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WATER VAPOR SORPTION BEHAVIOR OF SMECTITE-KAOLINITE MIXTURES

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Abstract—An experimental program was conducted to investigate the water-vapor sorption characteristics of smectite and kaolinite mixtures. End-member smectite and kaolinite were slurry-mixed together at mass-controlled ratios corresponding to 0%, 20%, 50%, 70%, 80%, 90% and 100% smectite. Vapor desorption isotherms for the mixtures were measured at 24°C for relative humidity (RH) ranging from ~95% to 0%.

Results show that the amount of water adsorbed by the clay mixtures at a given RH increases systematically with increasing smectite content. Derivative analysis of the sorption isotherms shows evidence of transitions between the two-, one- and zero-layer hydrate-states for the smectite-rich mixtures. The transitions become less apparent as the smectite content decreases. Monolayer coverage, specific surface area, and heat of adsorption were estimated from the isotherms using BET theory. It is shown that monolayer coverage and specific surface for the clay mixtures can be reasonably approximated by weighted averaging of the end-member clay properties. General methodologies are presented for predicting the sorption behavior (i.e. soil-water characteristics) and effective specific surface area from measurements of the end-member sorption isotherms.

Key Words—BET Analysis, Clay Liners, Kaolinite, Smectite, Sorption Isotherms, Specific Surface Area, Waste Containment.

INTRODUCTION

The design, construction and evaluation of hydraulic barriers for waste containment and remediation are major concerns for today’s geoenvironmental engineering community. Examples of engineered waste barriers include soil- or cement-based landfill liners, vertical barriers such as slurry, grout, or sheet-pile cut-off walls, and geotextile-based geosynthetic clay liners (e.g. Woods, 1987; Rumer and Mitchell, 1995).

In addition to meeting strength, durability and compressibility requirements, a primary design priority for waste containment systems is to minimize the hydraulic conductivity and thus the advective flux of contaminants through the system. For soil-based systems, these low hydraulic conductivities are achieved by mixing clayey soils with a high smectite content (e.g. bentonite) with controlled proportions of non-swelling clays, sand, or locally excavated materials. The small particle size, interlayer swelling capacity and tremendously high surface activity associated with the smectite fraction of the mix are primarily responsible for the low hydraulic conductivity and contaminant retardation properties of the containment system (e.g. Mesri and Olson, 1971; Jo et al., 2001).

For containment facilities constructed on or near the ground surface or at depth in relatively arid environments, the soils comprising the system tend to remain predominantly unsaturated and are subject to seasonal moisture fluctuation. In these cases, saturated advective flux becomes less important. Instead, the water sorption characteristics of the system at relatively low water content become the critical parameters governing its engineering behavior. These characteristics include hydraulic infiltration behavior, contaminant retardation behavior, and swelling, shrinkage and cracking behavior, all of which are important properties related to the system’s long-term performance. To the design engineer, therefore, a priori knowledge of the containment system’s sorption characteristics is highly desirable. Because waste containment systems are typically constructed by mixing two or more types of soil, methodologies for predicting the behavior of the mix from the properties of the end-member materials are ideal.

There have been numerous studies regarding the water vapor sorption behavior of clay. The work ranges from theoretical approaches based on consideration of molecular geometry (e.g. Barshad, 1949), experimental approaches using a wide variety of equipment for measuring sorption isotherms (e.g. Mooney et al., 1952; Collis-George, 1955; Van Olphen, 1965; Cases et al., 1992; Berend et al., 1995), experimental approaches using X-ray diffraction (e.g. Gillery; 1959; Del Pennino et al., 1981; Chipera et al., 1997), and most recently, numerical approaches using molecular dynamics computer simulations (e.g. Karaborni et al., 1996). In addition, analytical models such as Brunauer-Emmett-Teller (BET) and Frenkel-Halsey-Hill (FHH) theory have been developed and successfully applied for back-calculating important soil-water parameters like
monolayer coverage, specific surface area, and heat of adsorption from the experimentally-measured sorption isotherms (e.g., Keenan et al., 1951; Quirk, 1955; Lowell, 1979; Keren and Shainberg 1975, 1979; Parker, 1986).

