

ELECTRICAL CONDUCTIVITY AND DIELECTRIC CONSTANT OF BENTONITE MEASURED WITH TIME-DOMAIN REFLECTOMETRY

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ABSTRACT: The dielectric constant, ϵ , and bulk electrical conductivity (EC), σ , of Na- and Ca-bentonite samples were measured with time-domain reflectometry (TDR). Water retention characteristics were also determined. Na-bentonite retained much more water than Ca-bentonite at all suctions. Both bentonite pastes remained saturated for a volumetric water content $\theta \geq 0.60 \text{ m}^3 \text{ m}^{-3}$ (water content by weight $w \geq 0.50 \text{ kg kg}^{-1}$). The bentonite samples, although prepared by using distilled water, had a fairly high σ with a peak at $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$. For saturated conditions, the EC increased with decreasing θ and, hence, increasing dry bulk density, ρ_b . The greatest σ was found at the lowest θ for which the sample was still saturated with water: $\sigma = 3.88 \text{ dS m}^{-1}$ for Na-bentonite and 1.45 dS m^{-1} for Ca-bentonite. The EC decreased with decreasing θ for unsaturated conditions. Due to energy losses, the TDR waveform was almost completely attenuated for $0.45 \leq \theta \leq 0.87 \text{ m}^3 \text{ m}^{-3}$ ($0.31 \leq w \leq 2.50 \text{ kg kg}^{-1}$) for Na-bentonite and for $0.36 < \theta < 0.50 \text{ m}^3 \text{ m}^{-3}$ ($0.22 < w < 0.38 \text{ kg kg}^{-1}$) for Ca-bentonite. As the water content decreased, the quasi-crystals (tactoids), consisting of several clay particles with near-parallel alignment, came closer together and the diffuse double layers started to overlap. This resulted in good conductive pathways with the greatest σ for the lowest saturated water content of $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$. Additional decreases in θ promoted further overlap of the diffuse double layers, but electrical conductance decreased because air entered the system. The EC was higher in Na-bentonite than in Ca-bentonite for all water contents. Because of the more dispersed particles and larger number of quasi-crystal in the Na-system than in the Ca-system, the electrical conductance between the quasi-crystals would be higher for the Na-bentonite than for the Ca-bentonite. Similarly, water molecules will be adsorbed more strongly and might cause higher water retention in Na-bentonite than in Ca-bentonite at the same suction.

INTRODUCTION

Soil electrical conductivity is widely used to assess soil salinity, to map the spatial distribution of salts for arid-land agriculture (Corwin et al. 1995), and to calculate leaching requirements of salt-affected soils (Gupta 1994). As environmental concerns increase, it is recognized that salinity in soils is not only a problem in arid and semiarid regions, but also in humid areas including lowlands. It is important to prevent degradation of surface and subsurface water resources by salts, and toxic elements such as pesticides. The EC and soil-water content are essential parameters for the study of water flow and solute transport through the soil profile.

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Time-domain reflectometry (TDR) has become popular method to measure the dielectric constant, ε , of soils from which we can estimate the volumetric water content, θ . TDR can also be used to measure the bulk soil EC, σ , nondestructively (Dalton and van Genuchten 1986). Topp et al. (1980) developed an empirical $\varepsilon - \theta$ relationship usually independent of soil type, soil density, soil temperature and soil salinity expressed as:

$$\varepsilon = 3.03 + 9.3\theta + 146.0\theta^2 - 76.7\theta^3 \quad (1)$$

Equation (1) is of a universal nature and was applied with an accuracy of $\pm 0.01 \text{ m}^3 \text{ m}^{-3}$ of water content for relatively coarse-textured soils (Patterson and Smith 1981; Dalton and van Genuchten 1986; Zegelin et al. 1989). Less accurate results were obtained for organic soils (Herkelrath et al. 1991), fine-textured soils (Dobson et al. 1985), and highly saline soils (Wyseure et al. 1997). Organic matter in the soils reduces the dielectric constant. Because of the low dielectric constant (≈ 3.2) of water adsorbed on the surface of clay particles (Dobson et al. 1985), fine-textured soils were found to have a lower dielectric constant than coarse textured soils at the same water content. It may therefore be necessary to have a soil-specific $\varepsilon - \theta$ calibration for accurate estimations.

