

Intrinsic Relationship between Specific Surface Area and Soil Water Retention

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Abstract: Specific surface area (SSA) is a fundamental property of soil. A new methodology for SSA determination of both expansive and nonexpansive soil based on interpretation of the soil water retention curve (SWRC) is proposed and evaluated. The SWRC-based methodology relies on the Khorshidi-Lu water sorption model, where hydration of expansive soils is interpreted to occur on three distinct surfaces and in sequential order: exchangeable cations, intercrystalline surfaces, and external particle surfaces. Hydration at these different sites is responsible for the commonly observed hysteresis in specific moisture capacity (SMC) between adsorption and desorption paths. Hydration mechanisms for nonexpansive soils, where intercrystalline surfaces do not exist, are shown to be well captured by interpreting the Brunauer-Emmett-Teller (BET) multilayer sorption theory if the effect of cation hydration on the SWRC is considered. A suite of materials ranging from silty to clayey soils is used to demonstrate the validity of the SWRC-based methodology. A comparison of SSA values obtained using the SWRC-based methodology, two existing water-vapor-based methods, and the ethylene glycol monoethyl ether (EGME) method confirms the validity and the accuracy of the SWRC-based methodology. Agreement between SSA values calculated based on the SWRC approach and the EGME method for nonexpansive soils and expansive soils as estimated by root-square-mean error (RSME) is 9 m²/g and 80 m²/g, respectively. A limitation of the EGME method for the SSA determination of expansive soils is also identified. DOI: 10.1061/(ASCE)GT.1943-5606.0001572. © 2016 American Society of Civil Engineers.

Author keywords: Specific surface area; Water sorption isotherm; Specific moisture capacity; BET plot; Expansive soils; Nonexpansive soils.

Introduction

One of the fundamental properties of soil is specific surface area (SSA). In the geotechnical community, it is defined as the surface area of a soil per unit mass (m²/g). The SSA of a soil is dominantly controlled by the portion of clay in the soil. It has been related to various soil properties and engineering behavior such as swell-shrinkage (e.g., Ross 1978; Low 1980), hydraulic conductivity (e.g., Dasog et al. 1988), elastic modulus (e.g., Lu and Kaya 2014), fluid flow and diffusion (e.g., Santamarina et al. 2002; Sanzeni et al. 2013). In addition, cation exchange capacity (CEC) and Atterberg limits are correlated with the SSA (e.g., Farrar and Coleman 1967; Churchman and Burke 1991; Santamarina et al. 2002; Dolinar et al. 2007; Chittoori and Puppala 2011; Woodruff and Revil 2011). Atterberg limits and grain-size distribution are currently the primary tests for classifying soils; however, the SSA might be a better

property for the classification of fine-grained soils (Lutenegger and Cerato 2001).

The SSA might be determined based on the adsorption of gas or liquid on soil interlayer/particle surfaces (Likos et al. 2010), where the accumulation or loss of a probe substance on the soil interlayer/particle surface is measured to calculate the SSA. Nitrogen and water vapor are two popular probe molecules in gas adsorption techniques for SSA determination (e.g., Quirk 1955; Newman 1983; Środoń and McCarty 2008). Nitrogen theoretically can only cover external particle surfaces of soil, while water can penetrate into interlayers and cover interlayer surfaces as well (e.g., Kraehenbuehl et al. 1987; Pennell 2002; Środoń and McCarty 2008). Three main substances used in liquid adsorption methods are methylene blue (MB) dye (e.g., Hang and Brindley 1970; Kahr and Madsen 1995), ethylene glycol (EG) (e.g., Dyal and Hendricks 1950; Bower and Goertzen 1959), and ethylene glycol monoethyl ether (EGME) (e.g., Carter et al. 1965; Eltantawy and Arnold 1973; Cerato and Lutenegger 2002; Akin and Likos 2014). The molecules of these substances are polar; thus, both internal and external surface areas of particles are measured using them as the probe molecules.

The use of EGME has been widely accepted and is employed as a standard method for SSA determination of soils by Soil Science Society of America (Pennell 2002). Similar to other sorption-based SSA approaches, the mass of EGME retained by a sample at equilibrium is assumed to correspond to monolayer coverage on the mineral surface, such that SSA may be determined from

$$SSA_{EGME} = \frac{M_a}{2.86 \times 10^{-4}(M_s)} \quad (1)$$

where M_a (g) is the mass of EGME retained at equilibrium and M_s (g) is the initial dry mass of the sample. The constant 2.86×10^{-4}

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Note. This manuscript was submitted on April 7, 2015; approved on May 3, 2016; published online on July 20, 2016. Discussion period open until December 20, 2016; separate discussions must be submitted for individual papers. This paper is part of the *Journal of Geotechnical and Geoenvironmental Engineering*, © ASCE, ISSN 1090-0241.

has units of g/m^2 and quantifies the mass of EGME required to cover 1.0 m^2 of montmorillonite mineral surface.

Water-Vapor-Based SSA Calculation

The water-vapor-based SSA for all soils can be obtained by two well-known approaches: the Brunauer-Emmett-Teller (BET) (Brunauer et al. 1938) gas adsorption method and Newman (1983) single point method. Recently, Leao and Tuller (2014) introduced a t -curve method based on the energy layer density due to van der Waals attraction on a water film that is mainly applicable for non-expansive soils with $\text{SSA} < 150 \text{ m}^2/\text{g}$. This method is fundamentally similar to the Tuller and Or (2005) method that is considered to be applicable for soils with $\text{SSA} < 200 \text{ m}^2/\text{g}$ (Tuller and Or 2005). According to the BET and Newman methods, the SSA can be calculated from the following equation:

$$\text{SSA} = \frac{w_i N A}{\omega_w} \quad (2)$$

where ω_w = molar mass of water; N = Avogadro's number; and A = area covered by one water molecule ($10.8 \times 10^{-20} \text{ m}^2$). The parameter w_i for both the BET and Newman methods is the monolayer gravimetric water content w_m , which can be obtained from the BET equation

$$\frac{RH}{(1 - RH)_w} = \frac{c - 1}{c w_m} RH + \frac{1}{c w_m} \quad (3)$$

where w = gravimetric water content; RH = relative humidity; and c = BET sorption constant related to the heat of adsorption of water on the soil particle surface. It is assumed that the plot of $RH/(1 - RH)_w$ versus RH gives a straight line that is used to determine c and w_m . The w_m may also be obtained from the Newman (1983) single point method, where it was suggested that the w_m is equal to w_{47} , the gravimetric water content (water content hereafter) at 47% RH , for expansive soils, and $w_{47}/1.7$ for nonexpansive soils. The rationale for the RH value for expansive soil is based on the water content required to cover the inter-layer surface of Ca-Wyoming montmorillonite with theoretical SSA of $798 \text{ m}^2/\text{g}$ (obtained from X-ray measurements) up to two layers (Newman 1983). In addition, the coefficient 1.7 for nonexpansive soils is associated with an estimation of average water thickness at 47% RH that is 1.7 times greater than the monolayer thickness (e.g., Hagymassy et al. 1969; Newman 1983).

