Synchrotron x-ray study of hydration dynamics in the synthetic swelling clay Na-fluorohectorite

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We present time-resolved synchrotron x-ray diffraction from the swelling clay Na fluorohectorite during controlled hydration and dehydration. A comparison of bulk and surface scattering reveals that the time dependence of basal Bragg peak positions and intensities has two components, which come into play at distinct temperatures. Intercalation of water into the crystal structure commences at a temperature of about 60°C, on a time scale on the order of 1 hour. By contrast, percolation of water into the porous medium has a characteristic time constant of 3–4 h. This is the rate limiting process for hydration of the interior of the clay for $T > 40^\circ\text{C}$. We suggest that the temperature-dependent percolation step may account for some of the hysteresis reported in earlier diffraction studies of the hydration of similar systems.

1. INTRODUCTION

The ability of smectite clays to absorb water and swell is long known, and some of the earliest x-ray diffraction studies focussed on the changes in basal spacing that accompanied this absorption [1]. It was soon concluded that water was able to enter between the silicate layers in these clays, intercalating into the crystal structure. In the hydration of a bulk clay sample, this process accompanies the adsorption onto the exterior of the particles. Due to their small size, the available external surface area of the clay particles may be comparable to the internal area. For this reason, water adsorption studies of bulk clay samples must always attempt to take both processes into account. This is often complicated by sensitivity to initial conditions or hydration history [2]. And of course, internal and external water adsorption may not have the same dependence on well controlled variables such as the size or charge of the exchangeable cation in the interlayer space. This fact can make systematic trends in cation substitution difficult to observe.

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In this paper we present time-resolved synchrotron x-ray diffraction studies of a synthetic swelling clay, Na-fluorohectorite, conducted during controlled hydration and dehydration. Two aspects of this experiment distinguish it from previous work. First, the x-ray scans can be taken quickly (several per minute), revealing the time dependence of Bragg peak positions and intensities as water enters the clay. Second, we can conduct the scattering measurement either in transmission through the bulk sample, or in reflection from the surface. By this means we can detect intercalation either as it occurs at the surface, a direct result of the prevailing environment, or as it occurs in the bulk. We will show that in the latter case the percolation of water or vapor through the porous medium affects the apparent time scale and temperature dependence for the clay hydration.

2. EXPERIMENTAL DETAILS

Fluorohectorite clay was purchased from Corning [3] and ion-exchanged through dialysis to produce Na-fluorohectorite having the nominal chemical formula $\text{Na}_{0.3}\text{Mg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2$. The wet clay powder was compressed in a furnace to make monolithic solid samples with the flat clay particles aligned along their stacking directions to within 5–10 degrees. Rectangular pieces were cut from the furnace-pressed disk for x-ray diffraction along the stacking direction (c axis), either in reflection from a flat surface 5–10 mm long in the beam direction, or in transmission through 2–3 mm of material. For the transmission measurements, the surface signal was blocked using a thin cover of Pb tape.

The samples were mounted on a copper heating/cooling block with a thermocouple imbedded near the sample. Temperature control in the range 0–130°C was achieved with a combination of a thermoelectric cooling element, a commercial heating element connected to a Lakeshore 321 temperature controller, and external cooling water circulated through the bottom of the block. The sample block was contained within a vacuum-tight beryllium metal can which served as the x-ray window. A peristaltic pump was used to circulate air through the chamber and subsequently either filter it through a dessicant column, or bubble through saturated K_2SO_4 salt water, in a closed loop. Under these conditions the relative humidity as measured by a sensor in the room temperature section of the system stabilized at 0.5% and 97% respectively.

X-ray scattering measurements were carried out at beamline X22A at the National Synchrotron Light Source, with an x-ray wavelength of 1.24 Å. The beam was focussed to a spot size of $0.5 \times 0.5 \text{ mm}^2$. The resolution in momentum transfer q_z of 0.005–0.010 Å⁻¹ was established by 0.5 or 1.0 mm slits before the NaI single channel detector, 600 mm from the sample. This arrangement was optimal to get the maximum intensity with minimal instrumental broadening.

3. RESULTS

Diffraction patterns along the (00 L) direction show that three stable hydration states are found in Na-fluorohectorite, as has been reported previously [4]. From the dehydrated state with basal spacing $c = 9.7 \text{ Å}$ (Fig. 1, dashed line), the lattice spacing swells to 12.4 Å when the temperature is reduced to the range 30–60°C, depending on how much water vapor is available (Fig. 1, solid line). At lower temperatures under humid conditions, additional intercalated water increases the basal spacing to 15.0 Å (Fig. 1, dot-dash line).