Several dielectric mixture models have been proposed to account for the effect of adsorbed water on the average dielectric constant of fine-textured soils (Dobson et al. 1985; Roth et al. 1990). Dirksen and Dasberg (1993), however, found that such mixture models could describe the dielectric constant well for some clay soils but entirely failed to do so for bentonite. High salinity in soils limits the range of water content where TDR can be used because the dielectric constant will be overestimated (Wyseure et al. 1997) due to increased attenuation of the reflected signal (Mojid et al. 1998).

The application of TDR to measure water content and EC in heavy clays such as bentonite has not been yet widely studied, although heavy clays are prevalent especially in lowlands. Bentonite is a very fine-textured clay, which has a high swelling and shrinkage potential due to the considerable amount of smectite (montmorillonite). Almost all water in bentonite clays is influenced by the surface. The dielectric constant and conductive characteristics of adsorbed water are different from free water. Cremers and Laudelout (1966) used bentonite suspension prepared with distilled water. The EC reading that they obtained varied considerably depending on the type of adsorbed cations. TDR measurements in swelling bentonite would be influenced by changes in EC and bulk density. The objectives of this study were: (1) to evaluate the EC for Na- and Ca-bentonites at various water contents and their effect on TDR measurement of dielectric constant, and (2) to investigate the $\varepsilon - \theta$ relationship for the bentonites. We will discuss these properties in terms of the microstructure of the bentonite clay particles.

MEASUREMENT OF DIELECTRIC CONSTANT AND EC WITH TDR

Detailed background information on the use of TDR to measure dielectric constant and EC can be found in the literature (Topp et al. 1980; Dalton and van Genuchten 1986; Baker and Allmaras 1990; Heimovaara and Bouten 1990; Dirksen 1999). We only provide a brief description of the measurement procedure in the following. The TDR cable tester sends a high frequency transverse electromagnetic (TEM) pulse through a coaxial cable to a probe. The launched pulse reflects back when it encounters a change in impedance on its path of travel. The reflected pulses superimpose on the launched pulse and are displayed as a waveform. Figure. 1 shows a retrieved TDR waveform for a Na-bentonite sample. The horizontal axis

represents the distance from the output point of the TDR cable tester. The vertical axis provided the impedance of the TDR pulse.

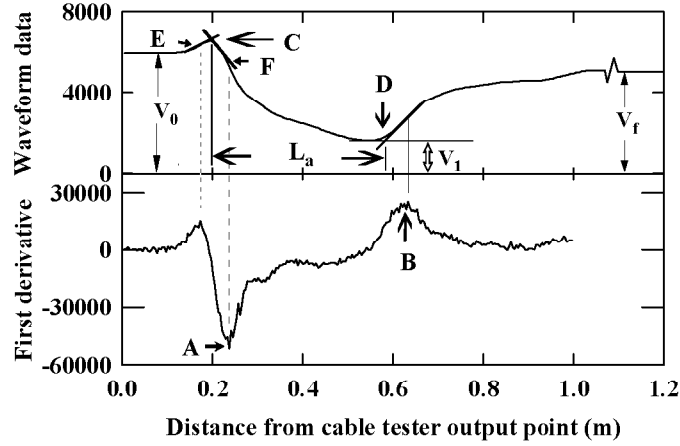


Fig. 1 A TDR waveform and its first derivative in a Na-bentonite sample with $\theta = 0.95 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.7 \text{ kg kg}^{-1}$).

The initial and final points of reflection from the starting and end points of the probe, respectively, are used to interpret the waveforms for the determination of the dielectric constant, ϵ . The dielectric constant of the soil controls the distance between these two points (Lorrain and Corson 1970). The initial reflection point (point C in Fig. 1) is determined by the intersection of a tangent passing through the rising branch of the waveform at E with the tangent through the falling branch at F. Both E and F are inflection points of the waveform. The final reflection point (point D in Fig. 1) is located at the intersection of a horizontal line passing through the global minimum of the waveform and a line tangent drawn to the waveform at the point of its highest first derivative (point B in Fig. 1). L_a is the apparent travel path of the TDR pulse used in Eq. (2) to calculate the dielectric constant, ϵ , and V_0 , V_1 and V_f are the impedances used in Eq. (3) to calculate the electrical conductivity, σ . The TDR support software (e.g., Baker and Allmaras 1990; Heimovaara and Bouten 1990; Evett 1998; Or et al. 1999) identifies these points almost in a similar way by utilizing the first derivative of the waveform.

