Determination of Cation Exchange Capacity from Soil Water Retention Curve

Morteza Khorshidi, Aff.M.ASCE¹; and Ning Lu, F.ASCE²

Abstract: Cation exchange capacity (CEC) has a significant influence on the physical and chemical behavior of soil. Quantification of the CEC is an essential yet challenging task. A new methodology for the determination of the CECs of soils by using the soil water retention curve (SWRC) in the extremely high suction range is presented. The methodology is based on a theoretical SWRC model that explicitly considers the contribution of the cation hydration on the matric potential. For a homoionic soil, the CEC governs the relationship among the type of exchangeable cations, matric potential, and the corresponding equilibrated soil water. Thus, the CECs of homoionic soils can be deduced from their SWRCs. For a natural soil with a multiple cation species, the CEC of bulk soil can be determined from the SWRC of the Na⁺-exchanged form of the soil. A suite of materials ranging from nonexpansive to expansive soils is used to demonstrate the validity of the proposed methodology. The CECs of these soils are also measured independently by using the ammonium acetate method for comparison purposes. The close match between the independently measured and the SWRC-based CEC values confirms the validity and illustrates the potential promises of the SWRC-based methodology in determining the CEC of soils. DOI: 10.1061/(ASCE)EM.1943-7889.0001220.

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Introduction

Soils containing clay minerals possess negatively charged particle surfaces that hold exchangeable cations. These cations can be exchanged without a mineral structure change. The amount of exchangeable cations a soil possesses is referred to as the cation exchange capacity (CEC). It is basically the sum of the permanent CEC resulting from the isomorphic substitution within the soil structure and the variable CEC, or pH-dependent CEC, resulting from the deprotonation (e.g., Ellis and Foth 1996; Mitchell and Soga 2005; Sposito 2008). CEC values are typically expressed in units of milliequivalent electric charges per gram.

The CEC of soil reflects the layer charge and particle surface properties. Thus, it has been recognized as a fundamental property that influences soil behavior. For example, the commonly used geotechnical engineering indices such as Atterberg limits as well as specific surface area (SSA) have been closely correlated with the CEC (e.g., Farrar and Coleman 1967; Smith et al. 1985; Churchman and Burke 1991; Petersen et al. 1996; Yukselen and Kaya 2006; Woodruff and Revil 2011). Numerous studies have also shown that the swelling potential of soil may be related to the CEC; the soil’s swelling potential is used for the expansive soil classification (e.g., Rengasamy et al. 1986; Christidis 1998; Thomas et al. 2000; Dontsova and Norton 2002; Yilmaz 2004). In addition, the CEC greatly influences water sorption, fluid flow, electric and chemical flows, and coupled fluid in clayey soils (e.g., Shainberg et al. 1980; Gaston and Selim 1990; Revil and Leroy 2004; Dontsova et al. 2004; Khorshidi and Lu 2016a).

Numerous methods have been proposed for the CEC measurement since the nineteenth century. The frequently used methods include ammonium acetate method at pH = 7.0 (e.g., Schollenberger and Dreisblib 1930), ammonium chloride method (e.g., Shuman and Duncan 1990), sodium acetate method (e.g., Bower et al. 1952), or barium chloride (e.g., Mehlich 1938; Bascomb 1964) at pH = 8.2, and methylene blue absorption (Nevins and Weintritt 1967). The steps in these chemical methods involve the saturation of the soil by index ions that replace exchangeable cations in the soil and the subsequent displacement of the index ions with another salt solution (i.e., the extracting solution). Finally, the amount of the displaced index ions that represents the CEC of the soil is measured by using inductively couple plasma spectrometry or atomic absorption. Ammonium acetate is the most commonly used method, particularly for soil-classification applications (e.g., Sumner and Miller 1996; Ross and Ketterings 2011). The index ion and extracting solution in this method are ammonium (NH₄⁺) and KCl, respectively.

