Freezing and thawing of montmorillonite — A time-resolved synchrotron X-ray diffraction study

Per Daniel Svensson a,b,⁎, Staffan Hansen b

a Swedish Nuclear Fuel and Waste Management Co, Åspö Hard Rock Laboratory, P.O. Box 929, SE-57229, Oskarshamn, Sweden
b Polymer & Materials Chemistry, Kemicentrum, Lund University, P.O. Box 124, SE-22100, Lund, Sweden

A R T I C L E   I N F O

Article history:
Received 14 September 2009
Received in revised form 16 April 2010
Accepted 26 April 2010
Available online 5 May 2010

Keywords:
Freezing
Thawing
Montmorillonite
Smectite
Clay
Bentonite
XRD
Time-resolved

A B S T R A C T

The evolution of phases over time during freezing and thawing of unconfined Na- and Ca-montmorillonites (Wyoming, MX-80) was studied with time-resolved synchrotron X-ray diffraction. The clay samples were: (i) powder equilibrated to ambient atmosphere and (ii) pastes of 30 mass% montmorillonite in pure water. The phases were characterised in-situ using a stream of nitrogen gas for temperature control. The behaviour of montmorillonite during freezing and thawing is important in final repositories for spent nuclear fuel that are using bentonite as a buffer material. The Na-montmorillonite equilibrated to ambient atmosphere (one-layer hydrate) was unaffected by freezing down to −50 °C. The Ca-montmorillonite equilibrated to ambient atmosphere (two-layer hydrate) showed a minor decrease in basal spacing (0.11 Å) by freezing down to −50 °C. The magnitude of the decrease in basal spacing was high compared to the thermal contraction of the similar minerals muscovite and pyrophyllite and some dehydration of the clay was likely to be involved. Wet Na-montmorillonite in pure water was highly affected by freezing causing the osmotic phase to collapse during ice formation to 19 Å (three-layer hydrate) and later to a mixture of two and three-layer hydrates (−15 °C) and at lower temperatures to two-layer hydrate (16 Å, −50 °C). The Ca-montmorillonite in pure water was present as a 19 Å three-layer hydrate at +20 °C and expanded upon cooling, producing two partly overlapping 001 reflections corresponding to three and four-layer hydrates prior to the ice formation. A mean d-value of the 002 peaks of the four-layer hydrate was determined to be 10.8 Å, which corresponded to a basal spacing of 21.6 Å. To our knowledge this is the first time a distinct four-layer-water hydrate is reported for Ca-montmorillonite in pure water. After the ice formation started, the montmorillonite was dehydrated to three-layer hydrate and at −15 °C to a mixture of two and three-layer hydrates. At −50 °C only two-layer hydrate was present. The ice formation and the dehydration of the montmorillonite occurred simultaneously. The effects of freezing on the montmorillonite were shown to be reversible during the thawing. The two dimensional diffraction rings gave information on the ice texture. The highly dispersed Na-montmorillonite (high surface area) in pure water facilitated the nucleation of the ice crystals and gave rise to uniformly sized crystals, while the Ca-montmorillonite (not dispersed, lower surface area) gave rise to non-uniformly sized ice crystals.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Around 50 years ago it was shown by X-ray diffraction that the freezing of montmorillonite-containing pastes led to dehydration and shrinking of the montmorillonite interlayer distance (Norrish and Rausell-Colom, 1962; Ahlrichs and White, 1962; Anderson and Hoekstra, 1965). They showed that the process was rapid and reversible. This behaviour should be of importance when swelling clays containing montmorillonite (bentonites) are used as engineered barriers for toxic or radioactive waste repositories. The closer to the ground level these deposits are situated, the more likely they are to be exposed to freezing temperatures and to freeze–thaw cycles during subsequent glaciations. For final repository of spent nuclear fuel, a time scale of 106 years is applied for performance assessment and the possibility of one or more glaciations must be taken into account for areas situated sufficiently close to the Earth’s poles (SKB, 2006). Also, surface drill holes used for the investigation of the rock and parts of the shaft are planned to be backfilled with smectite rich clays. Smectites such as montmorillonite are common minerals in some soils and are likely to have an impact on the soil properties upon freezing and thawing with respect to moisture transport and volume change. This makes enhanced understanding of the freezing and thawing behaviours of smectites important for many different fields. The effect of freezing on montmorillonite has received

⁎ Corresponding author. Swedish Nuclear Fuel and Waste Management Co, Åspö Hard Rock Laboratory, P.O. Box 929, SE-57229, Oskarshamn, Sweden. Tel.: +46 491767021, +46 706090026 (mobile); fax: +46 49182005.
E-mail address: daniel.svensson@skb.se (P.D. Svensson).

