

HYDRATION STATES OF SMECTITE IN NaCl BRINES AT ELEVATED PRESSURES AND TEMPERATURES

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Abstract—A high-pressure, high-temperature cell was used to monitor the basal X-ray powder diffraction spacing of Na-saturated Cheto montmorillonite in contact with NaCl solutions at temperatures as high as 200°C and hydraulic pressures as high as 6700 psi (456 bar). The 003 and 005 reflections were used to determine $d(001)$ of the smectite. The montmorillonite, in 1 molal NaCl, exhibited a $d(001)$ of 15.4 Å at room temperature and pressure and a $d(001)$ of 15.6–15.7 Å under 500–2200 psi hydraulic pressure. The basal spacing of the clay in 5 molal NaCl was 15.2 Å and 15.33–15.45 Å at 1 bar and 750–6700 psi (53–456 bar), respectively. Because no changes in the basal spacing with increasing temperature to 200°C were detected in any of the experiments, this Na-smectite probably exists as a two-water-layer complex under diagenetic conditions.

Key Words—Brine, Diagenesis, Hydration, Pressure, Smectite, Temperature.

INTRODUCTION

Knowledge of the hydration state of smectite under burial conditions is an important step towards a thorough understanding of the smectite-to-illite transformation, as well as towards predicting the physical and chemical behavior of smectite in contact with a variety of subsurface fluids. Powers (1967) postulated that four one-molecule-thick water layers are situated between the 2:1 layers of a smectite. Burst (1969) proposed that smectites in the subsurface may contain one or two water layers at depth, whereas Perry and Hower (1972) hypothesized that subsurface smectite exists as a two-water-layer complex. Burst (1969) and Powers (1967) both proposed that the loss of interlayer water results solely from increases in pressure and temperature. Perry and Hower (1972) suggested, however, that an increase in negative layer charge on the silicate structure is a necessary condition for this reaction. Water loss occurs if the electrostatic attraction of the 2:1 layer for the interlayer cation exceeds that of the cation for its hydration shell (Eberl, 1980).

Smectites containing multilayers of water are stable under a variety of conditions. Na-smectite (Wyoming montmorillonite) is stable as a one-water-layer complex ($d(001) = 12.4\text{--}12.5$ Å) over the 20–70% relative humidity range (Bradley *et al.*, 1937; Keren and Shainberg, 1975). Smectite swells to 001 spacings in excess of 18 Å at relative humidities greater than 95% (Keren and Shainberg, 1975). Norrish and Quirk (1954) noted that the uptake of water by Na-smectites varies inversely with the concentration of the associated brine; however, at NaCl concentrations greater than 1.5 molal, the repeat spacing of Na-smectite is apparently constant at 15.5 Å (Posner and Quirk, 1964).

The effects of pressure and temperature on smectite hydration have received much attention. Thermal dehydration experiments, such as those by Méring (1946), Rowland *et al.* (1956), and Farmer and Russell (1971), have demonstrated that reversible interlayer water loss occurs between 100° and 150°C. Applied hydraulic pressure results in an increase in the temperature of dehydration, paralleling the liquid-vapor curve for H₂O (Stone and Rowland, 1955; Koster van Groos and Guggenheim, 1984). van Olphen (1963) estimated that lithostatic pressures in excess of 30,000 psi must be applied to Ca-smectite to remove the last two water layers at 25°C.

The prediction of smectite hydration states in the subsurface from experimental data based on surface conditions has speculative value. Although important to the understanding of the controls on clay hydration, few of the studies cited above provided insight concerning the behavior of smectite at elevated temperature and pressure. The present paper presents the results of experiments performed to determine the hydration state of smectite in contact with brine, at temperatures and hydraulic pressures that simulate deep burial. These experiments were accomplished using a high-pressure, high-temperature cell, with which the $d(001)$ of Na-smectite was monitored by X-ray powder diffraction (XRD) under the conditions of interest.

