

## Electrical Spectroscopy of Kaolin and Bentonite Slurries

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### Abstract

The electrical conductivity and dielectric permittivity of clay-water systems were used to characterize the physicochemical state of kaolin and bentonite-water systems. The dielectric permittivity and electrical conductivity of kaolin and bentonite were determined at various water contents and NaCl concentrations as a function of frequency, ranging from 0.1 kHz to 13 MHz. The results indicate that kaolin and bentonite have similar dielectric behavior. An increase in the frequency produces a decrease in the dielectric permittivity of the soil-pore water mixture. As the ion concentration increases, the dielectric permittivity of the mixture increases at low frequency (kHz) whereas it decreases at high frequency (MHz). The electrical conductivity of kaolin and bentonite increases with an increase in the ion concentration in the soil-water mixture. The electrical conductivity of a kaolin-water mixture decreases with an increase in the solid concentration. In contrast, the electrical conductivity of a bentonite-water mixture increases with a decrease in the solid concentration. This indicates the importance of the surface conductivity of a bentonite-water mixture. Furthermore, the results of this study indicate that dielectric permittivity and electrical conductivity might be used to characterize the electrokinetic behavior of soil minerals to determine the physiochemical changes in clay soil-water systems, such as subsurface contaminations.

**Key Words:** bentonite, contamination, dielectric permittivity, electrical conductivity, kaolin, slurry

## Kaolen ve Bentonit Bulamaçlarının Elektrik Spektroskopileri

### Özet

Dielektrik geçirgenliği ve elektrik iletkenliği kil minerallerinin elektrokinetik özelliklerini belirlemek için kullanılabilir. Bu anlamda, kaolen ve bentonit minerallerinin dielektrik geçirgenliği ve elektrik iletkenliği, farklı NaCl içeriğinde ve mineral/su oranında 0.1 kHz- 13 MHz frekans aralığında saptandı. Sonuçlar gösterdi ki, genelde, kaolen ve bentonit benzer dielektrik geçirgenlik özelliği gösteriyor: ölçüm yapılan frekans arttıkça mineral-su karışımının dielektrik geçirgenliği azalıyor. İyon konsantrasyonu arttıkça, mineral-su karışımının dielektrik geçirgenliği düşük frekanslarda (kHz) artıyor, yüksek frekanslarda azalıyor (MHz). Sistemdeki iyon konsantrasyonu arttıkça hem kaolenin hem de bentonitin elektrik iletkenliği artmaktadır. Kaolen/su oranı arttıkça elektrik iletkenliği azalmakta fakat bentonit/su oranı arttıkça elektrik iletkenliği artmaktadır. Bu olay bentonit/su karışımında yüzeysel iletkenliğin olduğunu göstermektedir. Bu çalışmanın sonuçları gösteriyor ki dielektrik geçirgenliği ve elektrik iletkenliği ölçülerek kil minerallerinin elektrokinetik davranışı belirlenebilir. Yine benzer şekilde yeraltı kirlenmesinin oluşup oluşmadığı veya uygulanan yer altı temizleme yönteminin etkin olup olmadığı benzer şekilde tespit edilebilir.

**Anahtar Sözcükler:** Kaolen, bentonit, dielektrik geçirgenlik, elektrik iletkenlik, yer altı kirlenmesi

## Introduction

Subsurface contamination of soil and water is a worldwide problem. The development of effective clean-up programs requires characterization of contaminants in a rapid, non-destructive, and economic way. However, characterization is difficult because the clay-water and contaminant interaction is complex, and there is no simple technique for understanding it. The electrokinetic properties of clay may be a relatively simple and direct means of determining contamination and to understand clay-water and contaminant interaction.

Electrical spectroscopy offers advantages for studying the electrokinetic properties of clay-rich soils, such as dielectric permittivity and electrical conductivity, over a wide range of frequencies. These properties provide information on temporal processes in the Stern and diffuse double layer associated with the particles (Arulanandan and Michell, 1968; Myers and Saville, 1989). In addition, information is obtained on soil fabrics, such as whether the soil is disturbed or compacted (Shang et al., 1999), and on changes in physicochemical state (Kaya and Fang, 1997; Klein and Santamarina, 1996). Where water and soil particles come into contact, H<sub>2</sub>O molecules interact with clay surfaces and produce a diffuse double layer. The electrochemical diffuse double layer and surface conductance can significantly affect the electrical behavior of heterogeneous media depending on the degree of surface interaction. Low-frequency electrical spectroscopy may be used to study the behavior of the particle surface and its double layer, because polarization and relaxation processes typically affect response at frequencies below 100 kHz (Barchini and Saville, 1995; Klein and Santamarina, 1996; Kaya and Fang, 1997). In this study, the effect of the interaction of H<sub>2</sub>O molecules and ions with clay particles on dielectric permittivity and electrical conductivity were investigated within the frequency range of 0.1 kHz to 13 MHz.

