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NOTES

TRANSMISSION X-RAY DIFFRACTION TECHNIQUE FOR MEASURING CRYSTALLINE SWELLING OF SMECTITES IN ELECTROLYTE SOLUTIONS*

Key Words—Crystalline swelling, Electrolytes, Smectites, XRD.

The crystalline swelling of smectites in electrolyte solutions can be controlled by varying the salt concentration of the solutions (Norrish and Quirk 1954, Norrish 1954a, Slade *et al* 1991). Such osmotic control offers a convenient means of studying the energetics of crystalline swelling. Several X-ray diffraction (XRD) techniques have been developed for measuring the basal spacing of smectites in equilibrium with salt solutions (Norrish 1954b, Posner and Quirk 1964).

Norrish (1954b) placed an oriented flake of Na-saturated montmorillonite (Wyoming bentonite) (about 0.03 mm thick) in a plastic capillary, saturated the clay with a desired cation by passing a concentrated salt solution through the tube, and then equilibrated the clay by passing a solution with the desired concentration of the same salt through the capillary. The capillary then was sealed and a modified X-ray camera technique was used to measure basal spacings up to 400 Å. With this technique, Norrish observed both the initial stepwise swelling of smectites up to 20 Å and an increase in basal spacings > 40 Å that varied linearly with the inverse square root of the electrolyte concentration. This technique requires a powder camera, a device that is not widely available with modern X-ray diffraction instruments.

Posner and Quirk (1964) separated a clay paste from equilibrated clay suspensions by centrifugation and by sedimentation. Then they spread a layer of the paste on a ceramic tile, and covered the oriented paste with a thin, polyethylene film to prevent drying which could cause a change in concentration of the external solution. The oriented specimens were analyzed by XRD using the normal symmetrical reflection geometry. The technique used by Posner and Quirk (1964) is simple; however, measured basal spacings of the clay may be affected by the phase separation procedure, sample drying, and inaccurate positioning of the swollen clay at the reference plane of the goniometer.

In this note, we describe a technique for measuring the crystalline swelling of clays in electrolyte suspensions, employing symmetrical transmission geometry (Klug and Alexander 1974, p. 389–391) for XRD with a thin (~1 mm) liquid sample cell. The liquid sample cell allows analyses of basal spacings of randomly oriented clays dispersed in electrolyte solutions.

MATERIALS AND EXPERIMENTAL METHODS

Clay samples

Twenty grams of Wyoming bentonite (Baroid Division, National Lead Co., Houston, TX) were shaken overnight with 1 liter of 1 M NaCl and then washed once with deionized water. The <0.2-, 0.2–2.0-, 2.0–20-μm equivalent-size fractions of the Na-clay were obtained by centrifugation and sedimentation. The clay suspensions were concentrated on a rotary evaporator and the final concentration of clay in each suspension was determined gravimetrically.

Swelling in salt solution

For each equivalent-size fraction, aliquots of clay suspension, containing 25, 50, 100, 250 mg of clay, respectively, were shaken in 50-ml centrifuge tubes for 48 h with 5 ml of 0.5 or 3.0 M NaCl. After shaking, the clay was allowed to settle and the supernatant was decanted. This procedure was repeated once, then the samples were resuspended in 5 ml of 0.5 or 3.0 M NaCl so that the final clay concentrations were 5, 10, 20 and 50 mg/ml. Clay gels (80 to 150 mg/ml, depending on equivalent size) were also prepared for each equivalent-size fraction by centrifugation.

Transmission cell

A diagram of the transmission cell used in this study is shown in Figure 1. The cell consists of two 0.5-mm-thick plastic plates glued together with silicone sealant. An 18-mm-diameter hole was cut in the center of the cell, and two pieces of Mylar film were attached to the external surfaces to act as windows. The sealed hole served as the sample chamber with a volume of about 0.3 cm^3. The cell was constructed such that the mid-

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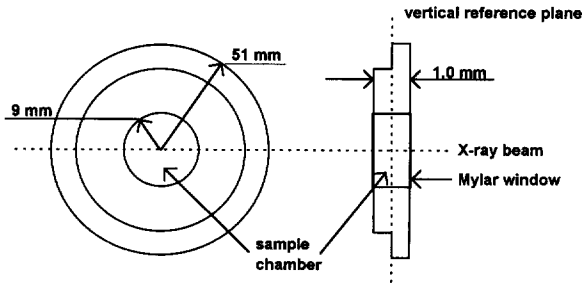

Figure 1. Diagram of the transmission cell used for XRD analyses of clay suspensions.

plane of the sample chamber could be positioned to coincide with the vertical reference plane of the goniometer (i.e., perpendicular to both the horizontal reference plane and the plane of the goniometer circle). The transmission cell was inserted in a circular sample holder which was placed on a transmission sample stage and held in position by a magnetic clamp. Preliminary tests indicated that the thickness of the sample chamber should be about 1 mm because the intensity of the X-ray beam passing through clay suspensions thicker than 1 mm was significantly reduced (Klug and Alexander 1974, p. 391). A 3-ml syringe was used to inject clay suspensions and gels (about 0.3 ml) into the sample chamber of the transmission cell. To enhance peak intensity of the gels, the sample cell was gently squeezed to produce a thin (<1 mm) film of gel.