The CEC of soil may change depending on the type of saturation and extracting solutions used in the CEC measurement. This change can only occur through the variable CEC, because it depends on the soil pH, which might change when the saturating or extracting solution is added to the natural soil. The less the change in the soil pH after treatment with a saturation or extracting solution is, the lower the error in the CEC measurement (Sumner and Miller 1996; Laird and Fleming 2008). Therefore, each of the chemical methods can be more appropriate for a particular soil situation. For example, the ammonium acetate method works well for basic soils, while it overestimates the CEC of acidic soils (Sumner and Miller 1996).

The methods described previously are cumbersome time-consuming approaches that are subject to errors associated with salt or sample loss during the decantation steps (e.g., Jaynes and Bioham 1986; Sumner and Miller 1996). To overcome these problems, this present study investigates the potential application of the
soil water retention curve (SWRC) in the determination of the CEC. The SWRC is an important constitutive function of the soil that can be used in the prediction of numerous soil properties and processes in the soil such as water flow, solute and contaminant transport, coupled heat and mass transfer, stress and deformation, specific surface area, and swell potential (e.g., Beven and Germann 1982; Padilla et al. 1999; Hansson et al. 2004; Lu and Likos 2004; Lu et al. 2010, 2014; Leao and Tuller 2014; Akin and Likos 2014; Moradi et al. 2015; Khorshidi and Lu 2016b).

Following the SWRC approach to obtain soil properties, a new SWRC-based methodology for determining the CEC of soil is proposed. This methodology is based on the relationship between the cation hydration and matric potential of soil at the very dry end of the SWRC. More specifically, the CEC of the soil can be estimated given the SWRC at high suction values (soil water sorption isotherm) of any bulk soil saturated with Na⁺ cations. Furthermore, independently measured CEC values by the ammonium acetate method are also used to verify the proposed method for the CEC determination.

**Methodology**

**Relationship between Matric Potential and Cation Hydration**

The SWRC is the relationship between the total potential and corresponding equilibrated soil water (e.g., Brooks and Corey 1964; van Genuchten 1980; Lu and Likos 2004; Khorshidi 2015). The total potential consists of three forms of potential: matric, gravitational, and osmotic. Due to the negligible effects of gravitational and osmotic potentials compared to matric potential for problems concerning total potentials less than −100 MPa, matric potential can be effectively considered as total potential (Khorshidi et al. 2016d).

There exist three water retention regimes. Starting from high matric potentials to low matric potentials, they are capillary water, adsorbed water, and tightly adsorbed water (McQueen and Miller 1974; Lu and Likos 2004). The pertinent range to these regimes depend on type of soil; but in general, matric potential ranges between 0 to −400 kPa, −400 kPa to −10 MPa, and −10 to −1,200 MPa were proposed for these regimes, respectively (e.g., Tuller et al. 1999; Frydman and Baker 2009; Lu and Khorshidi 2015).

Since the water sorption is controlled solely by cation and surface interactions in tightly adsorbed water regime, two main fundamental soil properties determine the amount of equilibrated soil water at low matric potentials: CEC and SSA (e.g., Tuller et al. 1999; Dontsova et al. 2004; Srodon et al. 2008; Khorshidi and Lu 2016a; Khorshidi et al. 2016c). The former property is important at very low water contents, where cation hydration is the governing mechanism to retain water in the soil (e.g., Berend et al. 1995; Cases et al. 1997; Prost et al. 1998; Laird 1999; Xu et al. 2000; Sposito 2008; Woodruff and Revil 2011; Khorshidi et al. 2016d). Water molecules at these water contents are located in the first hydration shell of the exchangeable cations, as illustrated in Fig. 1. The exchangeable cation in the homoionic soils shown in Fig. 1 is the Na⁺ with a hydration shell distance of 0.24 nm. The cation hydration is followed by surface hydration until the monolayer surface coverage on soil particles becomes complete. The boundary between these two mechanisms depend on the type of exchangeable cations in soils and it can occur at relative humidity values between 5 and 30% (Khorshidi and Lu 2016a).