Studies in the past have focused primarily on the adsorption of water vapor by relatively pure clay minerals. This paper presents the results of an experimental program conducted to investigate the sorption behavior for a series of mixed clay minerals. Relatively pure smectite and kaolinite were mixed at seven different mass-controlled ratios. The end-member smectite and kaolinite are intended to represent the highly expansive and non-expansive soils that are mixed together during the construction of typical waste containment systems. Sorption isotherms for the mixtures were measured using a specially developed humidity-control apparatus and analyzed using BET theory (Brunauer et al., 1938). The primary goal of the work is to facilitate the design of waste containment systems by determining whether or not the sorption behavior and engineering characteristics (e.g. specific surface area) of typical soil mixtures may be estimated by superimposing the properties of the end-member soils.

MATERIALS AND METHODS

End-member clays

The kaolinite used in this work was supplied by the Georgia Kaolin Company. Wyoming bentonite was supplied by the Rototin Clay Company. Na⁺-exchanged forms of the clays were prepared by saturating the bulk materials with 1.0 M NaCl solution for 24 h. The particles were separated from the salt solution in a high-speed centrifuge and re-suspended in fresh salt solution a total of three times. The samples were then repeatedly rinsed with distilled water until no excess chlorides were detected in the supernatant liquid. Chloride was presumed to be absent when the supernatant tested negative with AgNO₃ (Moore and Reynolds, 1997).

Mineralogy and engineering properties

Oriented clay-aggregate samples for X-ray diffraction (XRD) analysis were prepared by evaporating dispersed suspensions of the Na⁺-exchanged samples onto a glass slide. The samples were not fractionated by particle size prior to XRD testing. Samples were scanned from 2°20 to 35°20 using an automated Scintag XDS-2000 XRD system employing CuKα radiation. Both clays were scanned under air-dry conditions. The Wyoming bentonite was equilibrated with ethylene glycol vapor and scanned a second time.

Figure 1 shows XRD diffraction patterns obtained for the Georgia kaolinite and Wyoming bentonite. Qualitatively, the results indicate that the former is composed of relatively pure kaolinite with a minor quartz component. The latter is primarily discrete smectite, with a quartz component also.

Atterberg limits were determined following procedures outlined in ASTM testing standard D4318 (ASTM, 2000). The liquid (LL) and plastic limits (PL) for the Na⁺-exchanged kaolinite are 45% and 28%, respectively.

Figure 1. XRD diffraction patterns of the end-member clay samples: (a) Georgia kaolinite, and (b) Wyoming bentonite. S: smectite; K: kaolinite.
The LL and PL for the smectite are 485% and 132%, respectively. Hydrometer analysis (ASTM D421) showed that the kaolinite comprised 35% clay-sized particles (<2 μm). Hydrometer tests for the smectite were inconclusive because the material tended to 'gel' when placed in suspension.

**Preparation of smectite-kaolinite mixtures**

The end-member smectite and kaolinite materials were oven dried to constant mass at 105°C. Mass-controlled proportions corresponding to 0%, 20%, 50%, 70%, 80%, 90% and 100% smectite were weighed out and mixed together in a glass beaker. Distilled water (50 mL) was added and the suspension was stirred for 24 h to promote complete homogenization and redistribution of the cations in the exchange complex. The suspensions were then oven dried, pulverized with a mortar and pestle to pass a #200 (75 μm) sieve, and stored in the oven at 105°C for subsequent sorption testing.

**Sorption testing apparatus**

Water vapor sorption isotherms were measured using a computer-automated humidity-control system developed previously for testing applications for expansive soils (Likos and Lu, 2001, 2002). Relative humidity control is achieved by computer-proportioned mixing of vapor-saturated, or 'wet', N₂ gas and desiccated, or 'dry', N₂ gas in a closed environmental chamber (e.g. Chipera et al., 1997). To develop sorption isotherms, the equilibrium mass of soils placed in the chamber is measured using an integrated electronic balance as water vapor is adsorbed or desorbed.

