

## EFFECTS OF RELATIVE HUMIDITY ON THE BASAL EXPANSION OF Mg-SMECTITE EQUILIBRATED WITH ETHYLENE GLYCOL AT LOW VAPOR PRESSURE

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**Abstract**—The effects of relative humidity (RH) on the expansion of Mg-smectite, equilibrated with low vapor pressure of ethylene glycol (EG), was studied. Four smectite samples were equilibrated with EG vapor from: (1) saturated vapor of pure EG, (2) an EG-CaCl<sub>2</sub> solvate, and (3) 0.05 relative EG vapor pressure at 65°C. X-ray powder diffraction (XRD) analyses of the clays under different RH conditions indicated that without EG, the basal spacing of Mg-smectite samples could only be expanded to 16 Å, even at 0.97 RH. The basal spacing of Mg-smectite samples equilibrated with saturated EG vapor was expanded to 17.1 Å and was not significantly affected by RH in the range 0.1–0.9. The basal spacing of the Mg-smectite samples equilibrated with vapor from the EG-CaCl<sub>2</sub> solvate and 0.05 relative EG pressure at 65°C was expanded by an amount that depended on the RH during the XRD analysis. The basal spacing increased from 14.2 to 17.1 Å as the RH increased from 0.6 to 0.75, except for sample API 23, which expanded to 17.1 Å at RH > 0.9. This sample did not expand beyond 16 Å when it was equilibrated with 0.05 EG relative vapor pressure. Sorption of moisture from air caused the one-layer EG-Mg-smectite complex (basal spacing = 14.1 Å) to rearrange itself to a double-layer EG-Mg-smectite complex (basal spacing = 17.1 Å). A small amount of the adsorbed EG in Mg-smectite, much less than was needed to cover a one-layer of the interlayer surfaces, caused an expansion of the basal spacing to 17.1 Å at high RH during the XRD analysis. The minimum amount of adsorbed EG which caused the one-/two-layer EG complex conversion was about 20–30 mg EG/g. The conversion was fast (<5 min) and was relatively reversible.

**Key Words**—Basal expansion, Ethylene glycol, Relative humidity, Smectite, X-ray powder expansion.

### INTRODUCTION

The basal spacing of homoionic smectite samples is a function of the interlayer cation and relative humidity (Mooney *et al.*, 1952; Keren and Shainberg, 1975). In a study of the basal spacing expansion of smectite as a function of unsaturated vapor pressure of ethylene glycol (EG), Hsieh *et al.* (1984) found that variation in relative humidity (RH) during the X-ray powder diffraction (XRD) analysis was the main cause of the uncertainty in basal spacing measurements. They indicated that: (1) RH significantly affected the basal expansion of Mg-smectite samples, if they had been equilibrated with low EG vapor pressure; and (2) the effect of RH on basal expansion of partially EG-solvated samples was fast, i.e., 90% of the expansion was attained in 10 min.

Current knowledge concerning the basal expansion of smectite under low EG vapor pressure is limited, and almost no information exists in the literature concerning the effect of RH on the basal expansion of Mg-smectite equilibrated with low EG vapor pressure. The basal expansion of smectite apparently depends on the degree of solvation of its interlayer cations and surfaces by solvents and, in turn, is controlled by the distribution of interlayer charges (Shainberg and Kemper, 1966; Hsieh *et al.*, 1984). Knowledge of the RH-EG interaction on the basal expansion of smectite under low EG vapor pressure might provide insight into the

nature of the interlayer surface and charge distribution of smectite, which is not available from a common EG smectite test.

The present experiment was designed to study the basal expansion of smectite samples equilibrated with low EG vapor pressure, as influenced by the relative humidity during XRD analysis.

### MATERIALS AND METHODS

The source and charge characteristics of the smectite samples examined in this study are listed in Table 1. The samples were saturated with Na<sup>+</sup> in 1 N chloride solution, washed twice with distilled water, dispersed in water whose pH was adjusted to 9.5 using 0.1 M sodium carbonate solution, and fractionated into <0.2-, 0.2–1-, and >1- $\mu$ m size fractions by centrifugation, following the procedures of Jackson (1969). A preliminary test indicated that the <0.2- and 0.2–1- $\mu$ m fractions of the reference smectite samples were free of XRD-detectable impurities. The 0.2–1- $\mu$ m fraction was selected for the study.