## Electrical Properties of Soils

The electrical conductivity, dielectric permittivity, and magnetic susceptibility of the constituent minerals mainly control the electrical properties of soils. The dielectric permittivity of a material is a measure of its ability to store a charge (electrical energy) for an applied field strength. The dielectric permittivity is a complex number composed of real and imaginary parts. The real part results from the

polarization of material, whereas the imaginary part is related to ohmic and polarization losses. There are several mechanisms for polarization, including electronic and ionic resistance, orientation polarization, double layer polarization and interfacial Maxwell-Wagner relaxation (Chelkowski, 1980).

Dielectric permittivity,  $\epsilon$ , is a function of frequency. Relative dielectric permittivity is the ratio of the complex dielectric permittivity,  $\epsilon$ , to the dielectric permittivity of free space,  $\epsilon_0$ . Complex dielectric permittivity,  $\epsilon^*$ , can be expressed as

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) \quad (1)$$

where  $\epsilon'$  = the real part of the dielectric permittivity,  $\epsilon''$  = the imaginary part of the dielectric permittivity,  $\omega$  = angular frequency; and  $i = \sqrt{-1}$ .

The dielectric permittivity of dry soil particles, independent of mineral type, is  $\approx 4$ , whereas that of water  $\approx 80$  (20°C) in the MHz frequency range (Arulanandan, 1991). Many researchers have discussed the relationship between the water content and dielectric permittivity of soil-water systems to describe mathematical models for soil-water-air systems (Topp et al., 1980; Kaya and Fang 1997; and Saarenketo, 1998). However, nearly all models fail to predict the water content owing to surface interactions at the particle-water interface. Because the surface interactions between soil particles and H<sub>2</sub>O molecules depend on the mineralogical composition of the soil particle, it is difficult to define the dielectric permittivity and electrical conductivity of wet soil particles.

## Materials and Test Methods

The kaolin sample was obtained from Georgia Kaolin Company<sup>R</sup>, Georgia, and the bentonite sample was obtained from a drilling company in Bethlehem, PA. The physicochemical properties of these materials are given in Table 1. The capacitance and electrical conductivity measurements were performed using a 4192A LF Impedance Analyzer (Hewlett Packard). The capacitor was capable of determining capacitance measurements in a frequency range of 0.1 kHz to 13 MHz. One reason for these measurements within the wide frequency range was to determine the behavior of the dielectric value and electrical conductivity, thus identifying the general behavior of both materials. In addition, the most appropriate frequency for a reliable measurement of contaminate variations in soil-pore water mixtures

can be determined.

**Table 1.** The physicochemical properties of soils used in the study

Soil Type	Kaolin	Bentonite
Specific Gravity, $G_s^a$	2.55	2.60
Color	Light tan	Light cream
Liquid limit <sup>a</sup>	42	440
Plastic Index	13	370
Main Cation	Sodium	Sodium
CEC (meq/100g)	24	87
pH	6.3±1.2 (10% solid)	8.5± 1 (5% solid)
Surface Area (m <sup>2</sup> g <sup>-1</sup> )	13.00	27.7
Particle Diameter (μ m)	0.087	0.19

<sup>a</sup> Standard ASTM procedure

The clay samples were treated initially with ammonium acetate and then with distilled dionized (DDI) water until the electrical conductivity of the supernatant became constant. Water solutions were then prepared at various NaCl concentrations. Then, clay-water mixtures were prepared with various water contents. Before conducting measurements, the prepared clay-water mixtures were kept at constant temperature for ≈ 12 h to achieve both moisture and ionic equilibrium. Then, clay-water mixtures were placed in a U-shaped Plexiglas cell. The Plexiglas cell had dimensions of 2 x 4 cm, and the separation between the plates was 2 cm. The conductive areas of the cell were covered by silver plates to eliminate impurities. All measurements were taken within ≈ 3 min to prevent the effects of overheating by the applied current.