EXPERIMENTAL

Equipment

Schematics of the high-pressure, high-temperature X-ray cell (Graf, 1974) used in this investigation are given in Figures 1 and 2. The cell was made of Inconel 625 nickel alloy (International Nickel Company); accessory parts were either Inconel or stainless steel. The hydraulic pressure on the sample was controlled externally through the brine and across a moveable pres-

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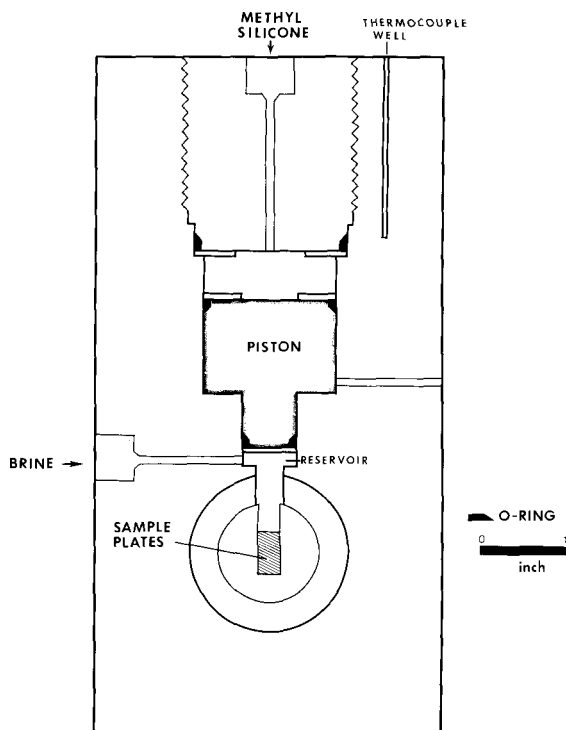


Figure 1. Schematic diagram of high-pressure, high-temperature X-ray cell: side view.

sure amplifier by a methyl silicone pressure system. The cell was heated by a ceramic resistance furnace. The temperature was monitored with an iron-constantan thermocouple. The X-ray cell was mounted on a General Electric XRD-3 X-ray diffractometer which was outfitted with a stepper motor and an Ortec 715 scintillation counter. The data were manipulated with an RT-LSI 11/2 microcomputer (Digital Electronics Corporation).

Sample preparation

The <2- μm fraction of Cheto montmorillonite from Chambers, Arizona, was saturated with sodium by soaking it in 1 N NaCl solution for one week, during which time the solution was changed 3 or 4 times. The clay was rinsed with deionized water until the AgNO_3 test for dissolved chloride was negative. The <0.5- μm fraction was removed by centrifugation, and the remaining clay (0.5–2.0 μm) was mixed 1:8 (clay : water) with deionized water. This suspension was used for making oriented mounts for XRD examination.

Because glassy-carbon sample plates are nonporous, a multiple step centrifugation technique was used to mount the clay until 30–40 mg of dry clay was on the plates. After the sample was loaded into the cell, 3–4 ml of brine was added by pipet to the brine reservoir and sample chamber. The sample was allowed to equilibrate

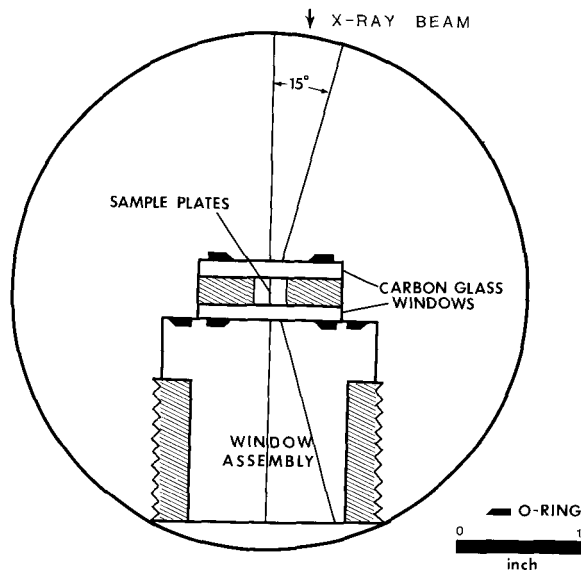


Figure 2. Schematic diagram of high-pressure, high-temperature X-ray cell: top view.

with the brine at room temperature and pressure for 2–3 days before the pressure or heat was raised.

Experimental conditions

Experimental conditions are given in Table 1. Each experiment consisted of first setting the pressure in the cell and then increasing the temperature in small increments. The pressure was adjusted periodically to keep it constant. After the temperature of interest was reached, the clay was kept at the pressure-temperature conditions overnight before it was examined by XRD.

X-ray powder diffraction procedure and data manipulation

Unfiltered Mo radiation was used in this investigation because its short wavelength ($K\alpha = 0.7107 \text{ \AA}$) was better able to penetrate the carbon windows than Cu radiation, and because it provided more basal reflections in the $30^\circ 2\theta$ range imposed by the 15° window apertures of the cell (Figure 2). Diffuse scattering by the glassy windows resulted in a broad maximum centered at $10\text{--}11.5^\circ 2\theta$ ($d = 4.09\text{--}3.56 \text{ \AA}$). To simulate the

Table 1. Experimental conditions for reaction of Na-saturated Cheto montmorillonite and NaCl brines.