0169-1317/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.clay.2010.04.015
little attention in connection with clay barriers, until recently, when Birgersson et al. (2008) investigated its effect on the swelling pressure of saturated and confined montmorillonite systems and showed that freezing decreased the swelling pressure. Access to synchrotron X-rays makes it possible to get much higher signal to noise ratios compared to traditional X-ray diffraction. Additionally, time-resolved data can be captured and this makes it possible to analyze this important process further. In the present study, we have investigated the evolution of phases over time during the freezing and thawing of unconfined Na- and Ca-montmorillonites in the dry state equilibrated to ambient atmosphere and as pastes with pure water. We describe the basal spacing of the montmorillonite in terms of the number of water layers. This is a simplified model. Using 3 Å as the approximate size of a water molecule (thickness of one layer), one can predict most observed basal spacings of smectite–water mixtures (Bradley et al., 1937). For simplicity we label these layer hydrates as: W1 (one-layer hydrate), W2 (two-layer hydrate), W3 (three-layer hydrate), W4 (four-layer hydrate) and WX (unknown number of water layers). A more detailed picture of the interlayer structure of smectite hydrates has emerged based on neutron scattering experiments and computer simulations, see for example Sposito et al. (1999). Basal spacings of smectites deviating from the ideal ones have also been reported (van der Gaast et al., 1986).

2. Experimental

2.1. Preparation of samples

The montmorillonite samples used in the present study were obtained by courtesy of Clay Technology AB, Lund. The Wyoming type of bentonite (MX-80, American Colloid Co.) consisted of around 80 mass% montmorillonite (mainly sodium form). Homo-ionic and dialyzed clay fractions (MX-80, American Colloid Co.) consisted of around 80 mass% montmorillonite. The analyses showed the clay fraction to consist almost exclusively of montmorillonite, with the following approximate layer composition per unit cell: (Al3.1Fe0.4Mg0.5)(Si7.9Al0.1)O20(OH)4 and either Na- or Ca-ions in the interlayer. The exchange capacity (CEC) of the dried material (105 °C, 24 h) was determined to be 86 cmol(+)/kg (Karnland et al., 2006, p. 23).

2.2. Mounting of specimens

(i) Montmorillonite samples equilibrated at ambient atmosphere were ground in an agate mortar, and the powder was used to partly fill a soda–lime–glass capillary (outer diameter 1.5 mm), which was then closed at both ends using modelling clay. The water content (mass of water divided by mass of solid hydrate) in the samples was estimated from the X-ray diffractograms by using the position of the montmorillonite 001 reflection. The unit cell parameters a = 5.21 Å and b = 8.97 Å and unit cell mass 734 g/mol (Karnland et al., 2006, p. 63). The approximated values were 6 and 17 mass% for the sodium and calcium montmorillonites respectively. This was equivalent to water ratios of 0.07 and 0.21 (defined as mass of water divided by mass of anhydrous solid).

(ii) Ground montmorillonite was mixed with deionized water to form a paste with 30 mass% of solid (25–27 mass% anhydrous solid), corresponding to a water content of 82–83 mass% (water ratio of 4.6). A capillary was partially filled with the paste using a syringe and the capillary was sealed with modelling clay. The samples used were thus essentially unoriented.