The dielectric permittivity of the mixtures was calculated using the capacitance measurements. The capacitance,  $C$ , of a material between two plates is given as

$$C = \frac{\epsilon\epsilon_0 A}{d} \quad (2)$$

where  $\epsilon$  = the dielectric permittivity of the medium,  $\epsilon_0$  = the permittivity of the vacuum ( $8.85 \times 10^{-12}$  C N<sup>-1</sup>),  $A$  = the area of the plates, and  $d$  = distance between plates. By knowing the geometric configuration ( $A$  and  $d$ ), and measuring the capacitance,  $C$ , the dielectric permittivity of the soil-water mixture was determined.

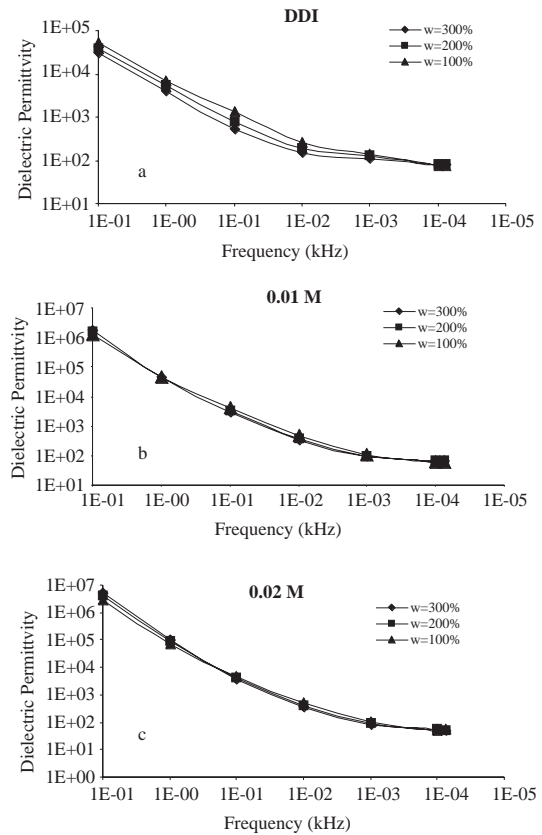
Repeated measurements of the dielectric constant of DDI water and soil were taken to test the reliability of the impedance analyzer. It was observed that

the dielectric constant of DDI at 20 °C was always between 78-80, the of dry soil was around 4-5, and that of air was 1.

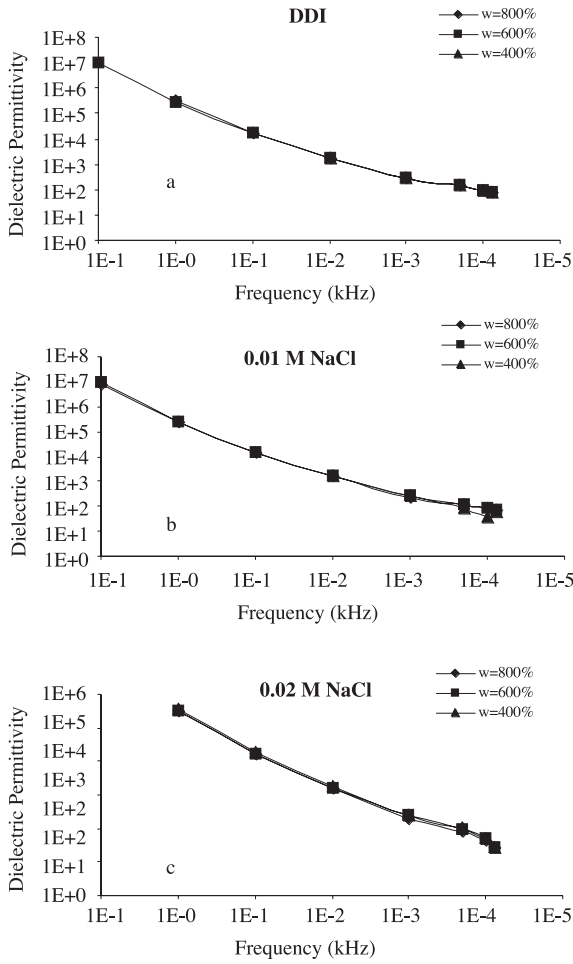
## Results and Discussions

### Dielectric permittivity

Figures 1 and 2 present the dielectric permittivity of kaolin and bentonite in different water contents. Both figures show that the dielectric permittivity of the clay-water mixture decreases with an increase in the frequency. However, the dielectric permittivity of bentonite-water is higher than that of kaolin at a given frequency. For example, when the pore water (solution water) is DDI, kaolin has a dielectric permittivity of  $10^5$  and bentonite has  $10^7$  at 100Hz. This trend is also observed for other ionic concentrations. However, the differences decrease with an increase in the ion concentration or an increase in frequency.