The 0.2–1- $\mu$ m fraction of the specimens was saturated with Mg<sup>2+</sup> in 1 N chloride solution and then washed twice with distilled water. A 1:2 clay/water paste (v/v) was prepared, and an aliquot containing 30 mg of clay was poured onto a glass slide and dried on a level surface at room temperature. After the clay had dried, the slides were placed in a vacuum desiccator

Table 1. Source and charge characteristics of smectite samples selected for the study (from Hsieh *et al.*, 1984).

Sample	Source	CEC (cation- exchange capacity) (meq/ 100 g)	Total layer charge (meq/ 100 g)	Tetra- hedral charge (%)
API 25	Upton, Wyoming; Ward's Natural Science Establish- ment.	91.5	91.8	30
API 27	Belle Fourche, South Dakota; Ward's Natural Science Establishment.	97.0	93.0	22
API 23	Chambers, Arizona; Ward's Natural Science Establish- ment.	109.7	109.4	15
SWy-1	Na-montmorillonite, Swy-1; Source Clays Repository of The Clay Min- erals Society.	87.8	91.1	35

and evacuated to  $<0.001$ -mm Hg pressure for one week before they were equilibrated with EG vapor.

Three EG equilibration treatments were used in this study: (1) One equilibration treatment used a saturated EG vapor at room temperature. Clay slides were placed in a vacuum desiccator over a small dish of fresh reagent grade EG. The desiccator was evacuated to  $<0.1$ -mm Hg pressure for 10 min and then closed. The clay slides were left to equilibrate with the EG vapor for three days at room temperature. (2) A second equilibration treatment used the vapor of an EG-CaCl<sub>2</sub> solvate. The procedure was the same as treatment (1), except that the dish of pure EG was replaced by a dish of a 1:5 weight ratio EG-CaCl<sub>2</sub> solvate. Both the chemicals were reagent grade, and the calcium chloride was an anhydrate. (3) A third equilibration treatment used 0.05 relative EG vapor pressure at 65°C. Clay slides were placed in an adsorption device similar to that described by Hsieh *et al.* (1984). The vapor pressure of EG was supplied from a flask of pure EG immersed in a water bath of 25°C, and the clay chamber was immersed in a water bath of 65°C. The EG vapor in the clay chamber was 5% saturation, according to the data of Boublic *et al.* (1973). The equilibration time was two days. Before and after an EG vapor treatment, clay slides were weighed on a balance enclosed in a chamber in which the RH was  $<0.1$ . The difference of the weights was taken as the amount of EG adsorbed by the clay.

The clay slides were examined after the equilibration treatments using a GE XRD-7 X-ray powder diffractometer and CuK $\alpha$  radiation. A chamber designed to enclose the entire sample holder of the X-ray goniometer was used to control the RH during the XRD

Table 2. Amount of ethylene glycol (EG) retained by smectite samples (mg/g) after various pre-equilibration treatments.

	Over free EG	Over EG-CaCl <sub>2</sub>	Over 5% EG rel. pressure
API 25	272.3	78.5	36.2
API 27	240.1	75.0	34.4
API 23	208.4	45.0	17.0
SWy-1	195.8	76.8	30.5

analyses. The chamber had two Mylar windows and two connectors for inlet and outlet of purging gas. The RH inside the chamber was controlled by purging with a mixture of a dry and a water-vapor saturated nitrogen gas. The mixing ratio of the dry and wet nitrogen gas was controlled by fine needle valves. The actual RH in the chamber was monitored by a needle-probe psychrometer (Cole-Parmer type K model) inserted into the outlet tube of the chamber. The accuracy of the psychrometer was 3% between 0.1 and 0.9 RH. Before the XRD analysis, the clay slide was allowed to equilibrate with a given RH in the goniometer chamber until no significant change in basal diffraction intensity either at 14.1 or 17.1 Å was noticed. Generally, the equilibration procedure took  $<5$  min. All XRD analyses were performed with a scan rate of  $2^\circ 2\theta/\text{min}$ .