2.3. Synchrotron X-ray diffraction

Time-resolved X-ray powder diffraction data were collected on the beam-line I711 at MAX-lab, Lund (Cerenius et al., 2000) using a Mar system with a flat CCD detector (Mar 165, 2048 × 2048 pixels). The X-ray beam had a wavelength of 1.09994 Å, as refined using a LaB6 reference sample, and a size of 1 × 1 mm. The capillary was not rotated during the measurements and was kept in a stream of flowing nitrogen with adjustable temperature (Cryojet, Oxford Instruments). After setting of the target temperature, the data collection was started. No continuous temperature monitoring was performed during the experiment. Each frame was monitored for 20 s with subsequent saving of data until the diffraction pattern did not change further. Before and after each run, the absence of any ice on the outside of the capillary was checked visually. The integrated intensity, scattering angle and width of the recorded diffraction rings were evaluated using the software Fit2d (A.P. Hammersley, ESRF). The minimum scattering angle that was measured was approximately 2θ = 1.7°, depending on the exact position of the beam stop in each experiment. This corresponded to a maximum observable d-spacing of 38 Å.

3. Results and discussion

3.1. Montmorillonite equilibrated at ambient atmosphere

In the two dimensional diffraction patterns of air-dry montmorillonites at +20 °C (Fig. 1a) the diffraction ring of the 001 reflection was closer to the central beam position in the Ca-montmorillonite compared to the Na-montmorillonite, indicating higher water content in the Ca case. The integrated diffractograms of dry montmorillonite at +20, −15 and at −50 °C (Fig. 1b) indicated a W1 hydrate for Na-montmorillonite and a W2 hydrate for Ca-montmorillonite in the samples, as would be expected for montmorillonite equilibrated at normal in-door environment (Brindley and Brown, 1980, p. 203). The first montmorillonite hk reflection was present at d = 4.48 Å (Fig. 1b, Fig. 1. (a) Two dimensional X-ray diffractograms of dry montmorillonite at +20 °C. (b) Integrated diffractograms of dry montmorillonites at +20, −15 and −50 °C. W1 and W2 denote one-layer and two-layer hydrates, respectively.
all montmorillonites and temperatures). The hk reflection was an in-plane reflection (within the 2:1 smectite layer) and was independent of the basal spacing and the level of hydration. No ice reflection was seen in the diffractograms during freezing (Fig. 1b, all montmorillonites and temperatures), which corresponded to W1. No systematic change in basal spacing with temperature was seen in the dry sodium montmorillonite by the temperature change (Fig. 2a). The reason for this was that the random noise in the determination of the basal spacing (weak 001 reflection) was larger than the thermal dependence of the clay mineral.

3.1.1. Na-montmorillonite (W1) at +20, −15 and −50 °C

In the Na-montmorillonite equilibrated at ambient atmosphere a rather weak basal 001 reflection was observed at \( d = 11.4 \) Å (Fig. 1b, Na-montmorillonite, all temperatures), which corresponded to W1. The freezing of the air-dry montmorillonite was done in two steps, (i) from +20 down to −15 °C and after stabilization of the basal spacing, (ii) further down to −50 °C, as indicated in the figures by different symbols.

3.1.2. Ca-montmorillonite (W2) at +20, −15 and −50 °C

The basal reflection located at \( d = 15.1 \) Å (Fig. 1b, Ca-montmorillonite, all temperatures) corresponded to W2. At \( d = 5.0 \) Å a weak 003 reflection was seen (Ca-montmorillonite, all temperatures). The basal spacing in the calcium two-layer hydrate was slightly affected by the stepwise temperature change (by −0.11 Å in total, Fig. 2b). The decrease of the basal spacing without any signs of ice formation was interpreted as thermal contraction of the clay mineral. The thermal expansion coefficient was calculated as:

\[
\alpha = \frac{\Delta L}{L_0 \Delta T} = -0.111 A / (15.11 A \times -70 K) = 1.0 \times 10^{-4} K^{-1}
\]

This value was larger than the corresponding constant for muscovite and pyrophyllite (0.18 × 10^{-4} and 0.15 × 10^{-4} K^{-1}; McKinstry, 1965) and likely some dehydration of the montmorillonite was involved. Bulk water expands by 0.48% during lowering the temperature from +20 to −20 °C (CRC, 1972–1973, p. F-5). If we assumed that the interlayer water behaved exactly as bulk water, the expansion of the interlayer water was counteracting the contraction of the mineral due to dehydration. The theoretical increase in the basal spacing of a two-layer hydrate by lowering the temperature from +20 to −20 °C, without any dehydration or thermal contraction of the anhydrous mineral itself, would then amount to approximately +0.03 Å. The water removed from the montmorillonite by the lowered temperature most