Determination of the SSA using water vapor as a probe molecule has two main advantages. First, because of the presence of water in natural soils, it can best represent the field conditions. Second, the total SSA is obtained due to the access of water to both internal and external particle surfaces (e.g., Newman 1983; Akin and Likos 2014). However, the SSA values determined from the BET and Newman methods differ from the SSA results obtained from the EGME measurements with the difference increasing as the SSA increases (e.g., Akin 2014). For expansive soils, this difference becomes much greater, thus limiting the applicability of the BET or Newman method.

The main objectives of this work is to propose a methodology to determine SSA that are (1) based on the soil water retention curve (SWRC) to better represent the field environment; (2) able to predict SSA values much closer to the EGME-based SSA values than the previous BET-based methods; and (3) able to estimate much more realistic SSA values as an intrinsic soil property for expansive soils. The methodology is based on the Khorshidi and Lu (2016) water sorption model derived from the Lu and Khorshidi (2015) SWRC hysteresis model. According to the model proposed by Khorshidi and Lu (2016), the monolayer water content w_m can be uniquely determined by the specific moisture capacity (SMC) method for expansive soils and the BET plot for nonexpansive soils. An expansibility coefficient (EC) will be defined later to represent the susceptibility of soil to swelling. More details of the physical meaning and mathematical definition of EC will be provided later. In order to find the SSA of soil using the proposed SWRC methodology, the SMC method is utilized when the soil's EC is greater than 0.12; otherwise, the BET plot is used.

Material and Experimental Methods

The relationship between matric potential (in terms of relative humidity, suction head, or matric suction) and soil water content (in terms of the degree of saturation, gravimetric water content, or volumetric water content) is called the SWRC (e.g., Brooks and Corey 1964; van Genuchten 1980; Khorshidi et al. 2016). In order to calculate the SSA of soils based on water vapor sorption, SWRCs in the high suction range (water sorption isotherms hereafter) of various soils representing a wide range of expansibility from nonexpansive to expansive soils were measured here. The soil samples include nine different natural soil specimens from various locations in the United States and China, various mixtures of Georgia kaolinite (nonexpansive soil) and Wyoming sodium montmorillonite (highly expansive soil). The latter two were obtained from

Table 1. Origin, Mineralogy, and Geotechnical Properties of Test Soils

Soil	Mineralogy	Clay (%)	LL (%)	PL (%)	PI (%)	USCS	
						classification	Origin
Georgia kaolinite	K	35	44	26	18	CL	Georgia, U.S.
Wyoming montmorillonite	Discrete S, trace Qtz	100	485	353	132	CH	Wyoming, U.S.
Na ⁺ /Ca ⁺⁺ bentonite	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Denver bentonite	Discrete S, trace K, Qtz., K-Feld	90	118	45	73	CH	Colorado, U.S.
Denver claystone	Mixed layer I/S, trace K, Qtz., Gypsum	55	44	23	21	CL	Colorado, U.S.
Bonny silt	N/A	14	25	21	4	ML	Colorado, U.S.
BALT silt I	N/A	14	26	19	7	CL-ML	California, U.S.
BALT silt II	N/A	5	28	23	5	SM	California, U.S.
Hopi silt I	N/A	3	26	19	7	SC-SM	Arizona, U.S.
Hopi silt II	N/A	2	N/A	N/A	N/A	ML	Arizona, U.S.
Iowa silt	N/A	10	33	24	9	ML	Iowa, U.S.
Heifangtai silt	N/A	N/A	26	21	5	ML	Gansu, China

Note: K = kaolinite; I = illite; Qtz. = quartz; K-Feld = K-Feldspar; S = smectite; USCS = Unified Soil Classification System.

the Georgia Kaolin Company (Georgia) and Rototin Clay Company (Wyoming), respectively. Georgia kaolinite (GaK)-sodium montmorillonite (NaS) mixtures were prepared in seven oven-dried, mass-controlled proportions corresponding to their respective GaK and NaS content. Five additional samples of $\text{Na}^+/\text{Ca}^{++}$ bentonite soils with various isomorphically substituted mono-cations were prepared to represent materials with known cation exchange complexes. The mono-cation natural bentonite specimens were prepared by treating the clay with solutions of chloride of Li^+ , Na^+ , K^+ , Mg^{++} , and Ca^{++} (Akin and Likos 2014). The basic physical and geotechnical properties for each of the test soils, as well as their origins, are summarized in Table 1.

Water sorption isotherms of the soils were measured using a vapor sorption analyzer (Khorshidi 2015). Both relative humidity and gravimetric water content during drying (desorption) and wetting (adsorption) paths are measured dynamically with this device (e.g., Likos et al. 2011; Revil and Lu 2013; Khorshidi and Lu 2016). In this study, the soil specimens were first oven-dried at 105°C , and then cooled in a chamber containing desiccant to ambient temperature. Water sorption isotherms were then obtained for RH ranging between 4 and 95% along wetting and drying paths at $25 \pm 0.2^\circ\text{C}$.

Measured water sorption isotherms for all soils used in this study are shown in Fig. 1. Figs. 1(a and b) present measured drying water sorption isotherms for various GaK and NaS mixtures as well as different mono-cation bentonite soils, respectively. These soils are mostly expansive soils. Fig. 1(c) shows measured drying water sorption isotherms for the suite of natural soils, which are mainly nonexpansive soils. The desorption path is more representative to be used in inferring to the properties related to the surface or exchangeable cations (Mooney et al. 1952; Quirk 1955; Likos and Lu 2006; Lu and Khorshidi 2015). In addition to the measurements of water sorption isotherms for the soils, the tests for the determination of SSA based on the conventional EGME retention on soils are conducted. The details of the testing procedure can be found in Akin and Likos (2014).

