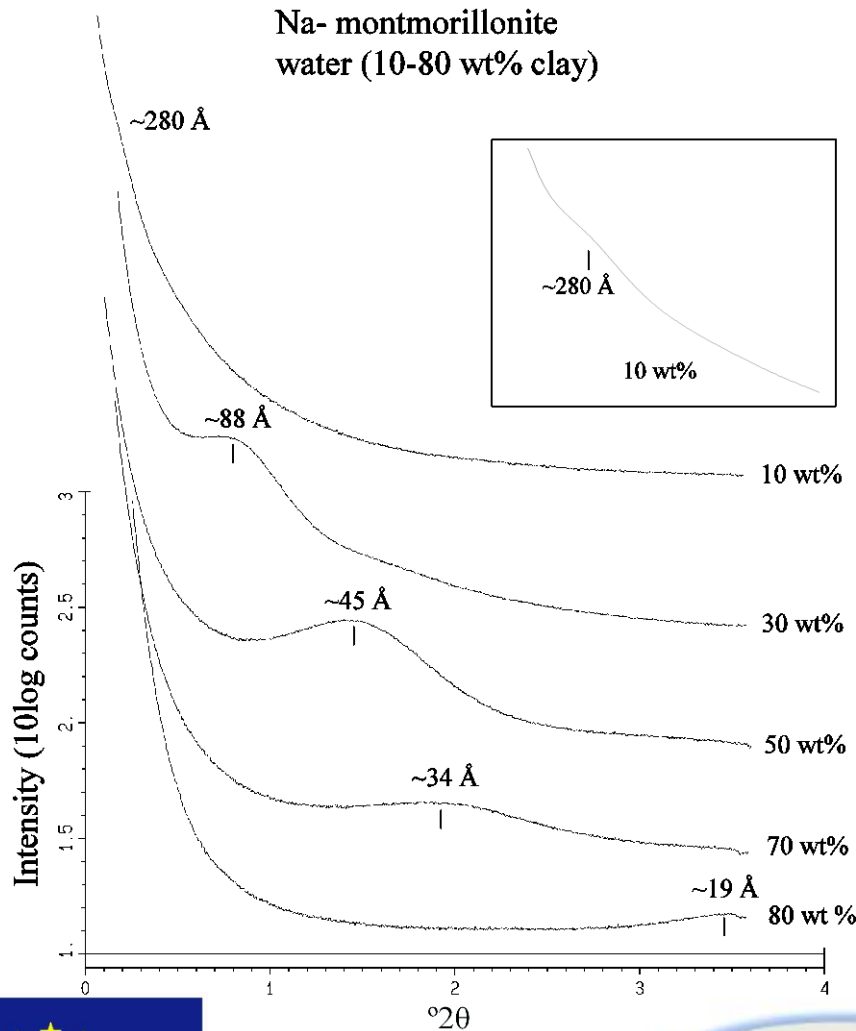
The third parameter is the layer charge. Higher charge means that the Coulombic interaction between the montmorillonite layers increase, and any expansion of the clay mineral have to counteract this.



# OSMOTIC SWELLING – CHEMICAL EROSION

In a pure Wyoming Na-montmorillonite the clay may expand more or less infinitely. The expansion is limited by the amount of water present and also by gravity.

This is why osmotic swelling may contribute to erosion.



**Figure 20.** Small angle scattering of Wyoming Na-montmorillonite, showing the relation between basal spacing and water content (Svensson and Hansen, 2013a).  $\lambda = 1.09994 \text{ \AA}$ .

# OSMOTIC SWELLING– CHEMICAL EROSION



The colloid coagulation concentration is the salt concentration that is needed to cancel the osmotic swelling. Higher layer charge increase the attraction between the clay layers and decrease the CCC.

This is also confirmed by experimental data for the investigated montmorillonites (Birgersson et al 2009).

It was indicated by the experiments that lower charge montmorillonite may form 21 Å spacing but the higher charge did not. In the case of Wyoming montmorillonite both 19 and 21 Å spacings were present.

This indicate that two populations were present with higher and lower layer charge, and different extent of the charge present in the octahedral sheet compared to the tetrahedral sheet.

Hence, parts of the MX80 seem to act more like a Milos or Kutch montmorillonite, while parts may act differently and swell more.



# SUMMARY



The layer charge was found to be non-uniformly distributed in the bentonites, and the layer charge impact the ability for osmotic swelling. Heterogeneously distributed layer charges have also been described earlier e.g. by **Christidis and Eberl (2003)**.

The presence of montmorillonites with heterogeneously distributed layer charges is of interest when it comes to release of colloids, as potentially the fractions that most easily form colloids will do this initially and later the release may stop.

The experimental methodology used (Svensson and Hansen, 2014) may potentially be used for indirect screening of various montmorillonites and other smectites in the search of a clay mineral with a layer charge corresponding to no or very little osmotic swelling, hence reducing the possible release of colloid particles at conditions of low salinity and high  $\text{Na}^+$  to  $\text{Ca}^{2+}$  ratio.

This is planned to be studied further in the future.



## REFERENCES



More information can be found in these publications:

**Freezing and thawing of montmorillonite – a time resolved X-ray diffraction study.** P. D. Svensson and S. Hansen (2010) *Applied Clay Science*, **49**, 127-134

**Combined salt and temperature impact on montmorillonite hydration**  
P. D. Svensson and S. Hansen (2013) *Clays and Clay Minerals*, **61**, 328-341.

**Determination of layer-charge characteristics of smectites.** Christidis, G. E., Eberl, D. D. (2003) *Clays and Clay Minerals*, **51**, 644-655.

**Swelling transition of a clay induced by heating.** Hansen, E. L., Hemmen, H., Fonseca, D. M., Coutant, C., Knudsen, K. D., Plivelic, T. S., Bonn, D., Fossum, J. O. (2012). *Scientific Reports*, **2**, 618.

**Bentonite erosion. Final report.** Birgersson, M., Börgesson, L., Hedström, M., Karnland, O., Nilsson, U. (2009) *Swedish Nuclear Fuel and Waste Management Co (SKB) Technical Report*, TR-09-34.