The distance between the initial and final points is the apparent travel length, L_a , of the pulse through the probe (Fig. 1). The average dielectric constant, ϵ , of the soil sampled by the TDR probe is calculated from the electrodynamic equation given by (Dalton and van Genuchten 1986; Dirksen 1999):

$$\epsilon = \left(\frac{L_a}{L_s v_p} \right)^2 \quad (2)$$

where L_s is the length of the probe (0.045 m in this study) and v_p is the ratio of the velocity of the TDR pulse in a medium to that in free space (obtained from the TDR setting). The volumetric water content, θ , is related to ϵ by Eq. (1) for relatively coarse-textured soils.

The ordinate of a TDR waveform representing the impedance of the TDR pulse is proportional to the energy of the generated signal. This energy is continuously lost with increasing EC of the medium through which the TDR pulse propagates. The dependence of

the amplitude of the reflected signal on the EC of the medium provides the basis for measuring the EC with TDR. Note if the medium surrounding a TDR probe has a high EC, the signal is rapidly attenuated and dielectric constant and EC cannot be accurately measured.

The thin-section approach of Giese and Tiemann (1975) is usually applied to calculate the EC for soils, σ (dS m⁻¹). The Giese and Tiemann equation may be written as:

$$\sigma = \frac{10\varepsilon_0 c}{L_s} \frac{Z_0}{Z_u} \left(\frac{2V_0}{V_f} - 1 \right) \quad (3)$$

where ε_0 is the dielectric permittivity of free space (8.9×10^{-12} F m⁻¹), c is the velocity of the TDR pulse in free space (3×10^8 m s⁻¹), Z_0 is the characteristic impedance of the probe (Ω), Z_u is the output impedance of the TDR cable tester (50Ω for Tektronix 1502C cable tester), V_0 is the incident pulse voltage, and V_f is the reflected pulse voltage after multiple reflections have been suppressed (Fig. 1). The associated software selects V_0 and V_f from the waveform. Z_0 is determined in a separate calibration by immersing the probes in pure water with a known dielectric constant, ε_w (78.39 at 25 °C), according to:

$$Z_0 = Z_u \sqrt{\varepsilon_w} \left(\frac{V_1}{2V_0 - V_1} \right) \quad (4)$$

where V_1 is the minimum voltage on the waveform between the initial and final reflections of the pulse obtained from the waveforms (Fig. 1).

MATERIALS AND METHODS

Two types of bentonite samples, Na- and Ca-saturated bentonites, were used in this study. The Na-bentonite (Kunigel-V1, Kunimine K.K. Co. Ltd., Yamagata, Japan) consists of approximately 50% smectite (montmorillonite) and has a particle density $\rho_p = 2.6$ Mg m⁻³, cation exchange capacity (CEC) ≈ 60 meq/100g, and an exchangeable sodium percentage (ESP) ≈ 90 (Ito et al. 1994). Air-dried Na-bentonite was mixed with distilled water using a stirrer to prepare samples with water content for $0.84 \leq \theta \leq 0.96$ m³ m⁻³ ($2.0 \leq w \leq 10.0$ kg kg⁻¹) with an every 0.5 kg kg⁻¹ increment. For $\theta < 0.84$ m³ m⁻³, the stirrer could not mix water with bentonite uniformly. Therefore, several samples with lower water contents were prepared by spraying water on the bentonite and manual mixing. The samples were kept for three months in plastic bags to attain uniform water content distributions.

The Ca-saturated bentonite was prepared by washing the Na-bentonite of $\theta = 0.95$ m³ m⁻³ ($w = 7.0$ kg kg⁻¹) with 1 N CaCl₂ solution several times in a pressure plate chamber. The Ca-saturated bentonite was then washed several times with distilled water in the pressure plate chamber to remove excessive calcium ions until the EC of the drainage water became less than 0.007 dS m⁻¹. The washed Ca-bentonite was mixed again with distilled water at $\theta \approx 0.95$ m³ m⁻³. Eight Ca-bentonite samples were prepared in 5-cm diameter acrylic columns with a ceramic plate at the bottom. Suction was applied at the bottom of these samples by using hanging water columns ranging from 0 to 0.217 bar for three weeks to reach an equilibrium water content distribution. Eight samples for lower water contents were also prepared by spraying water on air-dried Ca-bentonite, which were then kept for one month in plastic bags to obtain a uniform distribution.