In order to determine the SSA based on the SWRC, water content corresponding to the monolayer hydration around cations and interlayer/particle surfaces (for both expansive and nonexpansive soils) or water content corresponding to the bilayer hydration on cations and interlayer surfaces (only for expansive soils) must first be obtained. To identify these values, the exact process of water hydration on soil should be investigated and defined. In the following, therefore, different hydration mechanisms and their order of hydration process on particle surfaces and in interlayer spaces are discussed.

Hydration Mechanisms in Soils

The water sorption isotherm for Wyoming montmorillonite exhibits a stepwise pattern, while this behavior cannot be observed in SWRC of Georgia kaolinite [Fig. 1(a)]. These patterns in the SWRC can be well explained by distinguishing the different hydration mechanisms in a soil and the order of occurrence of each one. Three hydration mechanisms are recognized to occur during water sorption on soils: exchangeable cation hydration, particle surface hydration, and interlayer surface hydration (e.g., Cases et al. 1997; Sposito 2008; Khorshidi and Lu 2016). The first two hydration mechanisms occur in any type of soil, while the third type of hydration mechanism occurs only in expansive soils with an expandable interlayer. Beyond the hydration water, there can also be an osmotic stage, where water can be sorbed on soil due to the attraction between a water molecule and various cations and

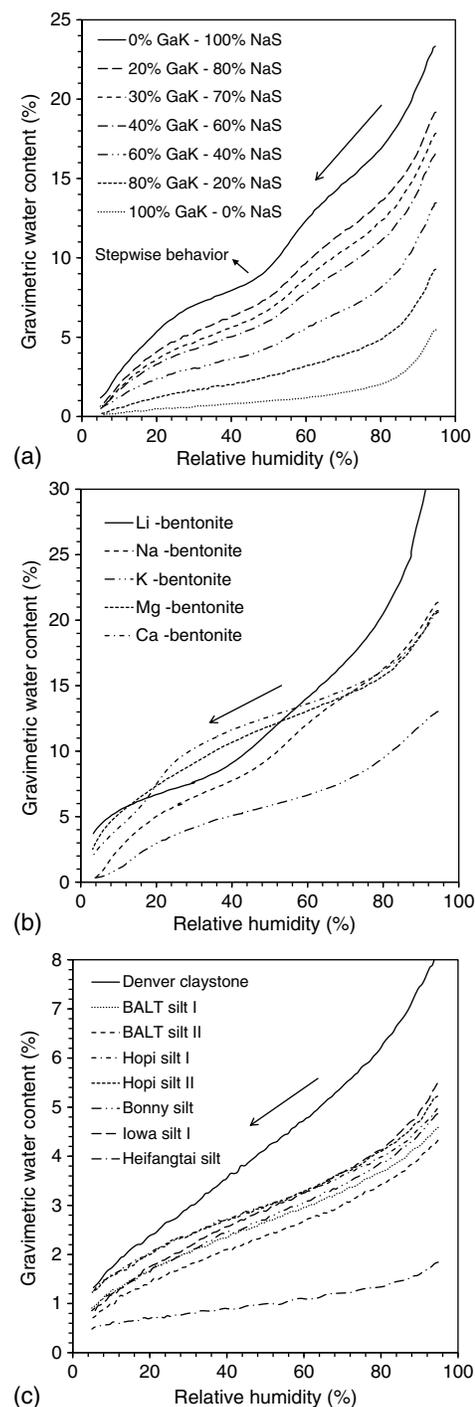


Fig. 1. Measured drying sorption isotherms of (a) various mixtures of Georgia kaolinite and Wyoming sodium montmorillonite; (b) various cation-exchanged bentonites (data from Akin and Likos 2014); (c) various natural soils

soluble salts in the soil solution (e.g., van Olphen 1977; Lu and Likos 2004).

Sequence of Hydration Mechanisms

In the literature, it is considered that at low relative humidity, cation hydration followed by interlayer/particle surface hydration occurs during water sorption on soils (e.g., Chiou and Rutherford 1997;

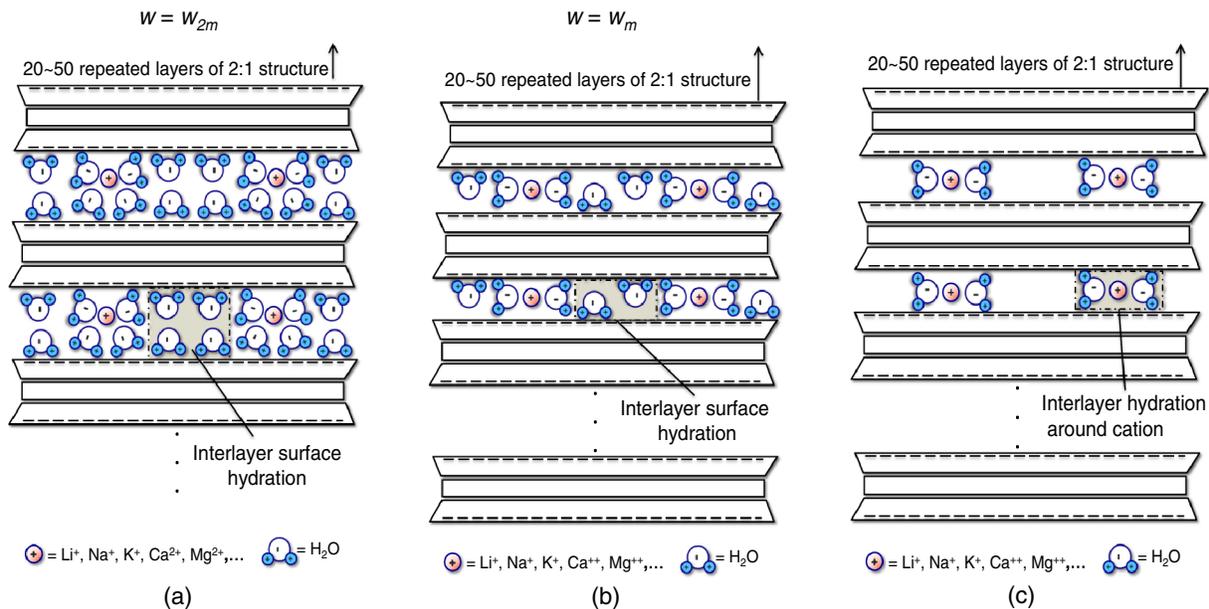


Fig. 2. Conceptual arrangements of water layers hydrating on exchangeable cations or interlayer surfaces for a typical expansive soil along desorption path: (a) bilayer cation and interlayer surface coverage; (b) monolayer cation and interlayer surface coverage; (c) monolayer cation coverage