The contribution of the cation hydration on the matric potential has been recently identified by Khorshidi et al. (2016d) by considering all different types of works (such as pressure work, temperature work, surface tension work, and surface hydration work) acting on water molecules during sorption of water on soil. Using Gibbs free energy in the range of very low water contents, the matric potential Ψ (Pa) in homoionic soils due to all water sorption mechanisms, particularly the exchangeable cation-water molecule (charge-dipole) interaction, has been captured by (Khorshidi et al. 2016d)

\[
\psi = -3 \times 10^{-10} \frac{V_c \kappa_1 r_1}{\kappa_1 r_1}
\]

(1)

where \(V_c\) = cation type \(i\) valence; \(r_1\) (m) = distance between the cation and water molecules in its first hydration shell (as shown in Fig. 1); and \(\kappa_1\) = parameter used to include the works due to the electric force and cation-water interaction in the matric potential expression. Due to the hydration hysteresis, Eq. (1) was developed for the drying path since this path is more representative to infer surface and exchangeable cation-related properties of soils (e.g., Lu and Khorshidi 2015). The value of \(\kappa_1\) is directly related to the number of water molecules around each cation \(N_i\) in the soil, regardless of the type of the exchangeable cation \(i\). The relationship between \(\kappa_1\) and \(N_i\) can be obtained by back-calculation of \(\kappa_1\) values by fitting Eq. (1) to the measured water sorption isotherms of

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**Fig. 1.** Arrangement of water molecules around exchangeable cations at very low water contents in: (a) typical nonexpansive soil; (b) typical expansive soil (adapted from Khorshidi et al. 2016d)
cation-exchanged bentonites. Resultantly, Fig. 2 demonstrates the relationship between $\kappa_i$ and $N_i$, which can be approximated as (Khorshidi et al. 2016d)

$$\kappa_i = 4.0N_i + 9.3$$  

(2)

Substituting Eq. (2) into Eq. (1) yields

$$\psi = -3 \times 10^{-10} \frac{V_{c_i}}{(4N_i + 9.3)r_i^2}$$  

(3)

Assuming the cation hydration as the only mechanism for holding water, $N_i$ for homoionic soils can be obtained by dividing the number of water molecules by the number of exchangeable cations. Regardless of the location of exchangeable cations in a diffuse double layer (either in inner sphere, outer sphere, or in diffuse double layer), all ions in water are hydrated as the water dipole is attracted to the charged ion and forms a structure with it (Appelo and Postma 2005). Accordingly, $N_i$ is yielded from (Khorshidi et al. 2016d)

$$N_i = \frac{w_c}{w_{w,\text{CEC}}}$$  

(4)

where $w_c$ = molar mass of water; and $w = \text{gravimetric water content}$ of the soil. Substituting Eq. (4) into Eq. (3) yields the SWRC model at very low water contents

$$\psi = -\frac{3 \times 10^{-10}V_{c_i}\text{CEC}}{r_i^2(4V_{c_i}w + 9.3\text{CEC})}$$  

(5)

Eq. (5) is valid for water contents up to the monolayer cation hydration water content at which all exchangeable cations in the soil are covered with monolayer water. At this water content, $N_i$ is equal to the cation hydration number (Khorshidi and Lu 2016a). The SWRC model of Eq. (5) can be used to determine the CEC of natural soils with a multiple cation species.

**Determination of the CEC from Soil Water Sorption Isotherm**

The SWRC model in Eq. (5) was established for homoionic soils. In these soils, $V_{c_i}$ and $r_i$ can be replaced by their associated values, yielding the SWRC model as a function of the CEC. In order to use Eq. (5) for natural soils containing multiple cation species, the bulk natural soils should first be treated with saturating solutions to produce the homoionic soils. More specifically, NaCl can be used as the saturating solution to replace all exchangeable cations in the soil with Na\(^+\). This solution is sometimes used as the saturating solution for the quantification of the CEC (Pearcy et al. 2012). The basic assumption in the SWRC-based CEC measurement is that the CEC of the bulk soil is equal to the CEC of Na\(^+\)-exchanged soil.