Figure 2a illustrates the general layout of the testing system. Following the schematic from left to right, bottled nitrogen (>99.995% N₂) is split into two separate
gas streams through ¼" nylon tubing. A pair of computer-controlled mass-flow valves (MKS Instruments, Type 1179A) regulates the flow of each gas stream between zero and 200 cm³/min based on a DC signal from a control computer. One of the gas streams is vapor-saturated by bubbling it through a gas-washing bottle (Fisher-Milligan 07-513) filled with distilled water. The second gas stream is routed through a cylinder filled with desiccant media (i.e. silica gel). The vapor-saturated (or ‘wet’) and desiccated (or ‘dry’) gas streams are then reintroduced in a three-neck flask at a combined flow rate of 200 cm³/min. The resulting gas stream (labeled ‘humid’ on Figure 2a) has a RH that is a direct function of the ‘wet’ to ‘dry’ gas flow ratio (w/d) maintained by the control PC. Electrical heat tape is wrapped around the ‘wet’ and ‘humid’ gas lines and connected to a variable voltage transformer to allow the option for elevated temperature testing.

The ‘humid’ gas stream is routed into an acrylic environmental chamber containing a soil sample (Figure 2b). Relative humidity and temperature are continuously monitored with a capacitance-film humidity/temperature probe (Vaisala Corporation, Model HMI-35). The probe measures humidity between 0% RH and 99% RH at 0.01% RH resolution. Temperature is measured to 0.01°C. Signals from the humidity probe form a feedback loop with the control PC for automated regulation of the ‘wet’ to ‘dry’ gas flow ratio (w/d) using the two mass-flow controllers. Prior to adsorption testing, the accuracy of the humidity probe was checked using six saturated salt solutions. Figure 3 compares RH values measured using the probe with theoretical values based on the various salt solutions. A one-to-one slope is included on the figure for comparison.

![Figure 3. Check on the accuracy of the RH probe: comparison of measured humidity with theoretical values for five saturated salt solutions.](image)

An electronic balance (Mettler-Toledo, Model SAG204) with 210 g range and 0.0001 g resolution forms the bottom plate of the environmental chamber (Figure 2b). Soil samples are placed directly on the balance for testing. The RH is stepped up or down incrementally by proportioning the ratio of ‘wet’ to ‘dry’ gas flow under feedback from the RH probe. The water content of the soil is monitored continuously with the balance through the PC serial port as water vapor is adsorbed or desorbed at each step in RH. When the steady-state value at a given RH is reached, the water content is recorded and the humidity in the chamber is stepped (up or down) to the next increment. Typically, RH is stepped in increments of 10%. The electronic balance is automatically calibrated prior to each run using an internal 200 g mass.

Sorption testing procedure

Water sorption isotherms were measured for the end-member materials and the smectite-kaolinite mixtures to obtain the relationship between soil moisture content (w%) and RH%. All isotherms were determined along drying paths from relatively high soil moisture content to relatively low moisture content, i.e. desorption isotherms.

Samples were prepared for testing by sprinkling ~0.5 to 1.0 g of the pulverized clay onto a pre-weighed glass slide. A second glass slide was used to spread the sample out evenly and compress it to a thickness of ~2 mm. The mount was then dried to constant mass at 105°C and transferred to the environmental chamber in a sealed container. Samples were subjected to 0% ‘wet’ flow (RH ≈ 0.5%) for 24 h to establish a baseline mass for subsequent water content calculations. A preliminary series of tests showed that the water content of typical clays after the near-zero-humidity drying period is roughly equivalent to oven drying at 105°C (Likos, 2000). The RH was then ramped to ~95% RH until the sample reached constant mass. This initial equilibration time ranged from ~30 h to 130 h, where samples with the highest smectite content required the most time. After the initial equilibration, the samples were tested for desorption characteristics by decreasing the RH in increments of ~10%. The mass of the sample during desorption was monitored continuously to detect steady state. Typically, the samples required at least 48 h for each increment. During all stages of testing, the temperature in the chamber was elevated and stabilized at ~24°C using the electrical heat tape.