![Fig. 2. (a) Evolution of montmorillonite basal spacings as a function of time for dry clay fractions during freezing from +20 to −15 (squares) and further to −50 °C (triangles). (b) Expanded diagram.](image1)

![Fig. 3. Two dimensional diffractograms of montmorillonite pastes with pure water at +20, −15 and −50 °C. The peripheral ring at low temperatures comes from ice.](image2)
likely formed ice crystals. However, the amount was lower than the detection limit of the X-ray diffraction.

3.2. Wet montmorillonite pastes with pure water (30 mass% in water)

In the two dimensional diffraction patterns of wet Na-montmorillonite and Ca-montmorillonite at +20, −15 and at −50 °C (Fig. 3), the 001 diffraction ring moved further from the centre at lower temperature, which indicated dehydration of the montmorillonite. In the corresponding integrated diffractograms the intensity of the ice reflection increased gradually with decreasing temperature (Fig. 4). The freezing and the formation of ice occurred between −10 and −15 °C (by stepwise decreasing the temperature from +20 to −5, −7.5, −10 and −15 °C with a delay of about 5 min at each temperature). The freezing temperatures were lower than observed by Anderson and Hoekstra (1965), who found freezing between −5 and −6 °C in a similar system (a wet paste of Wyoming ion-exchanged clay fractions).

3.2.1. Wet Na-montmorillonite (WX) at +20, −15 and −50 °C (30 mass% in water)

In the wet Na-montmorillonite at +20 °C strong scattering was observed at low angles close to the beam stop (Fig. 3). No 001 reflection was seen (Fig. 4, Na-montmorillonite, +20 °C) indicating osmotic or non-crystalline swelling (the separation of the montmorillonite layers were mainly limited by the water content as the main attractive electrostatic forces were smaller than the repulsive osmotic forces; Norrish, 1954). Norrish claimed that no crystalline swelling was observed at low angles close to the beam stop (Fig. 3, Ca-montmorillonite, +20 °C). Initially, during freezing to −15 °C the basal spacing as a function of time compared to the relative intensity of the ice reflection is shown in Fig. 5. The basal spacing as a function of time compared to the relative intensity of the ice reflection is shown in Fig. 6. During the early stage of freezing of the Na-montmorillonite to −50 °C, a high level of low angle scattering and no signs of any 001 basal reflections (Fig. 5, 0.4 min) indicated the WX hydrate. After 2.7 min a small ice reflection occurred together with a very weak reflection corresponding to basal spacing at around 19 Å. After 3 min the ice reflection intensity more than doubled (Fig. 6) and the low angle scattering disappeared (Fig. 5). Two distinct basal spacings appeared corresponding to W2 (d = 16.0 Å) and W3 (d = 18.7 Å, Fig. 5 at 3.0 min, Fig. 6). After 3.4 min it was no longer possible to fit any W3 component in the diffraction data. After 8 min the intensity of the ice reflection was constant, and the phase was W2 (Fig. 6).

After 0.3 min of thawing Na-montmorillonite from −50 °C pure W2 hydrate was present (d = 15.8 Å, Figs. 5 and 6). After about 5 min some amounts of the W3 hydrate were formed, but the intensity of the ice reflections did not decrease (Fig. 5 at 5.8 min, Fig. 6). After 7 min the ice intensity started to decrease and the montmorillonite hydrate was pure W3 (Figs. 5 and 6). After 9 min no ice was detected and no 001 reflection was seen, indicating osmotic swelling of the montmorillonite (Fig. 5, 9.0 min).