The reason for the use of NaCl as the saturating solution, instead of other solutions (e.g., KCl and MgCl\(_2\)), can be explained by employing Fig. 2. Based on this figure, the obtained experimental $\kappa_i$ values for the Na\(^+\) cation (in Na\(^+\)-bentonite) are found to fit much better than the other cations to the average line indicated by Eq. (2) [Eq. (2) was ultimately used in Eq. (5)]. The good fitting also covers a wider range of $N_i$ values for the Na\(^+\) cation, as compared with the other cations. Thus, using Na\(^+\) as the saturating cation by employing NaCl, instead of the other solutions, reduces the errors introduced by Eq. (5) for the determination of the CEC. In addition, NaCl has a negligible effect on the soil pH (Pearcy et al. 2012). Therefore, there would be a negligible difference between the variable CEC of the bulk soil and that of the Na\(^+\)-exchanged form of the soil.

The SWRC model for the Na\(^+\)-exchanged soils can be obtained by using Eq. (5). The $V_{c_i}$ and $r_i$ values for Na\(^+\) are 1 and 0.24 nm (Chang et al. 1998; Mähler and Persson 2012), respectively; therefore, Eq. (5) reduces to

$$\psi = -\frac{5.40 \times 10^9\text{CEC}}{0.23w + 9.66\text{CEC}}$$  

(6)

In this equation, the CEC can be used as the fitting parameter that will be determined. The SWRC model of Eq. (6) should be fitted to the measured isotherm in the range of $-350,000$ kPa < $\psi$ < $-300,000$ kPa by using a least-squares regression to determine the best fit value of the CEC. A fitting in this range of matric potentials, which corresponds to $1 < N_i < 2$, provides the lowest error in the CEC estimation. This is because the predicted $\kappa_i$ values obtained by Eq. (2) match the experimental $\kappa_i$ values for the Na\(^+\) cation very well, as depicted in Fig. 2.

Overall, the CEC of each soil can be deduced by using Eq. (6) and the SWRC of the Na\(^+\)-exchanged form of the soil in the range of $-350,000$ kPa < $\psi$ < $-300,000$ kPa [$\approx 7\% < \text{relative humidity(RH)} < 11\%$]. The experimental program to validate the proposed SWRC-based methodology is addressed in the next section.

**Experimental Program**

A suite of natural silty and clayey materials ranging from expansive to nonexpansive soils was used to demonstrate the validity of the SWRC-based methodology for the CEC determination. All but one soil sample was collected from different places in the United States; the last sample was collected in China. The engineering properties of the soils are summarized in Table 1. The soil samples were treated to produce Na\(^+\)-exchanged soils for the purpose of measuring their water sorption isotherms. Na\(^+\)-exchanged soils were prepared by saturating a bulk soil with 1 M NaCl for 24 h. The particles of the soil samples were separated from the salt solution in a high-speed centrifuge, and the soils were suspended again in fresh NaCl two more times. The samples were then repeatedly rinsed with deionized water to remove the chlorides detected in the supernatant. In the absence of chloride in the supernatant, the supernatant tested negative with AgNO\(_3\) (no salt forms; Moore and Reynolds 1997).
One of the common issues that occurs during rinsing Na\(^{+}\)-saturated clays (e.g., montmorillonite) with water is colloidal dispersion, which makes soil settlement by centrifuge almost impossible. In the case of a colloidal dispersion, a 50\% ethanol-deionized water mixture, instead of deionized water, was used to rinse the soils with chlorides (Moore and Reynolds 1997).

The CECs of the tested soils were independently measured by using the ammonium acetate method to validate the new methodology. The detailed procedure for the ammonium acetate method is described in ASTM D7503 (ASTM 2010).

The water sorption isotherms of Na\(^{+}\)-exchanged soils were measured by using a vapor sorption analyzer (VSA), an automated device that has recently become widely used for measuring isotherms in the drying (desorption) and wetting (adsorption) cycles (e.g., Arthur et al. 2013; Lu and Khorshidi 2015). VSA works based on the chilled-mirror dewpoint technique, continuously measuring RH (or ψ) and w (e.g., Lu and Khorshidi 2015). Soil samples were oven-dried at 105°C and cooled down to ambient room temperature. Soil water sorption isotherms were then measured at 25 ± 0.2°C with the VSA. The measurement for the drying and wetting cycles typically lasts between 24 and 48 h. However, the time required to measure the isotherms in the range of matric potentials recommended for the determination of the CEC favorably reduces to 1–3 h, depending on the type of the soil.