RESULTS AND DISCUSSION

Select results from a typical sorption testing cycle are shown in Figure 4a (30% kaolinite ~70% smectite). The cycle took ~600 h (25 days) to complete. Adsorbed water content (w%) is expressed as the mass percentage of adsorbed water relative to the soil solids. Relative
humidity and temperature (see inset) were measured directly by the RH/temp probe. Typical for all testing, the mean and standard deviation in measured temperature during the cycle were 24.03°C and 0.10°C, respectively. Desorption isotherms were determined for all samples from the time series data by averaging the adsorbed water content and RH values obtained during the final 30 min of each step in RH. The measured isotherms are shown in Figure 4b.

**General discussion**

The sorption isotherms display several distinct features. Foremost, the amount of water adsorbed by the clay mixtures increases with increasing smectite content. The adsorbed water content at approximately 95% RH ranges from as much as 21% for the smectite-rich mixtures to as little as 6% for the kaolinite end-member. The relatively large amount of water adsorbed by the smectite-rich mixtures reflects the greater surface area and interlayer swelling characteristics of the smectite.

The kaolinite end-member displays characteristics of a standard type II isotherm (e.g., Brunauer, 1945). The general shape indicates that adsorption occurs incrementally as molecular monolayers until the adsorbed film grows to a thickness such that it is no longer strongly influenced by the particle surface. The inflection occurring near 85% RH may indicate the point where continued sorption occurs as capillary condensation in the interparticle pore-space (Parker, 1986).

The isotherm for the pure smectite, which most closely represents a type IV isotherm (Brunauer, 1945), displays characteristics that indicate successive desorption of molecular water layers from within the interlayer of the expansive crystalline structure. The isotherm may be qualitatively described as ‘wavy,’ with an ill-defined double step. Similar characteristics have been noted by numerous researchers for the sorption of polar adsorbate molecules (e.g., H2O) on expansive clay minerals (e.g., Mooney et al., 1952; Collis-George, 1955; Van Olphen, 1965; Cases et al., 1992; Berend et al., 1995).

Figure 4. Sorption testing results for end-member and mixed samples of kaolinite and smectite: (a) RH, water content and temperature response for a mixture of 30% kaolinite and 70% smectite; and (b) desorption isotherms measured for all samples.
The ‘wavy’ characteristics of the isotherms become less evident as the smectite content of the mixed samples decreases. For example, Figure 5a shows the derivative ($\Delta w/\Delta RH$) of each isotherm as a function of equilibrium RH. The smectite-rich mixtures display distinct peaks in the derivatives. Two peaks occur at RH values between ~5% to 15% and 50% to 60%. As the kaolinite percentage increases, the peaks become less well defined.

The peaks in the isotherm derivatives indicate relatively large changes in moisture content for a given change in humidity. The peaks occurring between 50% and 60% RH are interpreted to indicate transitions from the two-layer to the one-layer hydrate state associated with the smectite fraction of the clay mixtures, i.e. crystalline swelling (Van Olphen, 1991). Similarly, the peaks occurring between 5% and 15% RH are interpreted to indicate transitions from the one-layer to the zero-layer hydrate state. These interpretations are supported by numerous humidity-controlled XRD studies that have noted distinct transitions in basal spacing (i.e. $d_{001}$) corresponding to the one- and two-layer hydrate states of smectite (e.g. Mooney et al., 1952; Gillery; 1959; Del Pennino et al., 1981; Chipera et al., 1997). The transitions noted in the XRD studies have typically been observed between the same ranges of relative humidity for Na$^+$-exchanged smectite.