Prost et al. 1998; Sposito 2008). The first conceptual model to explain several SWRC characteristic behaviors, among them hydraulic hysteresis in high suction regimes, was recently proposed by Lu and Khorshidi (2015). According to this conceptual model, Khorshidi and Lu (2016) developed a water sorption model to quantitatively describe the sequence of water sorption processes on soil by defining the ranges of relative humidity relative to exchangeable cation and interlayer/particle surface hydration mechanisms. According to this model, the order of hydration mechanisms along the desorption path is conceptually illustrated in Fig. 2. The soil in this figure is a typical expansive soil with a 2:1 mineral structure (two tetrahedral and one octahedral sheets in each unit layer).

Following the water sorption model by Khorshidi and Lu (2016), the desorption process for a typical expansive soil can be described as follows: in the range of high relative humidity, desorption removes water molecules from interlayer/particle surfaces. During a decrease in the relative humidity, at a certain relative humidity, there is a state where the water content corresponds to the bilayer hydration on cations and interlayer surfaces, as shown in Fig. 2(a). The gravimetric water content at this state is defined as w_{2m} hereafter. Further reduction in relative humidity removes water molecules from the second layer on interlayer surfaces, resulting in monolayer hydration of cations and interlayer surfaces of soil particles as illustrated in Fig. 2(b). The gravimetric water content at this state is shown by w_m . It is assumed that the number of water molecules in the second layer is almost equal to that of the monolayer. It will be shown in the assessment section of this paper that this assumption is valid. By further decreasing the relative humidity, dehydration occurs first on the interlayer surfaces, followed by dehydration around cations. At the end of interlayer surface dehydration, all the water molecules are adsorbed by the exchangeable cations [Fig. 2(c)].

On the other hand, based on the water sorption model by Khorshidi and Lu (2016) for nonexpansive soils, the arrangement of water molecules in a monolayer is shown in Fig. 3(a). In this state, the hydrated exchangeable cations are adsorbed on particle surfaces and the vacant spaces between them are filled with the water molecules that hydrate the particle surfaces. The water

content corresponding to this state is w_m . During a dehydration process, water molecules are first removed from the particle surfaces, leading to water coverage only around exchangeable cations [Fig. 3(b)]. For more details about the order of water dehydration

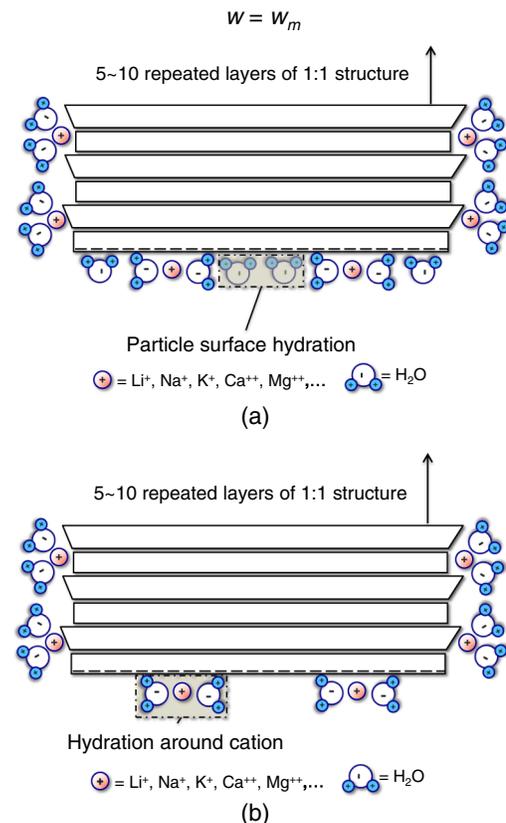


Fig. 3. Conceptual arrangements of water layers hydrating on exchangeable cations or particle surfaces for a typical nonexpansive soil along desorption path: (a) monolayer cation and particle surface coverage; (b) monolayer cation coverage (data from Khorshidi and Lu 2016)

and water molecules arrangements, the reader is referred to Khorshidi and Lu (2016).

The parameter w_i in Eq. (2) is the gravimetric water content where all the cations and interlayer/particle surfaces are covered with one layer of water molecules. Therefore, it is equal to the w_m for nonexpansive soils [as shown in Fig. 3(a)] and the w_{2m} for expansive soils [as shown in Fig. 2(a)]. For expansive soils, SSA can also be calculated by

$$SSA = \frac{w_m NA}{\omega_w} \times 2 \quad (4)$$

where w_m is the monolayer water content as indicated in Fig. 2(b).

The SSA can be found based on the SWRC methodology by using Eqs. (2) and (4). To do so, the w_m and w_{2m} should be determined in these equations. For expansive soils, the w_m and w_{2m} are determined by the specific moisture capacity (SMC) method. As described subsequently, the SMC method relies on the hysteric behavior of the SMC during adsorption and desorption paths. For nonexpansive soils, w_m is identified by the BET plot considering the impact of cation hydration on the SWRC. The details of the SMC and BET plot methods are described in the following.

Determination of Monolayer/Bilayer Water Content Based on the SMC Method

SMC [$C(w)$] is the amount of change in water content per unit change in total potential as expressed by (e.g., Lu and Likos 2004)

$$C(w) = \left| \frac{\partial w}{\partial \psi} \right| = \left| \frac{\partial w}{\partial RH} \frac{\partial RH}{\partial \psi} \right| \quad (5)$$

where RH = relative humidity and ψ = total potential (that is equal to the negative of total suction). According to the Khorshidi and Lu (2016) water sorption model, during water coverage on exchangeable cations, the value of the SMC on the desorption path (C_{des}) is greater than the SMC value on the adsorption path (C_{ads}) at any given RH . On the other hand, during water adsorption and desorption on the interlayer/particle surfaces, the SMC of the adsorption path is almost equal to that of the desorption path. With regard to the aforementioned two rules, one can find the exact hydration mechanisms during adsorption and desorption of water on soil, resulting in the identification of the monolayer/bilayer water content on cations and interlayer surfaces.