Figure 1. X-ray diffraction patterns taken in transmission through the bulk Na fluorohectorite samples in three different hydration states. Intensities are normalized on the same scale, but shifted for clarity. Basal peaks are indexed. Sharp peaks labelled “q” are from quartz impurities. (—): dry air, 130 °C. (—): room temperature and humidity. (· - ·): humidified air, 10 °C.

And as with other swelling clays [5], the temperatures at which the various hydration states may be found is variable, dependent on the sample environment and history.

These hydration states are generally referred to in terms of the number of intercalated water layers which are supposed to incorporate into the structure — nominally zero, one or two layers in the case of Na-fluorohectorite. This identification would be adequate in the case of static, stable hydration states. However, it is recognized that structural changes occur during hydration [6]. These may include local rearrangements in water molecule positions [7–9], as well as the alternating intercalation patterns originally described by Hendricks and Teller [10,11].

Evidence for both, in some cases fleeting evidence, is obtained by in-situ diffraction during hydration. Figure 2 shows scans taken through the (001) peak positions at low q_z , while a sample in humid atmosphere is allowed to cool from a dry state at 130°C to below room temperature. In most of these scans, intensity is found simultaneously at two different (001) peak positions. This shows the extent to which regions of clay, probably separate domains or particles, coexist in different hydration states. During the process of hydration, intensity on “drier” peaks at higher q_z gives way to those corresponding to “wetter” states. We can also see that the peak at $q_z \approx 0.51 \text{ Å}^{-1}$ shifts in position during hydration, showing that the lattice constant associated with the one-water-layer hydration state is changing to accomodate some structural reorganization. And only for

Figure 2. X-ray diffraction scans taken in transmission during hydration. Solid lines: initial, high temperature traces, with intensity at zero-layer and one-layer (001) peak positions. Dashed lines: low temperature scans indicating hydration from one- to two-water-layer states.

the one- and two-water-layer states do we find the intensity between the Bragg peaks (at $q_z = 0.45 \text{ \AA}^{-1}$) that is indicative of irregular alternate layer intercalation. In short, the complete crystallographic picture promises to be quite involved, and to contain a wealth of information regarding motions of water molecules during the hydration process — analysis is underway.

The present paper will focus on the time scales for hydration, which we obtain from the time-dependent peak intensities measured during hydration. For this purpose, we take the total integrated intensity of each Bragg peak to be proportional to the volume of clay in the corresponding hydration state. This simplification ignores changes in the structure factor which may accompany hydration: for example, we assume that although the peak at $q_z \approx 0.51 \text{ \AA}^{-1}$ shifts in position, its magnitude relative to the corresponding sample volume is unchanged. Our analysis also requires that hydrated regions be structurally independent of each other. This is clearly not the case for the transition between the one- and two-water-layer states, which show evidence for Hendricks-Teller type alternating intercalation. But it is a plausible description of the hydration from the zero- state to one-water-layer state, where no peak at an intermediate position is observed.

Hence, we are concerned principally with the behavior of zero-water-layer (001) and (003) peaks, corresponding to the dry regions in the sample, and the one-water-layer (001) peak, corresponding to a hydrated state. Integrated peak intensities were determined from Lorentzian fits on a linear background. Figure 3 shows examples of integrated peak

Figure 3. Time dependence of Bragg peak integrated intensities (top panels) as temperature is controlled (lower panels). Solid lines are guides for the eye, labelled with exponential time constants in hours. Labels “dry” and “wet” refer to zero- and one-water-layer Bragg peaks. (a) Slow cool, bulk. (b) Slow cool, surface. (c) Fast cool, bulk. (d) Slow heat, bulk.

intensities monitored as a function of time (upper panels), while hydration was controlled by stepping the temperature (lower panels). Our aim is first to identify the temperatures at which hydration proceeds under these conditions, and then to determine the time constant for hydration in that interval. Figure 3(a) shows data taken in transmission through the bulk sample during a slow cool. For temperatures above 65°C, the Bragg peak intensities at the zero-water-layer (001) and (003) positions change very slowly, requiring > 30 hours to fall to 1/e of the initial value. When T is reduced below 65°C, however, intensity coming from these dry regions in the sample begins to decrease. As shown by guides in the figure, the time dependence can be roughly described by an exponential decay on the order of 3–4 hours. Surprisingly, further decrease of temperature has no obvious effect until $T < 45^\circ\text{C}$, at which point hydration proceeds much more rapidly, with time scales < 1 hour.