## RESULTS AND DISCUSSION

The amount of ethylene glycol adsorbed by the Mg-smectite samples under various conditions of equilibration is listed in Table 2. The apparent basal spacings of the Mg-smectite samples without any EG vapor treatment ranged between 13.6 and 16.0 Å, depending on the RH (Figure 1). The basal spacings were close to 14 Å between 0.2 and 0.6 RH, a typical basal spacing for a two-layer water-smectite complex. Mooney *et al.* (1952) and Keren and Shainberg (1975) observed that between RH 0.3 and 0.6, the amount of water adsorbed by a smectite increased continuously with increasing RH without change in the basal spacing. Between 0.7 and 0.95 RH, the first-order basal reflection of the Mg-smectite samples shifted to 15–16 Å and was not ac-

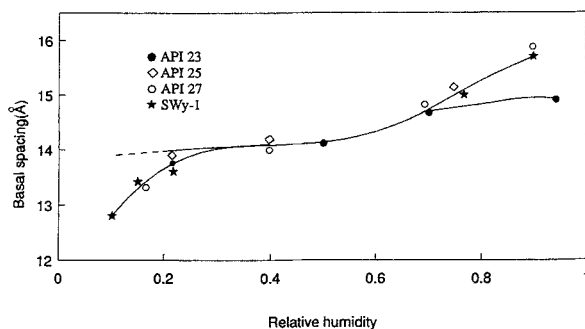


Figure 1. Basal spacing of Mg-smectite samples as a function of relative humidity during X-ray powder diffraction analysis.

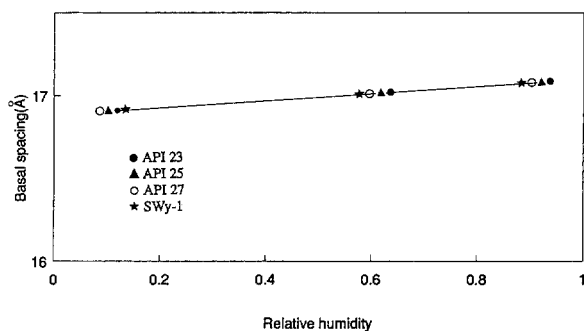


Figure 2. Basal spacing of Mg-smectite samples equilibrated with saturated vapor pressure of ethylene glycol, as a function of relative humidity during X-ray powder diffraction analysis.

accompanied by rational higher-order reflections. These materials were probably randomly interstratified, multi-layered water-smectite complexes. These results confirm previous reports that the basal spacing of a homoionic smectite is a function of RH (e.g., Mooney *et al.*, 1952; Keren and Shainberg, 1975) and that the basal spacing of Mg-smectite is  $<16 \text{ \AA}$  at 0.95 RH.

Mg-smectite samples pre-equilibrated with saturated vapor of EG expanded to a basal spacing of  $17.1 \pm 0.1 \text{ \AA}$  regardless of the RH (0.1 to 0.95) during the XRD analyses (Figure 2). Rational higher-order basal reflections were observed, suggesting that a two-layer EG-Mg-smectite complex formed. The EG adsorbed in the clays was estimated at 195–270 mg/g (Table 2). According to previous workers (e.g., Dyal and Hendricks, 1950; Morin and Jacobs, 1964), 248–260 mg EG/g is sufficient for a complete monolayer coverage of the smectite interlayer surfaces (i.e., two-layer EG in the interlayer space). Apparently, RH had no effect on the basal spacing expansion of the EG-Mg-smectite complexes that had been saturated or nearly saturated with EG. This fully solvated condition resembled that achieved in the common EG smectite test, in which the basal spacing expansion is not influenced by RH during the XRD analysis.

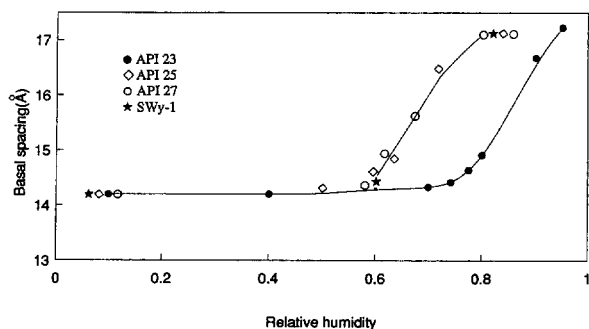


Figure 3. Basal spacing of Mg-smectite samples equilibrated with vapor of an ethylene glycol/CaCl<sub>2</sub> solvate, as a function of relative humidity during X-ray powder diffraction analysis.