The dielectric constant and electrical conductivity of the Na- and Ca-bentonite samples were measured with a Tektronix 1502C cable tester using the TDR support software WinTDR99, which was developed by Or et al. (1999). We used a 4.5-cm long TDR probe with three rods. The probe was inserted horizontally. The TDR waveform was recorded for each sample. The preparation and measurements of all samples were performed at constant room temperature (25 ± 1 °C). After the TDR measurements, gravimetric (w) and volumetric (θ) water contents were determined from the wet and dry weights as well as the volume of the wet samples. We confirmed that the sample was saturated for $\theta \geq 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w \geq 0.5 \text{ kg kg}^{-1}$) for both Na- and Ca-bentonites because the measured θ was almost identical to θ based on w , the particle density, ρ_p , and ρ_{water} ($= 1.0 \text{ Mg m}^{-3}$) assuming perfect saturation:

$$\theta = \frac{\rho_p w}{\rho_{\text{water}} + \rho_p w} \quad (5)$$

Since measuring the volume of the clay pastes was elastic, we decided to use θ based on Eq. (5) for saturated conditions.

The water-retention characteristics of the two bentonites were also measured. Saturated bentonite samples were prepared with $\theta = 0.95 \text{ m}^3 \text{ m}^{-3}$ ($w = 7.0 \text{ kg kg}^{-1}$) and increasing suction was applied to drain them. For small suctions below 0.217 bar, a hanging water column was used while the samples were put in a pressure plate chamber for higher suctions. In both cases, the water content was determined when equilibrium conditions had been reached when drainage had virtually ceased.

RESULTS AND DISCUSSION

Water Retention Curves

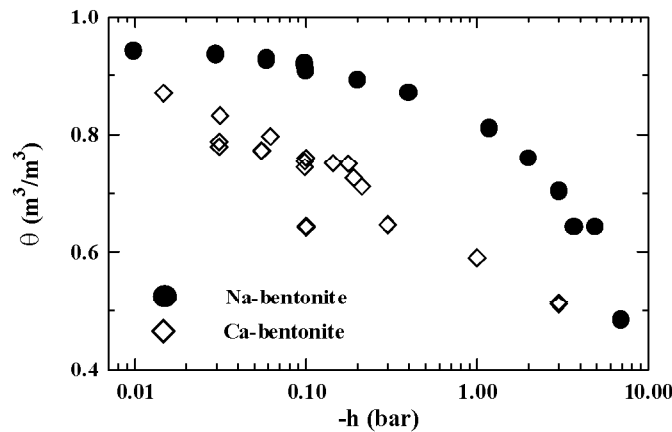


Fig. 2 Volumetric water content θ ($\text{m}^3 \text{ m}^{-3}$) as a function of suction $-h$ (bar) for Na- and Ca-bentonites

Figure 2 shows water content versus suction relationship for the Na- and Ca-bentonites. The water content of Na-bentonite was much higher than that of the Ca-bentonite at all suctions (Shainberg et al. 1971). While the air-entry value for rigid soils is generally less than

0.01 – 0.02 bar, bentonite remained saturated over a wide range of water contents. Note that the retention curves were identical to the shrinkage curves above the lowest saturated water content of $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.5 \text{ kg kg}^{-1}$) for both bentonites. As suction increased, since bentonite particles were compressed due to the release of some of the adsorbed water molecules, the pastes remained saturated even at lower water contents.