3.2.2. Wet Ca-montmorillonite at +20, −15 and −50 °C (30 mass% in water)

Wet Ca-montmorillonite at +20 °C showed only a small amount of low angle scattering (Fig. 3). The basal spacing was at d = 19.4 Å (Fig. 4, Ca-montmorillonite, +20 °C) corresponding to a W3 hydrate. The 002 reflection was visible at d = 9.7 Å (Ca-montmorillonite, +20 °C). The low angle scattering was no longer present at −15 °C (Fig. 3, Ca-montmorillonite). Diffraction spots from the ice crystals were clearly visible in the two dimensional diffraction pattern (Fig. 3, Ca-montmorillonite, −15 °C). The basal spacings indicated mainly W2 (d = 16.0 Å) with some minor W3 (d = 18.8 Å) (Fig. 4, Ca-montmorillonite, −15 °C). A small 002 reflection was located at d = 9.6 Å originating from the W3 component. The 003 reflection, which was somewhat larger than the 002 reflection was located at d = 5.3 Å originating from the W2 component. At −50 °C the 001 reflection indicated pure W2 (d = 15.8 Å, Fig. 4, Ca-montmorillonite, −50 °C). This was the same as in the sodium case. A 002 reflection was also present (d = 5.3 Å). As in the sodium case the intensity of the ice reflection increased between −15 and −50 °C (Fig. 4, Ca-montmorillonite).

3.2.3. Kinetic experiments — freezing and thawing of wet Na-montmorillonite

A selection of integrated diffractograms of the time-resolved process of freezing and thawing of wet pastes is seen in Fig. 5. The basal spacing as a function of time compared to the relative intensity of the ice reflection is shown in Fig. 6.

After 0.3 min of thawing Na-montmorillonite from −50 °C pure W2 hydrate was present (d = 15.8 Å, Figs. 5 and 6). After about 5 min some amounts of the W3 hydrate were formed, but the intensity of the ice reflections did not decrease (Fig. 5 at 5.8 min, Fig. 6). After 7 min the ice intensity started to decrease and the montmorillonite hydrate was pure W3 (Figs. 5 and 6). After 9 min no ice was detected and no 001 reflection was seen, indicating osmotic swelling of the montmorillonite (Fig. 5, 9.0 min).

3.2.4. Kinetic experiments — freezing and thawing of wet Ca-montmorillonite

In the two dimensional diffractogram before the freezing some minor scattering was seen at low angles (similar to Fig. 3, Ca-montmorillonite, +20 °C). Initially, during freezing to −15 °C of the wet Ca-montmorillonite two components W3 (d = 19.5 Å) and W4 (d = 22.2 Å) were present (Fig. 5). The mean d-value of W4 002 was 10.8 Å, corresponding to a basal spacing of 21.6 Å. This fitted the calculated value assuming that each layer of water is 3 Å thick (Bradley et al., 1937), i.e. 9.6 Å + 4 × 3 Å = 21.6 Å. With time the two overlapping 001 reflections became broader as the intensity of the W4 component increased. After about 3 min an ice reflection was seen in the integrated diffractogram (Fig. 5). After ice formation, the
Fig. 5. A selection of integrated diffractograms collected during freezing and thawing of montmorillonite pastes with pure water. Times are indicated in the diagram. W2, W3 and W4 denote two-, three- and four-layer hydrates, respectively.

Fig. 6. Montmorillonite basal spacings as a function of time compared to the relative intensity of the ice reflection ($d = 3.90 \text{ Å}$) for pastes with pure water during freezing and thawing. W2, W3 and W4 denote two-, three- and four-layer hydrates, respectively.
montmorillonite was simultaneously dehydrated from W4+W3 into W3+W2. As the intensity of the ice reflection increased, the ratio \(|I(W2)/I(W3)|\) also increased (Fig. 6). A weak maximum in the basal spacing of the W3 and W4 phases prior to the ice formation was seen, and after the ice formation the W4 phase was no longer present and the W3 basal spacing decreased from 19.5 to 18.5 Å. Because no measurement indicated a pure W4 phase, the relative intensities did not correspond to the true fractions of the phases, but illustrated the evolution of the phases over time. All the 001, 002 and 003 reflections were fitted using the Fit2D software (Fig. 7a, b). The W3 intensity decreased with time whereas the W4 intensity increased. Directly after the ice formation (at 3.2 min) only W3 was present, and later dehydrated into W2 (Fig. 7c). After ice formation the low angle scattering in the two dimensional diffractograms diminished (similar to Fig. 3, Ca-montmorillonite, −15 °C). A schematic illustration of the phase transitions in Fig. 8. Thawing from −50 °C to room temperature behaved as a reversed freezing and indicated that the process was fully reversible (Fig. 5).