Molality	Hydraulic pressure (psi)	Maximum temperature ¹ (°C)
1	500	150
1	2200	175
5	750	200
5	6700	200

¹ Maximum temperatures are the highest temperature at which X-ray powder diffraction analyses were made.

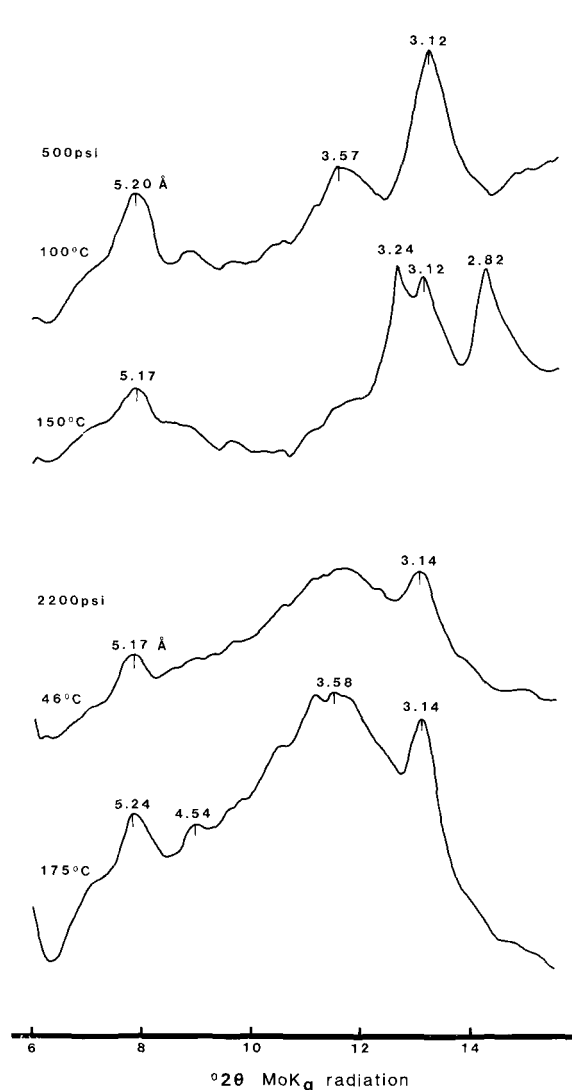


Figure 3. X-ray powder diffraction patterns of Na-saturated Cheto montmorillonite in 1 molal NaCl solution at hydraulic pressures of 500 and 2200 psi. The peak at 3.57–3.58 Å is the 005 K β reflection. Peaks at 2.82 Å and 3.24 Å are halite reflections.

scattering by the cell windows and brine, a series of background patterns was made. Kaolinite that had been heated to 600°C until it had become noncrystalline and the NaCl brines were used to simulate adsorption due to the clay and brine. Background patterns were run at several different temperatures, and the intensities were subtracted from the experimental patterns to make the hydrated montmorillonite peaks more distinct. A Gaussian smoothing function was applied to each data point; the standard deviation was set equal to the stepping increment. The XRD patterns presented here were normalized with respect to the maximum intensity and generally represent intensities between 30 and 80 count/s.

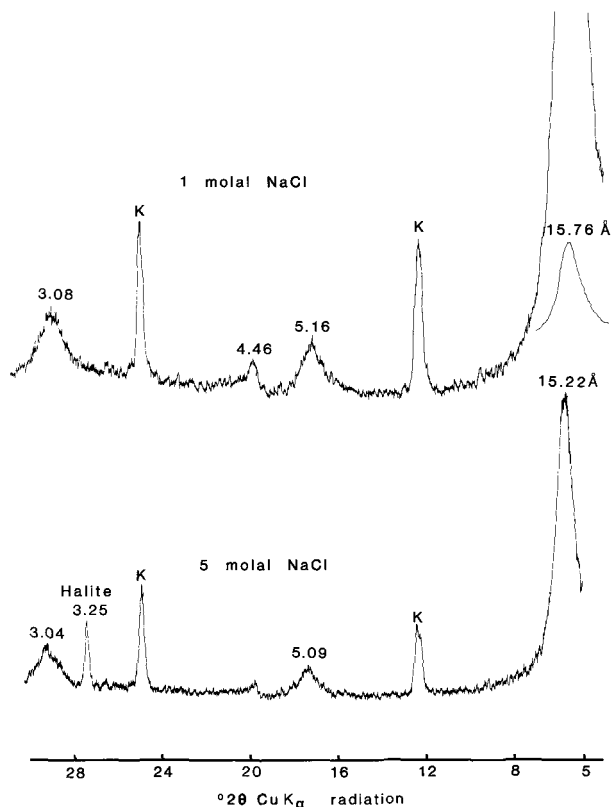


Figure 4. X-ray powder diffraction patterns of Na-saturated Cheto montmorillonite in 1 and 5 molal NaCl solutions at room temperature and pressure. Analysis made with Philipps X-ray diffractometer. Kaolinite (K) was added to the sample to help orientation.