TDR Waveforms

The bentonite samples caused significant energy loss of the launched and reflected TDR pulse in our experiments. Figure 3a shows the TDR waveforms for seven Na-bentonite samples with $\theta = 0.17, 0.23, 0.45, 0.61, 0.84, 0.87$ and $0.954 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.14, 0.20, 0.31, 0.50, 2.0, 2.5$ and 8.0 kg kg^{-1}). Figure 3b shows the waveforms for six Ca-bentonite samples with $\theta = 0.20, 0.24, 0.36, 0.50, 0.67$ and $0.91 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.14, 0.16, 0.22, 0.38, 0.78$ and 4.07 kg kg^{-1}). As the water content in the Na-bentonite decreased, the impedance of the waveform decreased due to loss of the signal energy. This continued until the water content reached $\theta \approx 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w \approx 0.50 \text{ kg kg}^{-1}$), the lowest water content at which the paste was still saturated. A further decrease in water content from $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$, energy loss of the signal decreased and the signal moved up again. For the 4.5-cm long TDR probe, the reflected signal was almost completely attenuated between $\theta = 0.45$ and $0.87 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.31$ and 2.5 kg kg^{-1}) for the Na-system. The waveform obtained for this range of water contents became unsuitable for analysis of the dielectric constant. This was because the final point of reflection D (Fig. 1) could not be determined accurately under such conditions, similar to the case of salt-affected soils (Mojid et al. 1998). For the Ca-system, on the other hand, the signal was almost completely attenuated between $\theta = 0.36$ and $0.50 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.22$ and 0.38 kg kg^{-1}).

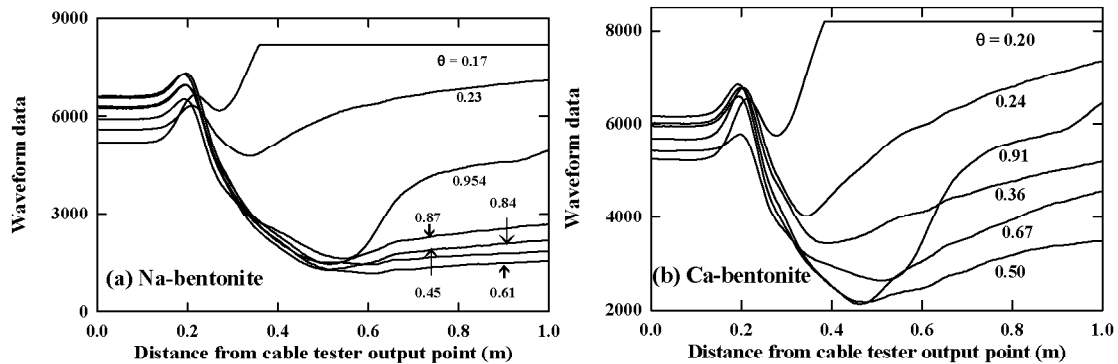


Fig. 3 TDR waveforms in seven samples with different volumetric water content θ ($\text{m}^3 \text{ m}^{-3}$) (a) Na-bentonite samples and (b) Ca-bentonite samples

Dielectric Constant – Water Content Relationship

Figure 4 shows the plot of θ versus ϵ relationship obtained from the Na- and Ca-bentonites. The dielectric constant ϵ of the bentonite samples, which depended predominantly upon their water content, decreased from 73.8 to 4.7 when θ decreased from 0.96 to 0.16 $\text{m}^3 \text{ m}^{-3}$ ($w = 10.0$ to 0.14 kg kg^{-1}) in the Na-system. In the Ca-system, ϵ decreased from 63.6 to 5.6 when θ decreased from 0.91 to 0.20 $\text{m}^3 \text{ m}^{-3}$ ($w = 4.07$ to 0.14 kg kg^{-1}).

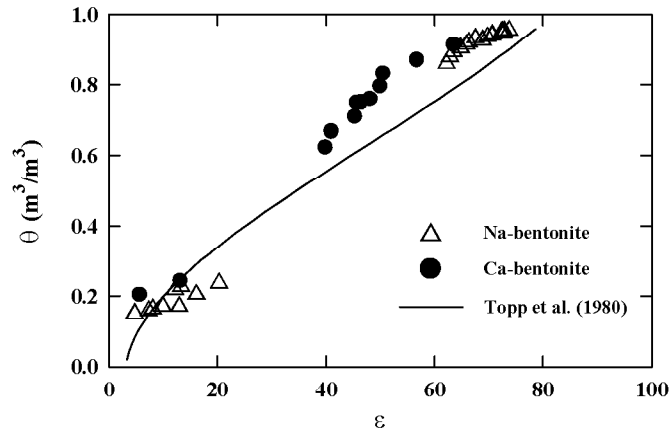


Fig. 4 Dielectric constant – volumetric water content ($\epsilon - \theta$) relationships for Na- and Ca-bentonites. The dotted line is based on Topp et al. (1980)