3.3. Ice crystal texture

It was noticed that the diffraction spots and thus the ice crystals in the case of Na-montmorillonite in pure water were more uniform in size compared to the ones in the Ca-montmorillonite in pure water. Fig. 9 shows the texture of the ice diffraction rings. The Na-montmorillonite in pure water was much less restricted in swelling (WX) compared to the Ca-montmorillonite. The highly dispersed sodium montmorillonite gave rise to a very large surface area compared to the calcium montmorillonite and the clay mineral platelets acted as sites for nucleation. Many nucleation sites produced many ice crystals of uniform size, few nucleation sites few ice crystals with a higher variability in size and shape. The water transport in the Na-montmorillonite gel was likely slower compared to the no gel forming Ca-montmorillonite dispersion.

![Fig. 7](image)

Evolution of hydrates W4, W3 and W2 as profile fitted reflections during freezing and thawing of Ca-MX80 and water. (a) 002 and 003 reflections integrated intensity as a function of time during freezing (+20 °C to −15 °C). (b) 001 reflection integrated intensity as a function of time during freezing (+20 °C to −15 °C). (c) A selection of integrated diffractograms showing 002 reflections during freezing (+20 °C to −15 °C). Ice formed at 3.2 min. (d) 002 and 003 reflections integrated intensity as a function of time during thawing (−50 to +20 °C). W2, W3 and W4 denote two-, three- and four-layer hydrates, respectively.

![Fig. 8](image)

A schematic illustration of the phase transitions in Ca-MX80 in pure water during freezing (+20 °C to −50 °C). The 19 Å-hydrate at room temperature is denoted W3' and the one in the presence of ice W3. W2, W3 and W4 denote two-, three- and four-layer hydrates, respectively.

![Fig. 9](image)

Texture of the ice diffraction ring for sodium and calcium montmorillonites in pure water.
3.4. Increased basal spacing after cooling and prior to freezing

To our knowledge this is the first time that a four-layer hydrate is identified for a Ca-montmorillonite in pure water. However, crystalline hydrates with a basal spacing of 22 Å in water were reported for Li- and H-montmorillonites (Norrish, 1954).

An increase of the basal spacing, i.e. the partial formation of W4, was noticed when the sample was cooled (before the ice formation) and heated (during the ice melting) for the Ca-montmorillonite paste (see Section 3.2.4). A similar behaviour was described by Hatharasinghe et al. (2000), when freezing a three component system of butylammonium vermiculite, butylammonium chloride and water between +5 and −5 °C. By X-ray diffraction the 001 reflection was studied and at 1 °C the intensity of the 001 reflection increased and simultaneously shifted towards lower angles and later at 0 °C the intensity again decreased. Also, Anderson and Hoekstra (1965), reported a small (0.4–1.3 Å), but systematic increase in 001-spacing of Wyoming bentonite (Ca-exchanged) during stepwise lowering of the temperature in steps of 1 °C from +4 to −20 °C. It should be kept in mind, that if the separate hydrates are not resolved, the interpretation will be a continuous change in the basal spacing, when a series of two-phase samples with varying amounts of two hydrates is analyzed. A small increase in swelling pressure was noticed by Birgersson et al. (2008) when lowering the temperature from +20 to 0 °C, followed by a stronger decrease when ice was formed and the montmorillonite was dehydrated. This change of the swelling pressure is compatible with the general change of the basal spacing observed in this study.