RESULTS

The XRD results for experiments using 1 molal NaCl brine, at 500 psi (34 bar) and 2200 psi (152 bar) are shown in Figure 3. The first-order reflection was not discernible in the patterns because of low-angle scattering; however, several higher order peaks were noted. The two most intense peaks at 5.17–5.24 and 3.12–3.14 Å are nearly integral reflections for a two-water layer smectite: the 5.20-Å peak is the third order reflection; the 3.14-Å peak is the fifth order reflection. The broad maximum at 3.57–3.69 Å is unresolved background. The peaks at 3.25 and 2.82 Å are for halite, indicating that the cell windows leaked.

The $d(001)$ value calculated from these spacings is 15.51–15.72 Å. This spacing is less than the spacing of 18.5 Å reported by Posner and Quirk (1964) for Na-saturated Wyoming montmorillonite in 1 molal NaCl and it is slightly greater than the spacing of 15.4–15.48 Å for Na-saturated Cheto montmorillonite saturated with 1 molal NaCl at room temperature and pressure (Figure 4).

The results of experiments in 5 molal NaCl at 750 psi (52 bar) and 6700 psi (456 bar) are presented in Figure 5. The $d(003)$ and $d(005)$ values are 5.11–5.14

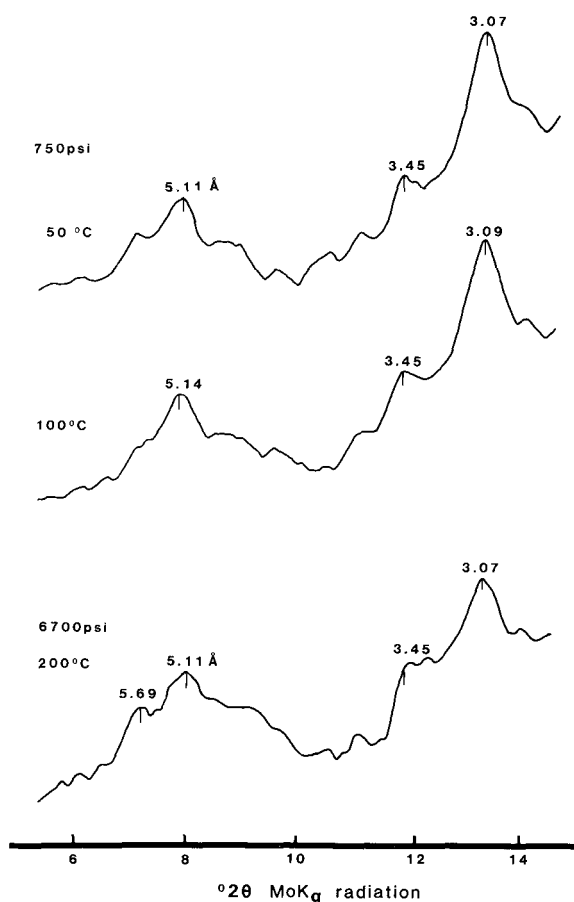


Figure 5. X-ray powder diffraction patterns of Na-saturated Cheto montmorillonite in 5 molal NaCl solution at 750 and 6700 psi. $003 K\beta = 3.45\text{--}3.48 \text{ \AA}$. $005 K\beta = 5.69 \text{ \AA}$.

and $3.07\text{--}3.09 \text{ \AA}$, respectively. The 003 and $005 K\beta$ reflections were also noted in these patterns at 5.69 and 3.45 \AA , respectively. The $d(001)$ value calculated for these patterns is $15.33\text{--}15.45 \text{ \AA}$, which is slightly less than the spacing of 15.5 \AA for Na-saturated Wyoming montmorillonite in 6 molal NaCl at room temperature and pressure (Posner and Quirk, 1964). The $d(001)$ of Na-saturated Cheto montmorillonite at room temperature and pressure is $15.22\text{--}15.27 \text{ \AA}$ (Figure 4).