The w_m and w_{2m} can be determined from the SMC– RH curve (SMC curve hereafter). Fig. 4 illustrates variations of the SMC during adsorption and desorption paths for a typical expansive soil with monovalent exchangeable cations. Starting from a low range of relative humidity, the SMC on the desorption path is greater than the corresponding SMC on the adsorption path; thus, the hydration mechanism is on the exchangeable cations. The interlayer space is opened up to the thickness of one water layer molecule; subsequently, the water molecules hydrate the interlayer surfaces (SMC of adsorption path is almost equal to that of desorption path). As relative humidity increases, the SMC on desorption path again becomes greater than the corresponding SMC on the adsorption path, implying the dominance of the second water layer hydration on the exchangeable cations. Therefore, the relative humidity at the completion of the monolayer cation hydration, RH_{mc} , and the relative humidity at the completion of the monolayer hydration around cations and interlayer surfaces, RH_m , can be determined as shown in Fig. 4. Similarly, the relative humidity at the completion of bilayer hydration on cations and interlayer surfaces (RH_{2m}) can be found as indicated in Fig. 4. Using the measured water sorption

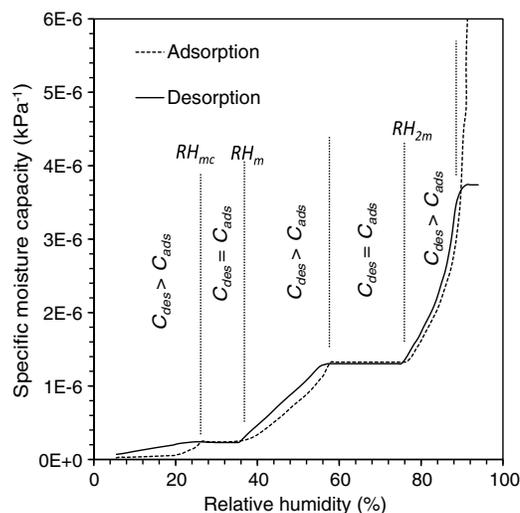


Fig. 4. Conceptual illustration of the variations of the SMC along adsorption and desorption paths employed for the determination of the RH_m (or w_m) and RH_{2m} (or w_{2m})

isotherm of the soils shown in Fig. 1, the water contents corresponding to RH_m (w_m) as well as the water contents corresponding to RH_{2m} (w_{2m}) are obtained.

The order of hydration mechanisms obtained based on the SMC variation in Fig. 4 represents the behavior of an expansive soil with dominant monovalent exchangeable cations. If the dominant exchangeable cations in the soil are divalent (such as Ca^{++}) or trivalent, the cations can usually adsorb the monolayer water (primary shell) followed by the second layer water (secondary shell) on themselves before the hydration of water on the interlayer surfaces is started (e.g., Khorshidi and Lu 2016). To quantify these variations in the order of hydration mechanisms during water adsorption/desorption by soils, the slope of the SMC curve is used. Moreover, for the cases of water hydration on exchangeable cations at the high relative humidity range where the difference between the SMCs on adsorption and desorption paths is not obvious, the slope of the SMC curve is applied to identify the hydration mechanism. There are two features for the slope of the curve that are useful to determine the hydration mechanism for the two aforementioned cases: (1) when one new layer of water gradually forms around cations, the SMC gradually increases with a shallow slope; and (2) as the number of water layers around cations increases, the slope of the SMC curve increases. For more details about these two features, the reader is referred to Khorshidi and Lu (2016).

Expansibility Coefficient

The SMC method is used for soils where the difference between the SMCs on the drying path and the wetting path is distinct and obvious. For other soils, the BET plot is used. To implement this criterion quantitatively, an expansibility coefficient is proposed. The EC is defined here as the area between the SMC curves during adsorption and desorption for monolayer cation hydration water divided by the mean SMC curve (average of adsorption and desorption SMC curve). It is defined as

$$EC = \frac{\int_0^{RH_{mc}} C_{des}(w) dRH - \int_0^{RH_{mc}} C_{ads}(w) dRH}{\int_0^{RH_{mc}} C_m(w) dRH} \quad (6)$$

where C_m = average of adsorption and desorption SMC values. The lower bounds of the integrals in Eq. (6) are zero. Due to the VSA

Table 2. SSA Values Calculated from Different Methods for a Wide Range of Soils from Nonexpansive to Expansive

Soil	EC	Soil type	SSA (m ² /g)						
			Existing methods			SWRC-based methodology			
			EGME	BET	Newman (1983)	SMC method		BET plot	
						Monolayer	Bilayer		
Li ⁺ -bentonite	0.21	Expansive	543	200	384	—	546	532	—
Na ⁺ -bentonite	0.93	Expansive	443	245	321	—	567	557	—
K ⁺ -bentonite	0.59	Expansive	305	161	203	—	522	—	—
Mg ⁺⁺ -bentonite	0.34	Expansive	417	268	419	—	578	533	—
Ca ⁺⁺ -bentonite	0.27	Expansive	518	436	446	—	—	543	—
Denver bentonite	0.50	Expansive	668	397	594	—	—	660	—
Denver claystone	0.30	Expansive	145	83	85	—	191	153	—
Bonny silt	0.33	Expansive	104	58	95	—	115	112	—
Iowa silt	0.18	Expansive	110	64	60	—	141	104	—
0% GaK - 100% NaS	1.03	Expansive	505	251	318	—	621	598	—
20% GaK - 80% NaS	1.07	Expansive	410	185	256	—	494	474	—
30% GaK - 70% NaS	1.04	Expansive	363	148	227	—	443	414	—
40% GaK - 60% NaS	1.00	Expansive	315	135	206	—	389	368	—
60% GaK - 40% NaS	0.94	Expansive	221	97	148	—	281	273	—
80% GaK - 20% NaS	0.74	Expansive	126	64	85	—	144	125	—
100% GaK - 0% NaS	0.12	Nonexpansive	31	22	20	—	—	—	28
BALT silt I	0.09	Nonexpansive	91	57	54	—	—	—	84
BALT silt II	0.11	Nonexpansive	96	51	49	—	—	—	76
Hopi silt I	0.10	Nonexpansive	94	66	62	—	—	—	92
Hopi silt II	0.03	Nonexpansive	81	66	61	—	—	—	85
Heifangtai silt	0.07	Nonexpansive	22	21	21	—	—	—	29

limitation in the measurement of lowest relative humidity, however, the lower bound of 5% (the lowest RH value measured in soil water sorption isotherms in this study) is used instead of zero in the integrals in Eq. (6). The RH_{mc} values are obtained based on the SMC method (as already explained) or the BET plot method as described in the next section. The reader is referred to Khorshidi and Lu (2016) for more details about the determination of RH_{mc} values. If the difference between the SMC values on desorption and adsorption paths during cation hydration becomes close to zero, as is the case for nonexpansive soils, the EC also gets closer to zero. As the percentage of expansive clay in a soil increases, the difference becomes greater, leading to a higher EC value.