### Validation of the Proposed SWRC-Based Method for the CEC Determination

To examine the performance of the proposed SWRC-based methodology, the CECs of the tested soils were measured independently using the ammonium acetate method. The CEC values, ranging from 0.08 meq/g to 1.02 meq/g for Denver bentonite, are listed in Table 2 (data from Akin 2014).

The measured water desorption isotherms of three Na\(^{+}\)-exchanged soils (Na\(^{+}\)-Georgia kaolinite, Na\(^{+}\)-Denver claystone, and Na\(^{+}\)-Wyoming montmorillonite) are plotted in Fig. 3. At a given RH, the values of equilibrated soil water content for these three soils differ significantly. These differences depend on the mineral type, CEC, and SSA of the soils. At approximately 94% RH, kaolinite was found to adsorb only 4.5% gravimetric water content, claystone (illite/smectite mixture) can adsorb 8.2% gravimetric water content, and montmorillonite can adsorb as much as 30.5% gravimetric water content. In addition, noticeable wavy or stepwise behavior is observed in montmorillonite, but is less prominent in claystone. This behavior is associated with two different hydration mechanisms (cation hydration and particle surface hydration) pronounced in the soils with a crystalline structure (Lu and Khorshidi 2015; Khorshidi and Lu 2016a).

The direct relationship between the CEC and the amount of equilibrated soil water content at low RH values can be deduced from Fig. 3. To illustrate this, the gravimetric water content values of Na\(^{+}\)-Georgia kaolinite, Na\(^{+}\)-Denver claystone, and Na\(^{+}\)-Wyoming montmorillonite at 10% RH were obtained. The corresponding water contents were 0.33, 1.12, and 2.57%, respectively. The CECs of these soils measured by the ammonium acetate method were 0.09, 0.32, and 0.71 meq/g (Table 2), respectively. The ratio of the CEC values of the soils compared with each other are almost the same as the ratios of their corresponding water contents. This implies that the CEC of the soil is the governing factor for the amount of water in the soil at low RH values, and can be correlated to the soil water sorption isotherm. On the other hand, the SSA of the soil is the governing factor at higher RH values. The methodology to calculate SSA by using isotherm at higher RH values is described in Khorshidi et al. (2016c).

The water desorption isotherms of Na\(^{+}\)-exchanged soils are used for the determination of their CECs. More specifically, Eq. (6) was fitted to the isotherms of Na\(^{+}\)-exchanged soils in the range of 7% < RH < 11%. Consequently, the CECs of the soils were calculated as the fitting parameter in this equation. Overall, the model fits the experimental data well, as shown in Fig. 4 for the three soils considered in Fig. 3. The SWRC-based CEC values obtained as the fitting parameter are listed in Table 2, along with the values measured by the ammonium acetate method. The difference