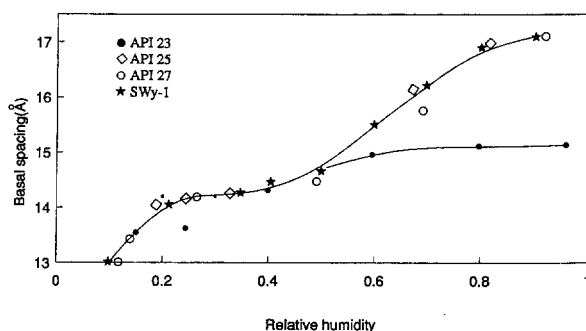


Figure 4. Basal spacing of Mg-smectite samples equilibrated with 0.05 relative ethylene glycol vapor pressure at 65°C, as a function of relative humidity during X-ray powder diffraction analysis.

If the Mg-smectite samples were pre-equilibrated with the vapor of the EG-CaCl<sub>2</sub> solvate (EG adsorbed was 45–78 mg/g), the apparent basal spacing of the smectites varied with the RH during the XRD analyses (Figure 3). The basal spacing of the smectite samples remained at  $14.1 \pm 0.3 \text{ \AA}$  at RH  $<0.45$ . Between RH 0.45 and 0.7, the basal spacing of the smectite samples, except sample API 23, was intermediate between 14.2 and 17.0 Å. At RH  $>0.75$  these clays expanded to  $17.1 \pm 0.1 \text{ \AA}$ . The API 23 specimen was an exception; its basal spacing did not start to expand until the RH exceeded 0.7 and expanded to 17.1 Å at RH  $>0.9$ . This specimen had the least EG retention among the specimens under low EG vapor pressure (Table 2) and had the highest layer charge of the smectite samples examined (Table 1).

If the Mg-smectite samples were pre-equilibrated with 0.05 relative EG pressure at 65°C, even less EG was retained (17–36 mg/g). The basal spacing expansion of samples API 25, API 27, and SWy-1, as a function of RH, was basically similar to those equilibrated with the EG-CaCl<sub>2</sub> solvate (Figure 4). The basal spacing of sample API 23 did not expand beyond 15.2 Å, even at 0.9 RH. The expansion behavior of sample API 23 was eventually similar to that of the Mg-clay without EG vapor treatment (Figure 1). This clay may not have adsorbed sufficient EG to produce a two-layer EG complex.

Apparently, the Mg-smectite samples equilibrated with low EG vapor pressure formed either one- or two-layer EG complexes depending on the RH. At low RH, adsorbed EG apparently distributed itself into a one-layer configuration such that only a 14-Å basal spacing was observed. At high RH, the sorption of water molecules provided energy for a rearrangement of the interlayer EG to a two-layer EG configuration such that the basal spacing was 17.1 Å. With the help of water molecules, a relatively small amount of EG (much less than is needed for a complete coverage of interlayer surfaces) probably formed a two-layer EG-smectite complex at high RH. The minimum amount of EG

needed for a smectite to form a two-layer EG complex at high RH is probably 20–30 mg/g. Unfortunately, the upper range of the adsorbed EG in which a two-layer EG complex may have been converted to a one-layer EG complex by low RH was not examined in this investigation. This upper range is apparently > 78 mg/g and may be about 100 mg/g.

The one-/two-layer EG-smectite complex conversion, as manipulated by RH, was apparently fast and reversible. To illustrate this effect, API 25 sample was first equilibrated with the vapor of the EG-CaCl<sub>2</sub> solvate, and then examined with XRD by setting the detector at a constant  $2\theta$  angle, which corresponded to 17.1-Å basal spacing. The XRD intensity was recorded as a function of RH (Figure 5), after the sample had equilibrated with a given RH (in terms of the basal XRD intensity). The conversion generally was complete in < 5 min after a given RH had been applied. Equilibrium in basal spacing expansion of smectites does not necessarily coincide with the equilibrium of water adsorption. In fact, the amount of water adsorbed may increase continuously without change in the basal spacing of smectites (Keren and Shainberg, 1975).