One possibility would be that the 001 reflection of a higher hydrate was present at lower angles than detectable with the equipment used in our experiments. The 19 Å reflection present at room temperature was denominated W3′ in Fig. 8. This W3′ would then represent the 002 reflection of a 38-Å hydrate and upon drying (cooling), and this 38-Å hydrate would then collapse to a 22-Å hydrate (W4) and later to 19 Å (W3). However, a 38 Å reflection would probably produce a 003 reflection at 12.7 Å and a 005 reflection at 7.6 Å, but these reflections were not detected above the random noise in the present measurements. The simultaneous presence of a 40-Å hydrate and a 20-Å hydrate was observed for Na-montmorillonite under certain conditions, but not for the Ca-form (Norrish, 1954; Anderson and Hoekstra, 1965). The existence of a higher hydrate would help to explain why confined Ca-montmorillonite retains its swelling pressure at relatively high water contents (Karlson et al., 2006, p.38), where the calculated average distance in a homogeneous system would correspond to 40–50 Å. However, in small angle X-ray scattering (SAXS) measurements on Wyoming Ca-montmorillonite, up to approximately 100 Å, no such distance was identified (Jönsson et al., 2009, p. 26). The presence of swelling pressure in such a low density Ca-montmorillonite system would then be the result of heterogeneity in the interparticle distances. Heterogeneity in this context implied that the average interparticle distance would be significantly larger than the basal spacing of the montmorillonite. However, due to the high background (partly due to the vicinity of the direct beam), interpretation of this low angle interval was difficult. In the case of Na-montmorillonite, osmotic swelling (WX) was easy to identify as the 001 reflection totally disappeared. On the contrary, in a system with a combination of crystalline and osmotic swelling (W3 + WX) the osmotic part (WX) would be difficult to identify in the case when the diffraction intensity from W3 dominates over the diffraction from WX.

Another possibility would be that the expansion of the hydrate was related to a change in the properties of the liquid water. The swelling of montmorillonite was controlled by the relation of the attractive and repulsive forces between the layers. If the repulsive forces were larger than the attractive ones, the clay mineral would expand and vice-versa. The dielectric constant (the static relative permittivity) of a medium controls the magnitude of the electrostatic interaction (Coulomb's law). By lowering the temperature from +20 to 0 °C the dielectric constant ε of water rises from 80.2 to 87.9 (Owen et al., 1961). Barshad (1952) examined the swelling of montmorillonite in mixtures of organic solvents (lower ε) and water, in order to establish the impact of the dielectric constant on the basal spacing. Barshad considered that an increase in the dielectric constant (due to the progressive addition of water to the organic solvent) decreased the Coulombic attraction between the exchangeable cations and the charged silicate layers and thereby explaining the observed expansion of the basal spacing. Brindley et al. (1969) studied Ca-montmorillonite swelling in organic–water mixtures and observed a similar expansion, when the mineral in pure organic solvent was compared to the one in pure water. In addition, a maximum in the basal spacing was observed at intermediate compositions (water–rich), which indicated the presence of a complex and delicate balance of attractive and repulsive forces rather than a simple dependence on the dielectric properties of the bulk solution.

The data presented in this paper, did not allow us to draw further conclusions concerning the formation of Ca-montmorillonite with four layers of water molecules, together with liquid water below room temperature. The observation of W4 in Wyoming Ca-montmorillonite at low temperatures is possibly an important step towards an increased understanding of the swelling of smectites.

4. Conclusions

Freezing of Na- and Ca-montmorillonites was rapid and reversible upon thawing. The effects from freezing on the swelling of the montmorillonite were shown to be greater in systems with high water content compared to drier systems. The formation of ice crystals changed the homogenou Na-montmorillonite water system (ideally one phase – montmorillonite hydrate) to a heterogeneous system (montmorillonite hydrate + ice). The texture of the ice crystals provided information about the difference in Ca- and Na-montmorillonite properties. The impact of confinement, electrolyte, solid–liquid ratio and perhaps other parameters will have to be investigated in order to draw further conclusions regarding applications such as engineered barriers for toxic or radioactive waste repositories.

Acknowledgements

Financial support by the Swedish Nuclear Fuel and Waste Management Co (SKB) is gratefully acknowledged. We want to thank Ola Karnland, Martin Birgersson and Magnus Hedström at Clay Technology AB, Lund for stimulating discussions.

References