### Table 1. Fundamental Engineering Properties of the Tested Soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Mineralogy</th>
<th>Clay (%)</th>
<th>LL (%)</th>
<th>PL (%)</th>
<th>PI (%)</th>
<th>USCS classification</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Georgia kaolinite</td>
<td>K</td>
<td>35</td>
<td>44</td>
<td>26</td>
<td>18</td>
<td>CL</td>
<td>Georgia</td>
</tr>
<tr>
<td>Wyoming montmorillonite</td>
<td>Discrete S, trace quartz</td>
<td>100</td>
<td>485</td>
<td>353</td>
<td>132</td>
<td>CH</td>
<td>Wyoming</td>
</tr>
<tr>
<td>Na(^{+})/Ca(^{2+}) bentonite</td>
<td>Discrete S, trace K, quartz, K-Feld</td>
<td>90</td>
<td>118</td>
<td>45</td>
<td>73</td>
<td>CH</td>
<td>Colorado</td>
</tr>
<tr>
<td>Denver bentonite</td>
<td>Mixed layer I/S, trace K, quartz, gypsum</td>
<td>55</td>
<td>44</td>
<td>23</td>
<td>21</td>
<td>CL</td>
<td>Colorado</td>
</tr>
<tr>
<td>Bonny silt</td>
<td>—</td>
<td>14</td>
<td>25</td>
<td>21</td>
<td>4</td>
<td>ML</td>
<td>Colorado</td>
</tr>
<tr>
<td>BALT silt I</td>
<td>—</td>
<td>14</td>
<td>26</td>
<td>19</td>
<td>7</td>
<td>CL-ML</td>
<td>California</td>
</tr>
<tr>
<td>BALT silt II</td>
<td>—</td>
<td>5</td>
<td>28</td>
<td>23</td>
<td>5</td>
<td>SM</td>
<td>California</td>
</tr>
<tr>
<td>Hopi silt I</td>
<td>—</td>
<td>3</td>
<td>26</td>
<td>19</td>
<td>7</td>
<td>SC-SM</td>
<td>Arizona</td>
</tr>
<tr>
<td>Hopi silt II</td>
<td>—</td>
<td>2</td>
<td>26</td>
<td>19</td>
<td>7</td>
<td>ML</td>
<td>Arizona</td>
</tr>
<tr>
<td>Iowa silt</td>
<td>—</td>
<td>10</td>
<td>33</td>
<td>24</td>
<td>9</td>
<td>ML</td>
<td>Iowa</td>
</tr>
<tr>
<td>Heifangtai silt</td>
<td>—</td>
<td>26</td>
<td>21</td>
<td>5</td>
<td></td>
<td>ML</td>
<td>Gansu, China</td>
</tr>
</tbody>
</table>

Note: I = illite; K = kaolinite; K-Feld = K-Feldspar; LL = liquid limit; PI = plastic index; PL = plastic limit; S = smectite; USCS = unified soil classification system.

### Table 2. Comparison between the Measured CEC Values of Soils Obtained by Ammonium Acetate Method and Those Obtained from the SWRC Model (Data from Akin 2014)

<table>
<thead>
<tr>
<th>Soil</th>
<th>Ammonium acetate-based CEC (meq/g)</th>
<th>SWRC-based CEC (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heifangtai silt</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>Georgia kaolinite</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Hopi silt II</td>
<td>0.18</td>
<td>0.22</td>
</tr>
<tr>
<td>Iowa silt</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>Hopi silt I</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>Bonny silt</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>BALT silt II</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>BALT silt I</td>
<td>0.23</td>
<td>0.20</td>
</tr>
<tr>
<td>Denver claystone</td>
<td>0.32</td>
<td>0.35</td>
</tr>
<tr>
<td>Wyoming montmorillonite</td>
<td>0.71</td>
<td>0.75</td>
</tr>
<tr>
<td>Na(^{+})/Ca(^{2+}) bentonite</td>
<td>0.76</td>
<td>0.74</td>
</tr>
<tr>
<td>Denver bentonite</td>
<td>1.02</td>
<td>1.69</td>
</tr>
</tbody>
</table>

can be concluded that the SWRC can readily be used to determine CEC values.

The high value of the coefficient of determination ($R^2$) in Fig. 5 indicates a very good match between the CEC values deduced from the SWRC model and those measured by the ammonium acetate method. Hence, it can be concluded that the SWRC can readily be used to determine the CEC of soils.

Discussion

The $R^2$ value in Fig. 5, calculated for all soils excluding Denver bentonite, is 0.99; this implies a very good match between the SWRC-based and ammonium acetate-based CEC values of the tested soils. In general, the former values are slightly larger than the latter values. However, the SWRC-based value for Denver bentonite is much larger than the ammonium acetate-based value.

A couple of reasons can be discussed as the possible sources of the large discrepancy for Denver bentonite. First, Denver bentonite is composed of smectite and calcite minerals, containing Ca$^{2+}$ and Mg$^{2+}$ as the main exchangeable cations in the soil (Likos et al. 2011). In soils with calcite and soluble salts, not all the exchange sites will be occupied by the saturating cation when using the ammonium acetate method for the CEC measurement (e.g., Sumner and Miller 1996). This results in the underestimation of the CEC. For these soils, the method of Amrhein and Suarez (1990) is recommended because it takes into account the dissolution of calcite and gypsum during the saturation and extraction steps (Sumner and Miller 1996). In addition, fixation of ions in some clay minerals (e.g., vermiculites and smectite) is a well-known problem that results in the underestimation of CEC (e.g., Bower 1950; Sumner and Miller 1996). The fixation of ions occurs when cations such as NH$_4^+$ and K$^+$ are trapped in the interlayers and are not readily available for cation exchange during the saturation or extracting processes.