Inasmuch as the amount of EG adsorbed in a smectite at a given relative vapor pressure of EG apparently depends on the layer charge of the specimen (Hsieh *et al.*, 1984), the low EG vapor pre-equilibration condition in which smectite began to show the one-/two-layer EG complex conversion under the influence of RH depended on the charge nature of the specimen. For example, sample API 23 retained the least amount of EG of the smectite samples in a given low EG vapor condition; it was also the only sample that required the highest RH to form a two-layer EG complex.

The adsorbed EG and water in a smectite are not stable if the sample is exposed to the ambient air, as they will eventually escape to the air (Kunze, 1955). Due to the very low vapor pressure of EG under ambient conditions (e.g., at 25°C, the saturated EG vapor pressure over a free pure liquid is only 0.1 mm Hg), the escape rate of the adsorbed EG from a smectite was very slow. On the contrary, water is much more volatile (the saturated water vapor pressure at 25°C is 23.8 mm Hg), and the escape rate of the adsorbed water from a smectite was much faster compared with the adsorbed EG. The great contrast in the desorption rate between water and EG in a Mg-smectite system was probably the cause for the RH-manipulated conversion of one-/two-layer EG-smectite complexes. The API 25 specimen that initially adsorbed 75 mg EG/g (over EG vapor of the EG-CaCl<sub>2</sub> solvate) continued to exhibit its one-/two-layer EG-complex conversion effect after the clay had been exposed to ambient air for one week (the adsorbed EG was still well above 30 mg/g); whereas the API 23 specimen which initially adsorbed 45 mg EG/g (over EG vapor of the EG-CaCl<sub>2</sub> mixture)

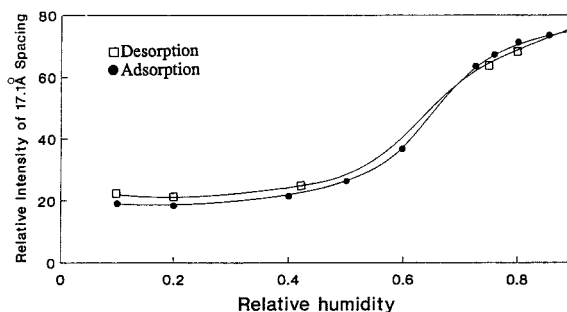


Figure 5. X-ray basal diffraction intensity of API 25 specimen, equilibrated with vapor of an ethylene glycol/CaCl<sub>2</sub> solvate, as a function of relative humidity during moisture adsorption-desorption processes.

failed to exhibit the one-/two-layer EG-complex conversion effect after it had been exposed to air for three days (the adsorbed EG fell to < 20 mg/g after three days).

#### SUMMARY AND CONCLUSIONS

The RH change (between 0.1 and 0.9) during XRD analysis did not affect the basal spacing of Mg-smectite samples that had been saturated, or nearly saturated, with EG. The basal spacing of the Mg-smectite samples that had been equilibrated with low EG vapor (over vapor of the EG-CaCl<sub>2</sub> solvate) expanded to 17.1 Å only if RH was high (> 0.75). Between 0.4 and 0.7 RH, the Mg-smectite samples formed a randomly interstratified one-/two-layer complex having a basal spacing between 14 and 17 Å. At RH < 0.4, the samples were all one-layer EG complexes, having basal spacings of 14 Å or less. High RH failed to expand the basal spacing of the API 23 specimen equilibrated with 0.05 relative EG vapor pressure at 65°C. Apparently, a minimum amount of the adsorbed EG was needed for the Mg-smectite samples to form a two-layer EG complex at high RH. This minimum is estimated to be 20–30 mg/g.

The one-/two-layer EG-Mg-smectite complex conversion as manipulated by the RH during XRD analyses was fast and relatively reversible. The equilibria of basal spacing expansion, with respect to the XRD intensity, were attained in 5 min under the conditions of the study.

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