Because of the almost complete attenuation of the reflected signal as shown in Fig. 3, the software algorithm could not interpret the waveform properly to determine ϵ for $\theta = 0.46$ to $0.87 \text{ m}^3 \text{ m}^{-3}$ in the Na-bentonite and for $\theta = 0.36$ to $0.50 \text{ m}^3 \text{ m}^{-3}$ in the Ca-bentonite. It appears from Fig. 4 that the same $\epsilon - \theta$ relationship can be applied for the saturated Na- and Ca-bentonites. The equation of Topp et al. (1980) underestimated water content especially for $\theta > 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w > 0.5 \text{ kg kg}^{-1}$).

Electrical Conductivity - Water Content Relationship

Figure 5 shows the EC for the Na- and Ca-bentonites, σ , as a function of water content θ . Data for a Wyoming bentonite under saturated conditions reported by Cremers and Laudelout (1966) are also plotted. The bentonite samples, although prepared by using distilled water, had a fairly high σ with a peak value at $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.5 \text{ kg kg}^{-1}$). The EC increased for lower θ and higher dry bulk density, ρ_b , when the sample was saturated. The greatest σ was found at the lowest saturated water content: $\sigma = 3.88 \text{ dS m}^{-1}$ for Na-bentonite and 1.45 dS m^{-1} for Ca-bentonite. On the other hand, the EC decreased when θ was lowered for unsaturated conditions.

Inoue et al. (2000) obtained the following relationship between the soil EC, σ , and the EC of the soil solution, EC_w , for various θ of a dune sand using NaCl solutions assuming a negligible surface conductance of the solid phase:

$$\sigma = 1.45\theta^2 EC_w + 0.102\theta \quad (6)$$

The maximum σ for Na-bentonite (3.88 dS m^{-1}) is equivalent to σ for a saturated sand with $\theta = 0.35 \text{ m}^3 \text{ m}^{-3}$ when EC_w is 21.6 dS m^{-1} (0.23M of NaCl solution). This implies that distilled water could not electrically isolate the bentonite clay particles and the surface conductance was important for bentonite clays.

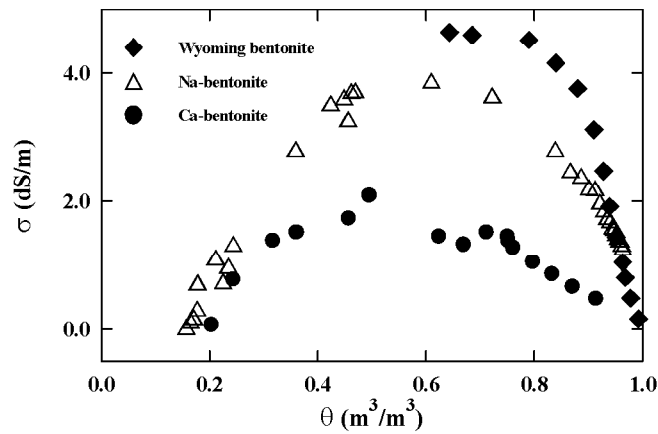


Fig. 5 Electrical conductivity σ (dS m^{-1}) as a function of volumetric water content θ ($\text{m}^3 \text{m}^{-3}$) for Na- and Ca-bentonites mixed with distilled water.

The EC of the Na-bentonite was higher than that of the Ca-bentonite at the same water content. The observed behavior of the EC with water content in the saturated bentonite is in agreement with the findings of Cremers and Laudelout (1966). These investigators reported that exclusion of intermicellar liquid led to an increase of the EC at a rate depending on the clay type. They found similar behavior of EC with water content (θ - σ relationship) for the saturated Wyoming bentonite clay, which is also shown in Fig. 5. The θ of the bentonite was calculated from the clay content in Fig. 1 of Cremers and Laudelout (1966). Figure 5 reveals that the θ - σ relationship of the Na-bentonite used in this study was close to that of the Wyoming bentonite under saturated conditions.