To calculate the SSA of soils according to the SWRC-based methodology, corresponding EC values should first be obtained. The calculated EC values are also listed in Table 2. The EC value of Georgia kaolinite, $EC = 0.12$, (dominant in 1:1 kaolinite mineral-one tetrahedral and one octahedral sheets in each unit cell) is defined here as the boundary between the nonexpansive and expansive soils. The kaolinite layers are held in place by hydrogen bonds and van der Waals forces, which are very strong. For this reason, kaolin does not swell. Therefore, for determination of SSA for soils with the EC values greater than 0.12, the SMC method is used; otherwise, the BET plot method is applied as described in the following section.

Determination of Monolayer Water Content Based on the BET Plot

The monolayer water content on cations and particle surfaces for nonexpansive soils can be identified by the BET plot method. The basic assumption in the BET method is that the soil surface is homogenous. Thus, plotting the experimental values of $RH/(1 - RH)_w$ versus the RH of soils (BET curve hereafter) yields a straight line. Khorshidi and Lu (2016) showed that this assumption is not valid because of the presence of exchangeable cations on

interlayer surfaces or particle surfaces. Fig. 5 demonstrates a conceptual BET curve for a typical fine-grained soil. As illustrated in the figure, the difference between the heat of adsorption of the cations and surfaces leads to the nonlinearity of the BET curve in the range of small RH values. The nonlinear segment is then followed by the linear segment corresponding to the particle/interlayer surface hydration of soil. After the completion of monolayer water coverage on the particle/interlayer surface, the dominant hydration mechanism is again due to the cations, resulting in deviation from the linear segment. Thus, surface hydration is confined by the second layer coverage around the exchangeable cations.

The w_m for nonexpansive soils is determined by drawing a line passing through the linear part of the BET curve. The range of

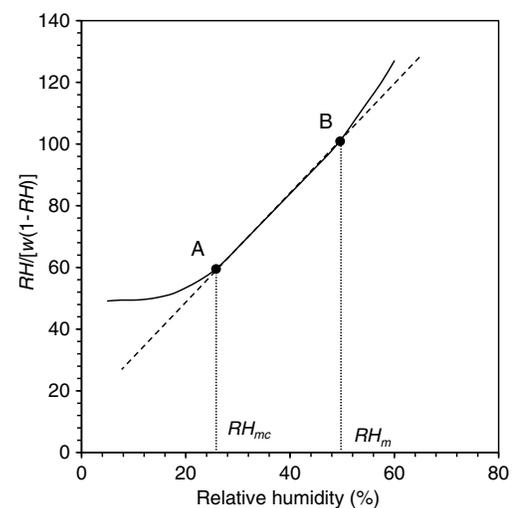


Fig. 5. Conceptual illustration of the BET plot of fine-grained soil for the determination of the RH_m (or w_m)

Table 3. Dominant Hydration Mechanisms in Different Ranges of Relative Humidity for Various Mixtures of Georgia Kaolinite and Wyoming Montmorillonite Obtained from SMC Method

Soil	Relative humidity (%)					
	$C_{des} > C_{ads}$	$C_{des} = C_{ads}$	$C_{des} > C_{ads}$	$C_{des} < C_{ads}$	$C_{des} = C_{ads}$	$C_{des} < C_{ads}$
0% GaK–100% NaS	5–28	28–46	46–59	59–78	78–90	90–95
20% GaK–80% NaS	5–27	27–45	45–59	59–77	77–89	89–95
30% GaK–70% NaS	5–28	28–45	45–61	61–76	76–89	89–95
40% GaK–60% NaS	5–27	27–45	45–61	61–75	75–91	91–95
60% GaK–40% NaS	5–27	27–45	45–58	58–77	77–90	90–95
80% GaK–20% NaS	5–28	28–40	40–57	57–74	74–89	89–95
Dominant hydration mechanism	Around cations	On interlayer surfaces	Around cations	On interlayer surfaces	Around cations	—

relative humidity pertinent to the interlayer/particle surface hydration is specified by the line segment AB in Fig. 5. Based on the preceding discussion, the relative humidities associated with point A and point B are the RH_{mc} and RH_m values, respectively. The w_m corresponding to RH_m can be found from the measured water sorption isotherms of the soil shown in Fig. 1.

Assessments of the SWRC-Based Methodology

The results of the SSA measurements for the soils based on various methods are presented here. These results include both water-based and EGME-based SSA measurements. Regarding water-based SSA measurements, three different methods are used: BET method, Newman method, and SWRC-based methodology. The SSA measurements based on the BET and Newman methods [Eqs. (2) and (3)] are listed in Table 2.

The dominant hydration mechanism in different ranges of relative humidity for various GaK–NaS mixtures is listed in Table 3. These ranges were obtained by applying the SMC method. Furthermore, the SMC variations of various monovalent cation-exchanged bentonites of Li^+ , Na^+ , and K^+ are illustrated in Figs. 6(a–c), respectively. According to the difference in the SMCs on the adsorption and desorption paths, the RH_m is obtained at the boundary of the range of relative humidity of both the monolayer interlayer surface hydration and bilayer cation hydration. Moreover, the RH_{2m} for Li^+ -saturated bentonite is determined at the completion of the second water layer on the interlayer surfaces before the SMC on desorption path becomes greater than the corresponding SMC on adsorption path. This variable since Na^+ -saturated bentonite is identified based on the slope change of the SMC drying curve at the point where the SMC starts to become greater than the maximum SMC value of the second hydration layer. Note that the second layer coverage is not yet completed up to 95% RH for K^+ -saturated bentonite [Fig. 6(c)].