XRD

Basal spacings of Wyoming bentonite in two salt solutions were measured using CuKα radiation (40 kV, 30 mA) on a Siemens D-5000 diffractometer in Θ-Θ configuration using a solid-state Si(Li) detector. Variable divergence and anti-scatter slits, a 0.1-mm detector slit, and Soller slits on both sides of the sample were employed. A scanning rate of 0.3°(2Θ)/min was used for all samples, but for comparison a few samples were also analyzed using a scanning rate of 0.015°(2Θ)/min.

RESULTS AND DISCUSSION

By using the liquid sample cell with Wyoming bentonite, we were able to monitor crystalline swelling from 15.5 to 18.5 Å even in dilute (10 mg/ml) clay-electrolyte suspensions. XRD patterns for Wyoming bentonite (0.2–2.0 μm fraction) in 3 M NaCl (Figure 2a) indicated a 15.5-Å first-order XRD peak, the intensity of which increased with increasing clay concentration. The basal spacing of 15.5 Å indicated the presence of two layers of water molecules in the interlayer position. Similarly, Posner and Quirk (1964) reported that Na-saturated Wyoming montmorillonite collapsed to 15.5 Å in 2.5 M NaCl and did not collapse further with increasing salt concentration of the solution.

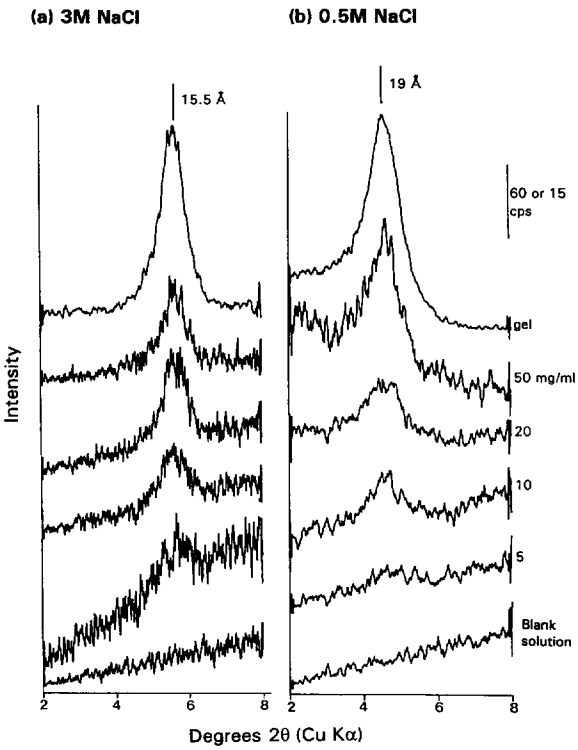

Figure 2. The effect of clay concentration on X-ray diffractograms of Wyoming bentonite suspensions: (0.2–2.0 μm equivalent-size fraction) in 3.0 M NaCl (a) and in 0.5 M NaCl (b). Similar results were obtained for the <0.2 and for the 2.0-2 μm equivalent-size fractions. The 60-cps scale refers only to the gel pattern of (b). The 15-cps scale refers to all other patterns.

The basal spacing of Wyoming bentonite (0.2–2 μm fraction) in 0.5 M NaCl was 18.5 Å, corresponding to three layers of water molecules in the interlayer position (Figure 2b). Other authors also have reported a basal spacing of 18.5 Å for Na-montmorillonite in 0.5 M NaCl (Norrish 1954b, Posner and Quirk 1964). XRD patterns for the 2–20- and <0.2 μm equivalent-size fractions in NaCl solutions (not shown) were similar to those in Figure 2.

At the lowest concentration of clay (5 mg/ml), Bragg diffraction peaks at 15.5 Å and 18.5 Å were very weak or absent. At higher clay concentrations, the peaks could be identified readily, and their breadth remained fairly uniform, suggesting that domain thickness remained constant. At low clay concentrations, the background intensities tended to increase with increasing degrees 2Θ. Some background was attributed to scattering of X-rays by air because a scan without the sample cell in place (not shown) revealed X-ray scattering unassociated with the clay sample, the salt solution, or the Mylar films. In addition to air scattering, the random

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orientation of coherent domains in the suspension as well as thermal motion of atoms in the clay contributed to the background signal by scattering X-rays (Klug and Alexander 1974). Clay concentration influenced the shape of the background signal because absorption of scattered X-rays increased with clay concentration. Slower scan speeds substantially increased the signal/noise ratio.

In this note, we have demonstrated a diffractometer-based technique that can be used to measure basal spacings of smectite suspension and gels. Increasing the concentration of clay in suspension enhanced the peak intensity by increasing the number of ordered domains per unit volume. In addition, background noise was diminished because scattered radiation was increasingly absorbed by the mass of the clay. However, if the transmission cell was too thick (>1 mm) or if the clay concentration was too high, absorption of X-rays decreased peak intensity. Strong peaks were obtained from thin films of gel (Figure 2), because sample thickness and, hence, absorption of diffracted radiation were minimized.

Agronomy Department C. SHANG
Iowa State University M. L. THOMPSON
Ames, Iowa 50011

USDA-ARS D. A. LAIRD
National Soil Tilth Laboratory
2150 Pammel Drive
Ames, Iowa 50011

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