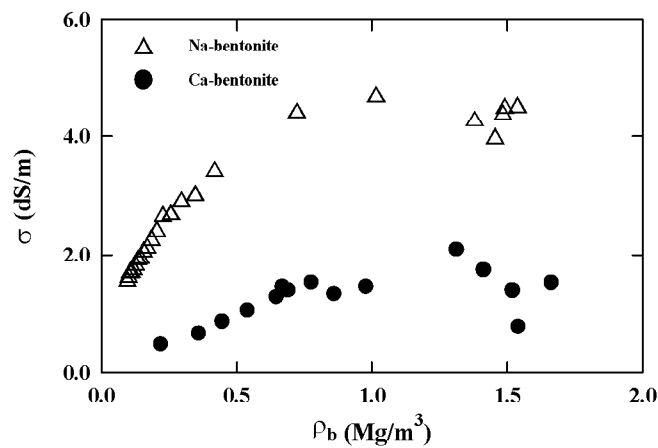


Fig. 6 Variation of electrical conductivity σ (dS m^{-1}) as a function of dry bulk density ρ_b (Mg m^{-3}) for Na- and Ca-bentonites

Since σ for these bentonites could be influenced by the clay content of the sample, we also plotted σ as a function of the dry bulk density of the sample, ρ_b , for Na- and Ca-bentonites in Fig. 6. For dilute suspensions with a low ρ_b , σ was small for both bentonites. As the water content decreased, ρ_b gradually increased for saturated conditions. At about $\rho_b = 1.0 \text{ Mg m}^{-3}$ ($\theta = 0.60 \text{ m}^3 \text{m}^{-3}$), σ reached its maximum. With further increases in ρ_b , the samples became

unsaturated and air entered the system. As the volume of air increased, the electrical contact between the particles decreased and σ become smaller

Micro-Structure and Physical Properties of Bentonite

Macroscopic physical properties, such as the water retention curve and the θ - σ and ρ_b - σ relationships, obtained for the Na- and Ca-bentonites were obviously influenced by the micro-structure of the clay particles (e.g., Mitchell 1993; van Olphen 1977). Clay colloidal systems are assumed to be composed of multiple quasi-crystals, often referred to as tactoids, consisting of several plate-shaped crystals with near-parallel alignment (Blackmore and Miller 1961; Quirk and Aylmore 1971). The number of clay particles in the quasi-crystals and the distance between clay crystals depends on double-layer repulsion and van der Waals attractions between particles. The repulsion force in a Na-system increases as the concentration decreases and the exchangeable sodium percentage (ESP) increases. When the diffuse double layer is fully developed, the clay particles disperse and the number of particles per quasi-crystal might become fewer due to greater repulsive forces. On the other hand, the thickness of the diffuse double layer is smaller in Ca-systems (Sposito 1984). The number of clay particles in the quasi-crystals for a Ca-system would be larger due to the weaker repulsive force. Blackmore and Miller (1961) reported that the distance between the clay crystals was 0.9 nm regardless of the condition in case of the Ca-montmorillonite.

Figures 7a, 7b, and 7c represent schematically samples of dilute suspension, saturated and unsaturated Na- and Ca-bentonites, respectively, with the same water content and solid content in both bentonites. For the sake of simplicity, we assumed a parallel association of three clay particles in the quasi-crystals for Na-bentonite and ten particles for Ca-bentonite. The total number of bentonite particles is the same (= 30) for both systems but the number of quasi-crystals is higher for the Na-bentonite (= 10) than for the Ca-bentonite (= 3). The dotted lines around the quasi-crystals represents the diffuse-double layer area.

As volume decreased for lower water contents (Fig. 7b), the quasi-crystals came closer together and the diffuse double layers outside of the quasi-crystals started to overlap. The card-house structure of the quasi-crystals having edge-to-edge and edge-to-face associations will rearrange mostly in edge-to-face position (van Olphen 1977). This would provide a good conductive pathway, which will result in the highest σ for a lower water content of $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$.

With further decrease in water content (Fig. 7c), the quasi-crystals might rearrange mostly in face-to-face position as assumed by van Olphen (1977). An additional decrease in θ would promote a further overlap of the diffuse double layers, but the electrical conductance was decreased because air entered the system when the system became unsaturated.