The SMC curves for bentonites with divalent-exchanged cations are depicted in Fig. 7. The RH_m and RH_{2m} for Mg^{++} -saturated bentonite are determined with the same procedure as explained for Li^+ -saturated bentonite [Fig. 7(a)]. However, for Ca^{++} -saturated bentonite, due to the formation of a complete bilayer coverage around cations before starting the interlayer surface hydration, the determination of RH_m is not possible. This order of hydration mechanism is inferred from Fig. 7(b). In the range of relative humidity below 21%, the SMC on the desorption path is greater than the SMC on the adsorption path, indicating that the cation hydration occurs. Meanwhile, a change in the slope of the SMC curve at about 10% RH shows the start of the secondary shell coverage around cations completed at 21% RH. Above 21% RH, the opened space for adsorption of two layers of water is filled with the water molecules that hydrate the interlayer surfaces.

Therefore, the RH_{2m} is obtained at 73% RH, where the SMC of the desorption path again becomes greater than the corresponding value on the adsorption path.

The BET plot method is applied to the soils with EC values less than 0.12. The RH_m values for the soils are obtained by passing a line through the linear segment of their BET curves, as explained before. After the determination of the RH_m and RH_{2m} for each soil based on the SMC or BET plot method, the w_m (corresponding to the RH_m) and the w_{2m} (corresponding to the RH_{2m}) is found from the soil's water sorption isotherm shown in Fig. 1.

Using Eq. (2) for nonexpansive soils as well as Eqs. (2) and (4) for expansive soils corresponding to bilayer and monolayer hydration, respectively, the SSA values of soils are calculated and listed in Table 2. The SSA results obtained from the SMC method independently based on the monolayer and bilayer hydration water contents are very close to each other, implying that our hypothesis for the arrangements of water molecules in Fig. 2(a) is valid. It follows that the second layer volume is almost equal to that of the first layer. However, the SSA calculated based using the bilayer hydration water content is more accurate and preferred for any natural soils containing monovalent and divalent cations.

Comparing the results of the BET method, Newman method, and the SWRC-based method with the EGME-based SSA results shown in Table 2 reveals that the results of the SWRC-based methodology are more compatible and closer to the EGME results. The agreement between the SSA values calculated based on the BET, Newman, and SWRC approach compared to the EGME method for nonexpansive soils as estimated by the RSME are 27 m²/g, 29 m²/g, and 9 m²/g, respectively. Similarly, these values for expansive soils are 183 m²/g, 104 m²/g, and 80 m²/g, respectively. Fig. 8 also shows the comparison between SSA values obtained from the SWRC-based methodology (using bilayer hydration for expansive soils) and the ones obtained from the EGME measurements for all test soils. Good correlations are found between these results with the coefficient of determination $R^2 = 0.94$.

Discussion

The comparison between the results of SSA measurements based on various methods is discussed. As shown in Table 2, there is a difference between the SMC-based SSA values and the ones obtained from the EGME method for expansive soils. The SSA values calculated by the SMC method are greater than those obtained by the EGME method. Since EGME molecules are large (compared to water molecules), they might clog the path for the other molecules to be adsorbed on cations or interlayer surfaces.

Considering the difference between the SSA values of the SMC and EGME method for all five cation-exchanged bentonites reveals that, generally, the difference increases as the hydration energy of

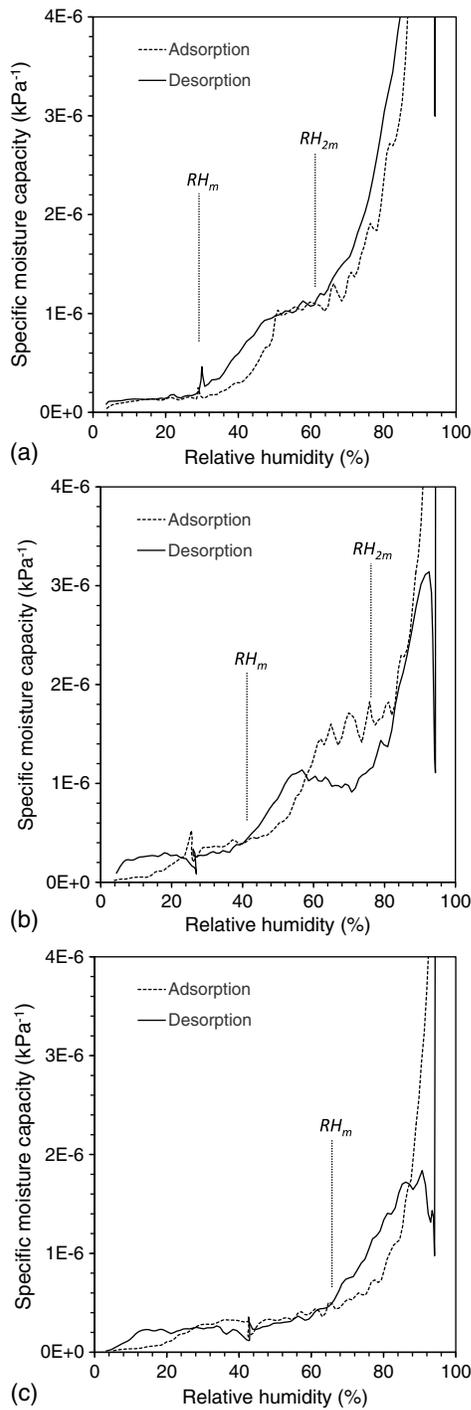


Fig. 6. Determination of the RH_m (or w_m) or RH_{2m} (or w_{2m}) by the SMC method for monovalent cation-exchanged bentonites: (a) Li^+ -saturated bentonite; (b) Na^+ -saturated bentonite; (c) K^+ -saturated bentonite

the cation decreases. Hence, this implies that the adsorption of EGME molecules on soil is highly affected by the type of cations in soil through their capabilities to draw the large polar EGME molecules through the interlayer space under the strong attractive forces such as electrostatic and hydrogen bonds. Therefore, they cannot represent the real SSA of the soil. The SSA of a soil is an intrinsic value (i.e., it should not vary when the type of cation in the soil changes). This is because the SSA is dependent on the dimensions of the soil sheets and particles that do not vary by the type