**Superposition of end-member sorption isotherms**

Sorption isotherms for the mixed clays were estimated from the end-member isotherms by weighted averaging following equation 1.

$$w_{\text{max}} = m_s w_s + m_k w_k$$

where $w_{\text{max}}$ is the water content of the smectite-kaolinite mixture at a given RH, $w_s$ is the water content of the end-member smectite at the same RH, $w_k$ is the water content of the end-member kaolinite at the same RH, $m_s$ is the dry mass fraction of the smectite, and $m_k$ is the kaolinite dry mass fraction.

![Figure 5. (a) Derivatives of the desorption isotherms showing peaks related to crystalline swelling in the smectite fraction. (b) Desorption isotherms estimated from superposition of the kaolinite and smectite end-members.](image-url)
Figure 5b shows measured data (symbols) and estimations based on superposition (dashed lines) by equation 1 for three of the clay mixtures. For RH < ~90%, the estimations are in reasonably good agreement with the measured data.

Superposition of end-member surface properties

The fact that the sorption isotherms of the clay mixtures are well represented by superpositions suggests that sorption behavior in the measured range is dominated by the specific surface area of the end-member clays. The mass of water required to form a monomolecular layer on the clay surfaces, the associated heat of adsorption, and the specific surface area of the particles were estimated from the sorption isotherms using BET theory (Brunauer et al., 1938).

According to BET theory, physical sorption involves the formation of many molecular layers of adsorbate on the adsorbent surface. Sorption is modeled by the following linear equation:

\[
P/P_0 = \frac{1}{X_m C} \cdot \frac{P}{P_0} + \frac{C - 1}{X_m C} \cdot \frac{P}{P_0}
\]

(2)

where \( X \) is the amount of adsorbate (e.g. H₂O) adsorbed in grams per gram of adsorbent (e.g. clay) at vapor pressure \( P \) and temperature \( T \). \( P_0 \) is the saturated vapor pressure of the adsorbate at the same temperature and \( X_m \) is the quantity adsorbed (g/g) when the adsorbent is covered with a molecular monolayer. The ratio \( P/P_0 \) is the relative vapor pressure or RH. The term \( C \) is a constant at any given temperature and is approximately equal to:

\[
C \approx \exp \left( \frac{E_1 - E_L}{RT} \right)
\]

(3)

where \( E_1 \) is the heat of adsorption of the first molecular layer of adsorbate, \( E_L \) is the heat of condensation of the adsorbate, \( R \) is the molar gas constant (8.314 J mol⁻¹ K⁻¹) and \( T \) is the absolute temperature (K). The difference (\( E_1 - E_L \)) refers to as the heat of adsorption (e.g. J/mol) and provides a quantitative measure of the energy of interaction between the first monolayer of adsorbed H₂O molecules and the active clay surfaces. Relatively high values of (\( E_1 - E_L \)) indicate relatively high forces of hydration between the clay surface and the monolayer H₂O.

If the cross-sectional area of the adsorbate molecule is known, the total surface area (\( S_t \)) and specific surface area (\( S \)) of the adsorbent may be approximated from the mass of adsorbate at monolayer coverage using equation 4 (e.g. Lowell, 1979).

\[
S_t = \frac{X_m N A}{M} \times 10^{-20} \text{m}^2
\]

(4)

where \( X_m \) (grams) is the total monolayer weight of the adsorbate, \( M \) is the molecular mass of the adsorbate, \( N \) is Avogadro’s number (\( 6.02 \times 10^{23} \) molecules/mol), and \( A \) is the adsorbate cross-sectional area in Å²/molecule. The cross-sectional area for adsorbed H₂O at 25°C can be approximated as 10.8 Å² (Lowell, 1979). Total surface area (\( S_t \)) is divided by the adsorbent mass to obtain the specific surface area (\( S \)).

According to equation 2, a plot of \( P/X(P_0 - P) \) vs. \( P/P_0 \) should give a straight line with the slope given by \( (C - 1)/X_m C \) and the intercept by \( 1/X_m C \). Values of \( X_m \) and \( C \) can be obtained from a plot of experimental sorption data to back-calculate the mass of H₂O at monolayer coverage and the heat of adsorption using equations 2 and 3.