INTERPRETATION AND DISCUSSION

The $d(001)$ spacings of Na-saturated Cheto montmorillonite in 1 and 5 molal NaCl brines varied between 15.7 and 15.2 \AA . Although no change in hydration state was apparent, these results affirm the previously demonstrated inverse relationship between salinity and swelling of smectite. Continuous variation in basal spacing is thought to be indicative of mixed layering of hydration states (Posner and Quirk, 1964; Keren and Shainberg, 1975). Slight variations in the positions of the third- and fifth-order peaks were noted,

suggesting that such mixed layering might indeed have been present. The shifts, however, were toward higher spacings and were probably a result of peak breadth. By Méring's rules (1949), shifts due to mixed layering should be toward lower d -spacings, rather than higher. Computer simulation of the XRD patterns using a program outlined by Reynolds (1980) confirmed such shifts.

The basal spacing of $15.6\text{--}15.7 \text{ \AA}$ of the Na-saturated Cheto montmorillonite in 1 molal brine in the X-ray cell was slightly larger than the 15.4 \AA spacing recorded at room pressure. A similar effect was noted for the 5 molal NaCl-clay system, for which the room pressure interplanar spacing was 15.2 \AA , whereas the spacing under pressure was $15.33\text{--}15.45 \text{ \AA}$. Although more work is necessary to establish whether these differences are beyond analytical error, the data suggest that increased pressure favors the hydration of clay. Increasing vapor pressure favors the hydration of smectite (Keren and Shainberg, 1975; Ormerod and Newman, 1983), and it is possible that increasing hydraulic pressure affects the hydration properties in a similar manner. A discussion of the effect of pressure on the properties of bulk and interlayer water was given in Colten (1985).

Glaeser and Méring (1968) observed a range in basal spacing of Na-smectite from 15.4 to 15.8 \AA between relative humidities of 70 and 90%. The existence of a two-water-layer complex with variable basal spacing suggests that variable amounts of water may be accommodated in the interlayer region. Slight adjustments in the interlayer water structure with changing water content may result in small changes in the basal spacing. Further work is necessary to establish more fully the relationship between water content and interlayer spacing.

One aim of the present study was to establish whether changes in the hydration states occur with heating under pressure. No significant changes in peak position with temperature were noted in any of the experiments, suggesting that dehydration did not occur under the experimental conditions. This interpretation is in agreement with that of Koster van Groos and Guggenheim (1984) who demonstrated by high-pressure differential thermal analysis that Na-saturated Wyoming montmorillonite does not dehydrate until temperatures of $40^{\circ}\text{--}100^{\circ}\text{C}$ in excess of the liquid-vapor equilibrium temperatures are reached.

The brines, temperatures, and hydraulic pressure conditions used in the present investigation were chosen specifically to simulate those of burial diagenesis. The 1 molal NaCl brine corresponds to 70,000 ppm total dissolved solids, a concentration common to brines at depths below 3000 feet (Kharaka *et al.*, 1979; Hanor and Bailey, 1983). Hydraulic pressure of 6700 psi simulates that of 15,000 feet of burial.

It should be noted that the effective stress in these experiments was zero; i.e., the pressure on the solids and fluids was equal. Increasing overburden pressure

might have enhanced the loss of interlayer water from smectites at depth; however, van Olphen (1963) and Steinfink and Gebhart (1962) demonstrated that applied lithostatic pressures must exceed 30,000 psi to affect loss of interlayer water from a two-water-layer complex. These pressures are far in excess of those encountered in normal sedimentary basins. Colten (1985) demonstrated that the effect of differential pressure in normal burial sequences favors the dehydration of clay at constant temperature. Thermodynamically, increasing lithostatic pressure should reduce the stability of the clay structure, thus making it more reactive with increasing burial.

The results of the experiments presented here suggest that smectite is stable as a two-water-layer complex at depth and that hydraulic pressures and temperatures associated with diagenesis do not affect dehydration. These results imply that changes in the clay structure and interlayer cation are required by the illitization reaction.

SUMMARY

These experiments demonstrate that the hydration state of Na-smectite under burial conditions may vary slightly with salinity. In NaCl brines of >70,000 ppm total dissolved solids, the dominant hydration state for dioctahedral smectite is a two-water-layer complex, with basal spacing between 15.3 and 15.7 Å. These data confirm the speculation of earlier workers, e.g., Burst (1969) and Perry and Hower (1972).

Simple thermal dehydration of the smectite was not achieved in the present experiments, suggesting that this process does not occur in diagenetic environments. Increased hydraulic pressure appears to favor hydration, as does decreasing salinity. This effect may be important in the deep subsurface where reversals in the salinity gradient are known to occur.

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