This observation of two significant temperatures, each with their own time constant, prompts us to consider how two different mechanisms may contribute to the hydration. An obvious consideration is the transport of water or vapor through the pores between the particles that make up the bulk clay sample. Such percolation is necessary to bring water into the sample, independent of the microscopic intercalation process that allows water molecules to enter the interlayer spaces in the clay crystallites. To test this idea, we conducted a similar experiment in reflection from the surface of the sample. Here, we directly observe the microscopic intercalation that influences the lattice spacing, without the limitation of transport through the bulk. Figure 3(b) shows that fast hydration begins at 55°C, with no need to wait until the temperature has been lowered to 45°C. This strongly suggests that the slower time scale belongs to bulk water transport through the porous medium, a process that limits the rate of bulk hydration at temperatures above 45°C.

To ensure that fast hydration was really the result of the drop below 45°C, and not simply the passage of sufficient time, we quenched the dry sample rapidly to 35°C in humid air, while measuring scattered intensity from the bulk (Figure 3(c)). It is clear that fast hydration commences right away at the lower temperature, even in the interior of the sample. The time dependence of the one-water-layer (001) peak shows that in about two hours, hydration of the sample is essentially complete.

Finally, to assess the temperature hysteresis, we subjected the hydrated sample to a slow heating profile, while taking data in transmission through the bulk. As Figure 3(d) shows, dehydration begins at about 60–65°C. This is evident from the decrease in intensity on the one-water-layer (001) peak, though it is several hours before any peaks corresponding to dry clay become visible.

4. DISCUSSION

We characterized the time dependence of the peak intensities in terms of exponential time constants. This assessment has no precise quantitative basis at present, since some data are nonlinear, and since Bragg peaks nominally belonging to the same clay volumes — the zero-water-layer (001) and (003) peaks — do not have identical time dependences in most regions. We expect that the discrepancies will be resolved by crystallographic modelling, in which all peaks will be described by a single structure at each time point.

By such analysis, the time dependence of structural parameters can be tracked and more profitably interpreted.

Nevertheless, our qualitative observations are quite clear. Water is found to intercalate on time scales of about an hour for temperatures below 55–60°C. But for temperatures above 45°C, the hydration is rate limited by percolation into the bulk, and proceeds three to four times more slowly. At the present, we have no physical model to explain this lower temperature limit. We are currently conducting similar measurements from Ni-fluorohectorite for comparison.

On heating, hydration also commences at about 60°. Therefore, we observe a temperature hysteresis of at most about 5°C. By contrast, an x-ray diffraction study of Na vermiculite has revealed a much larger hysteresis of about 26°C in temperature cycling: the zero-water-layer peak appeared at 58°C upon heating, and persisted to 32°C on subsequent cooling (at a water vapor pressure of ≈ 20 torr) [5]. However, the notable difference between the two studies is that for the Na vermiculite experiment, the system was allowed to stabilize for 6–12 hours at each temperature. Our experience with Na-fluorohectorite calls into question the notion of “stability” of a hydration state at a given temperature. As Figure 3(a), shows, the peak intensities are always changing; the temperature interval simply determines how fast this happens. Observation of temperature hysteresis in such systems probably depends strongly upon the time–temperature profile. It would be interesting to test this generalization with a greater variety of comparable studies.

Much more information is available in the literature regarding hysteresis in water adsorption isotherms. Indeed, the combination of water adsorption isotherm and x-ray diffraction measurements has laid a good foundation for the understanding of long-studied clays such as montmorillonites [2,12–14]. Even when the isotherms are hysteretic or have shapes that cannot be described by simple models, it has been possible to correlate steps or kinks in the isotherm with stepwise changes in the *c*-axis lattice constant. In the interpretation of these data, previous workers have also described two contributions to hysteresis [15]: that intrinsic to the process of physically pushing the smectite layers apart on the microscopic scale; and that resulting from other physical factors on the scale of the particle morphology. It seems possible that the latter, extrinsic hysteresis could be related to the percolation effect we describe here. It is difficult to follow up on this idea since hysteresis in temperature might not be directly comparable to hysteresis in adsorption isotherms. We suggest that time-resolved bulk and surface diffraction conducted during isotherm measurements may shed some light on the processes involved.

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