Figure 6 shows BET plots for the various mixtures of kaolinite and smectite clay. It is evident that the plots indeed yield linear relations for RH values < ~60% (\( P/P_0 < 0.6 \)). The slopes and intercepts of these portions of the relations were calculated to obtain \( X_m \), \( (E_1 - E_L) \), and \( S \). Figures 7a, 7b, and 7c show plots of these values for the...
end-member materials and the kaolinite/smectite mixtures, respectively. Each parameter is plotted as a function of the smectite percentage by mass. The results are also summarized in Table 1.

The monolayer coverage and specific surface area values for the end-member kaolinite and smectite ($X_m = 5.91 \text{ mg/g}$ and $58.40 \text{ mg/g}$ respectively; $S = 21.31 \text{ m}^2/\text{g}$ and $210.76 \text{ m}^2/\text{g}$ respectively) are in very good agreement with those reported by previous researchers using BET analysis for Na$^+$-exchanged clays (Quirk, 1955; Keenan et al., 1951; Keren and Shainberg, 1975). Specific surface values for pure Na$^+$-smectite as high as $840 \text{ m}^2/\text{g}$ have been reported (e.g., Mitchell, 1993). The relatively low value obtained in this analysis ($S = 210.76 \text{ m}^2/\text{g}$) may reflect the influence of the quartz component detected from the XRD analysis (Figure 1). The liquid limit (LL) of 485% measured for the end-member smectite, which is also low by comparison, may support this argument.

The heat of adsorption for the end-member kaolinite (1.76 kcal/mol, 7,366 J/mol) is in relatively close agreement with calculations based on sorption data for Na$^+$-exchanged kaolinite reported by Keenan et al. ($E_1 - E_L = 1.54$ kcal/mol, 6,440 J/mol). Keren and Shainberg (1975) reported much lower heat of adsorption values for Na$^+$-exchanged smectite as 0.34 kcal/mol (1,423 J/mol). There is no apparent trend in the heat of adsorption for the kaolinite-smectite mixtures (Figure 7b), indicating that the forces responsible for surface hydration are relatively independent of clay type and are more likely to be dependent on the properties (i.e., size and valence) of the predominant exchangeable cation, in this case Na.

For the kaolinite/smectite mixtures, there is an obvious upward trend in the monolayer coverage and specific surface area with increasing smectite percentage (Figures 7a,c). The question therefore arises as to whether or not these properties of the clay mixtures can be estimated by weighted averaging of the end-member values. Similar to the previous analysis, the dashed lines on Figures 7a and 7c were calculated from the end-member monolayer coverage and specific surface area, i.e.:

\[ X_{m} = m_{k} X_{ms} + m_{s} X_{mk} \]

\[ S_{mix} = m_{s} S_{s} + m_{k} S_{k} \]

where $X_{ms}$ and $X_{mk}$ are monolayer coverage for the end-member smectite and kaolinite, respectively, and $S_{s}$ and $S_{k}$ are the end-member specific surface areas. In both cases, the estimations by equations 5 and 6 match the measured data quite well, indicating that the properties of engineered soil mixtures may be reasonably estimated from the end-members comprising the design mix.

**CONCLUSIONS**

The adsorbed water content of the smectite-kaolinite mixtures at given RH increases systematically with increasing smectite content. Evidence of crystalline swelling was observed in the isotherms for the smectite-rich clay mixtures. Analysis of the isotherm
derivatives showed that the crystalline swelling behavior became less pronounced with decreasing smectite content. The sorption isotherms of the clay mixtures can be well predicted by superimposing the isotherms of the end-member clays, suggesting that the particle surface area is the dominant factor controlling the sorption process. Analysis using BET theory validated the superposition principle for particle specific surface area, indicating that the sorption characteristics for multi-soil mixtures used in typical waste containment systems may be reasonably established from the design mixture.

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REFERENCES