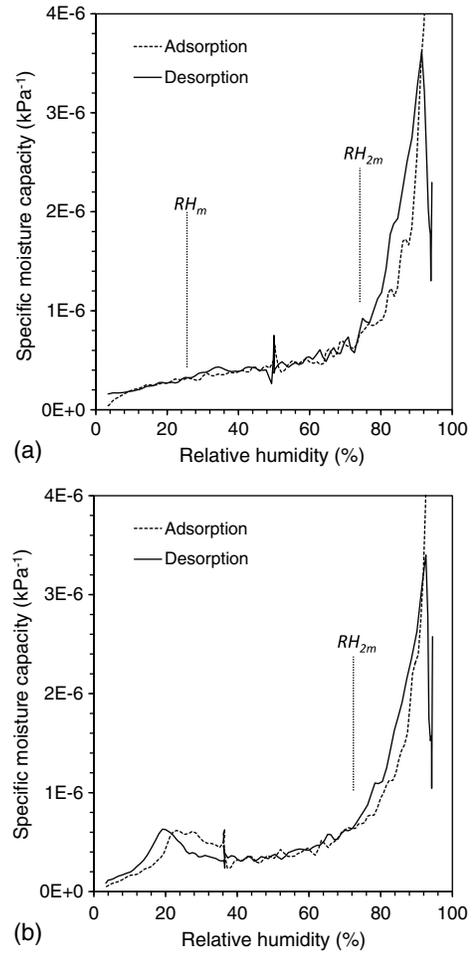


Fig. 7. Determination of the RH_m (or w_m) or RH_{2m} (or w_{2m}) by the SMC method for divalent cation-exchanged bentonites: (a) Mg^{++} -saturated bentonite; (b) Ca^{++} -saturated bentonite

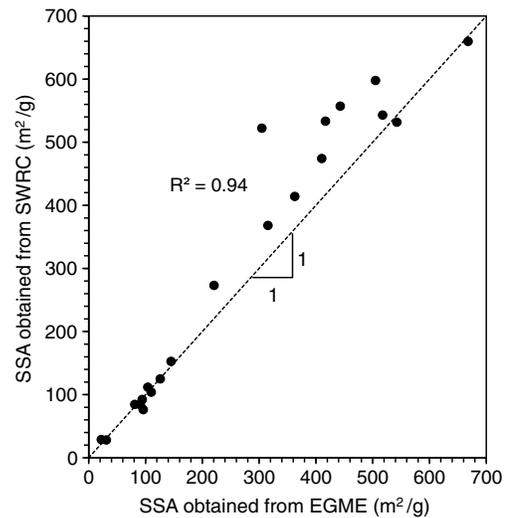


Fig. 8. Comparison between the SSA values obtained based on the SWRC methodology and the SSA values obtained from EGME measurements

of the exchangeable cations on the surface. The fact that there is a small discrepancy (less than 10%) between the SMC-based SSA values for various cation-exchanged bentonites (Table 2) confirms this assumption. Thus, the SMC-based SSA results seem to be more reliable and representative of the SSA of the soil in comparison to EGME-based results.

For nonexpansive soils (i.e., soils with $EC < 0.12$), the SSA measurements based on the BET plot are comparable with the ones obtained from the EGME method listed in Table 2. In most of the soils, the EGME results are greater than the BET plot results. In general, the difference between the EGME result and the BET plot result is proportional to the EC value of the soil. Thus, the small difference between the EGME and BET plot results could be due to the presence of a small amount of expansive clay in the natural soil. When applying the BET plot method for SSA determination [using Eq. (2)], if the portion of expansive clay in the natural soil is known, then the SSA value corresponding to the expansive clay should double [using Eq. (4) instead of Eq. (2)], leading to an increase in the SSA of the natural soil.

The SWRC methodology has several advantages over the EGME method. The procedure to measure soil water sorption isotherm is much simpler than EGME measurements; it requires less specimen handling, so the probable discrepancies due to the user effect is less; and most notably, the probe molecule is water, which is representative for soil–water interactions in nature. As indicated earlier in this section, there can be differences between EGME-based and water-vapor-based SSA measurements for expansive soils.

Summary and Conclusion

In order to calculate the specific surface area accessible to water and better represent the field conditions, a soil water retention curve-based methodology suitable for quantifying the SSA of both expansive and nonexpansive soils is developed. Here the hysteric behavior of the specific moisture capacity along adsorption and desorption paths (SMC method) is used for the SSA determination of expansive soils. For nonexpansive soils, the Brunauer-Emmett-Teller plot method is employed. The expansibility coefficient parameter indicative of the soil susceptibility to swelling is introduced for the classification of a soil as an expansive or nonexpansive one. The EC value of kaolinite is used as a benchmark to distinguish between expansive and nonexpansive soils. The SSA values obtained by the SWRC-based methodology are much closer to the EGME-based values than those of the BET-based method and Newman method.

There exist some discrepancies between the EGME-based SSA values and the SWRC-based SSA values. The BET plot SSA values are generally smaller than the EGME values. The reason is that in the calculation of SSA based on the BET plot, the effect of any expansive minerals in soil is not considered. On the other hand, the SSA results quantified by the SMC method for the bentonite soils are generally similar yet slightly greater than the EGME results. The adsorption of polar EGME molecules on expansive soils is highly affected by the type of interlayer exchangeable cations; therefore, completely different EGME-based SSA values are obtained for various cation-exchanged bentonites. In contrast, the SSA values calculated from the SMC method for these soils are close to each other, representing probably the real dimensions of the soil interlayers and particles that are independent of the type of interlayer exchangeable cations. Therefore, it can be concluded that for expansive soils, the SMC method is more realistic than the EGME method for determination of the SSA of soils.

Although the SSA depends on the chemical and physical properties of the probe molecule used to cover the surface, the SWRC-based methodology can realistically represent the SSA values for the surface accessible to water. Therefore, the intrinsic relation between the SSA and SWRC revealed here would provide a better linkage between SSA and other soil properties and geotechnical indexes such as cation exchange capacity, Atterberg limits, and hydrologic properties.

Acknowledgments

This research is funded by a collaborative grant from the National Science Foundation to NL (NSF CMMI 1233063) and WJL (NSF CMMI 1304119).

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