Overall, it is anticipated that the CEC measurement with the ammonium acetate method for Denver bentonite is underestimated. On the other hand, it is possible that all exchange sites in Denver bentonite with Ca$^{2+}$ and Mg$^{2+}$ cations were not replaced by the Na$^+$ cation when using NaCl as the saturating solution. Even a small amount of Ca$^{2+}$ and Mg$^{2+}$ remaining in the interlayers of Denver bentonite after saturation can substantially increase the amount of retained water because the hydration enthalpy of Ca$^{2+}$ and Mg$^{2+}$ are much greater than Na$^+$. Hence, the SWRC-based CEC value is possibly overestimated.

Several problems may arise when the chemical methods are used for the CEC measurement (Laird and Fleming 2008). These methods might not work properly when used for clay samples. Fixation of index ions in the interlayer positions of minerals, hydrolysis of water molecules during the process of rinsing soil with deionized water, change in soil pH by some of the saturating solutions, and dissolution of soluble salts or soluble minerals in soils containing them are among the problems that make the existence of a perfect method for CEC determination almost impossible (e.g., Sumner and Miller 1996; Laird and Fleming 2008).

Using the SWRC at very high suction for the CEC calculation resolves the problems associated with the fixation of index ions during the saturation and extraction processes, as well as the change in soil pH, because it is not required to extract the saturating solution in the new methodology anymore. Furthermore, the NaCl does not change the soil pH considerably. The new SWRC-based method is also much less labor intensive and time consuming, with less of a sample loss that typically occurs during the many decantation steps of the chemical methods. Therefore, it can be used as an alternative method for CEC determination in soils with calcite and soluble salts.
alternative method for the CEC measurement, as it will result in fewer errors, as compared to the existing chemical methods.

Along with all the advantages of SWRC-based methodology, it still might not work well for soils containing calcite, carbonate, and soluble salts. Indeed, some discrepancies might arise when using this method for soils with considerable amount of Al\(^{3+}\). It is also important to measure SWRC accurately because small change in water content can greatly change the obtained CEC value.

The new methodology for CEC measurement can become even simpler and more inexpensive if just a single-point soil water retention is used instead of measuring the whole range of isotherms. This can be achieved by equilibration of soil specimens in closed chambers containing saturated solution of sodium hydroxide or potassium hydroxide that produces RH of 8.2%. The CEC can then be estimated by using Eq. (6) for a single pair of \((w, \psi)\) corresponding to the RH of 8.2%.

**Summary and Conclusions**

The applications of SWRC for determination of fundamental soil properties have recently been explored. CEC is one of these properties that has great impacts on soil’s physical and chemical behavior. The CEC can be directly linked to the water content of soil at low relative humidity values. The linkage is provided by a theoretical SWRC model at high suction values that explicitly considers the effect of cation hydration on the soil water content.

A new experimental method is proposed to estimate CEC of soil based on the SWRC at the high suction range. In the experimental procedure, the bulk soil is first saturated with 1 M NaCl to produce the Na\(^+\)-exchanged form of the soil. The soil water desorption isotherm of the Na\(^+\)-exchanged soil in the range of the RH from 7 to 11% is then measured. Finally, the theoretical SWRC model is fitted to the measured isotherm to obtain the CEC.

The results reveal that the CEC values calculated by the SWRC model are comparable to those measured by the ammonium acetate method. One of the main advantages of the SWRC-based method as compared to the existing methods for CEC measurement is that the extraction process is no longer needed here. This indeed eliminates the errors that typically occur during the extraction process, leading to more accurate CEC measurement of soil. Moreover, the new method is much less cumbersome and time-consuming.

Overall, the proposed methodology presents new opportunities and potential promises in the fields of geotechnology, geoenvironmental, and soil sciences for the practical use of SWRC in determining the CEC of soils.

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**References**