In the solute-free Na-system, clay particles and quasi-crystals are more dispersed than in the Ca-system where the particles were more clustered, especially in the dilute suspension (Fig. 7a). The water molecules are more strongly adsorbed in the Na-system than in the Ca-system at the same water content. This could be the reason for the lower water content in the Ca-bentonite than in the Na-bentonite at the same suction as shown in Fig. 2. Because of the more dispersed particles and larger number of quasi-crystal in the Na-system than in the Ca-system, the electrical conductance between the quasi-crystals would be higher for the Na- than for the Ca-bentonite.

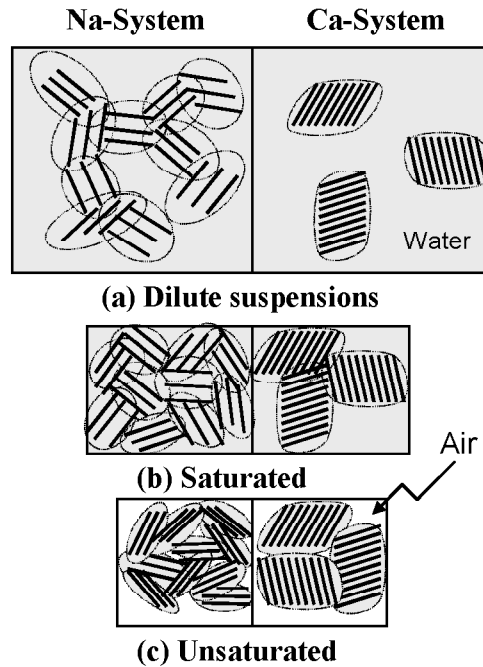


Fig. 7 Schematic representations of particle association in Na- and Ca-bentonites with the same water and solid fractions: (a) dilute suspensions, (b) saturated bentonites with a lower water content and (c) unsaturated bentonites

CONCLUSIONS

The water retention capacity of the Na-bentonite was much higher than that of the Ca-bentonite at all suctions. Both bentonites remained saturated for $\theta \geq 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w \geq 0.5 \text{ kg kg}^{-1}$). The TDR waveform was almost completely attenuated for $0.45 \leq \theta \leq 0.87 \text{ m}^3 \text{ m}^{-3}$ ($0.31 \leq w \leq 2.5 \text{ kg kg}^{-1}$) for the Na-bentonite and $0.36 \leq \theta \leq 0.50 \text{ m}^3 \text{ m}^{-3}$ ($0.22 \leq w \leq 0.38 \text{ kg kg}^{-1}$) for the Ca-bentonite. The attenuation of the waveform restricted the measurement of dielectric constant by TDR in this range of water contents. The so-called universal equation of Topp et al. (1980) significantly underestimated water content in the bentonites especially at higher water contents. Both the Na- and Ca-bentonite samples, although prepared with distilled water, had a considerable bulk electrical conductivity, σ , which varied with the water content and dry bulk density of the samples. The σ value for the unsaturated bentonite gradually increased with water content. At the lowest saturated water content of $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$ ($w = 0.5 \text{ kg kg}^{-1}$), the σ leveled off at its highest value and then decreased gradually with further increases in water content in response to decreasing the dry bulk density. The highest σ was 3.88 dS m^{-1} for the Na-bentonite and 1.45 dS m^{-1} for the Ca-bentonite.

The $\sigma - \theta$ relationships for the bentonites could be explained from the micro-structural association of the quasi-crystals (tactoids) consisting of several plate-shaped crystals with near-parallel alignment. As the water content decreased, the quasi-crystals came closer together and the diffuse double layers outside of the quasi-crystals started to overlap. This would provide a good conductive pathway that results in the highest σ for a lower water content of $\theta = 0.60 \text{ m}^3 \text{ m}^{-3}$. An additional decrease in θ would promote a further overlap of the diffuse double layers, but the electrical conductance decreased because of air entry. For the same water content under saturated conditions, a larger number of quasi-crystals with a

smaller number of clay particles dispersed for the Na-bentonite than for the Ca-bentonite. The difference in microstructure resulted in higher σ for Na-bentonite than for Ca-bentonite at all water contents.

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