**Figure 1.** Dielectric permittivity of kaolinite as a function of frequency.

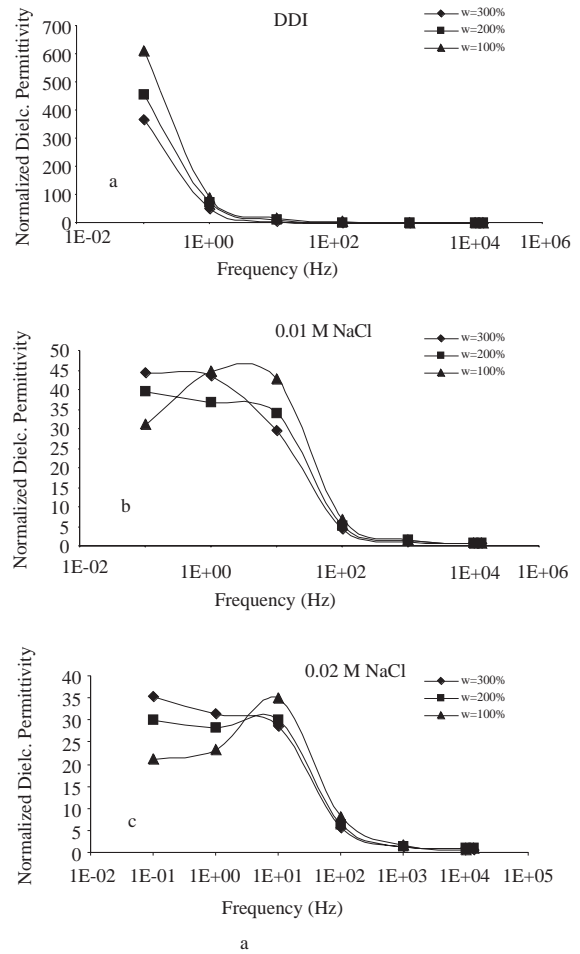


**Figure 2.** Dielectric permittivity of bentonite as a function of frequency.

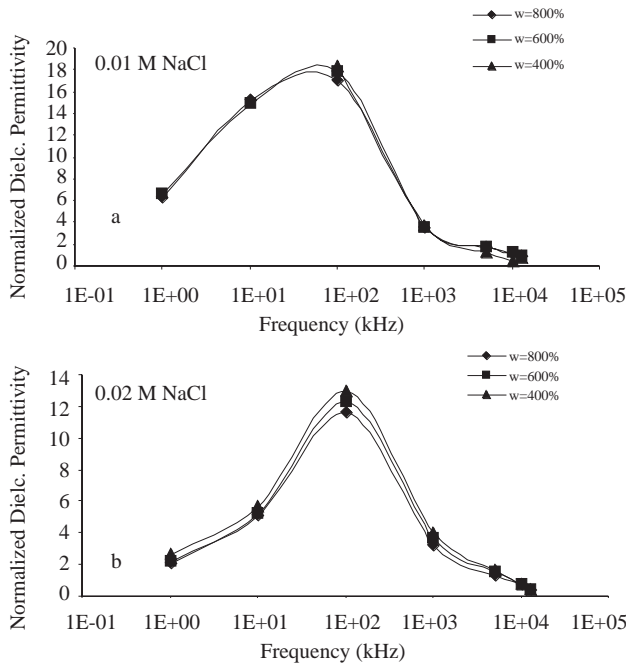
To determine the effect of surface interactions on dielectric permittivity, the dielectric permittivity of the clay-water mixture was normalized (Figures 3 and 4) with respect to water. The two clay minerals illustrate different dielectric behavior. Kaolin has the maximum normalized dielectric permittivity value, at 10 kHz, whereas bentonite has the maximum value, at 100 kHz. Although the values differ, an increase in the ionic concentration causes a decrease in the normalized dielectric permittivity. For example, when the ion concentration is 0.01 M NaCl, bentonite has a normalized dielectric permittivity value of 19, whereas this value is 13 for an ion concentration of 0.02 M NaCl at 100 kHz, the peak frequency value. This result is similar for kaolin; i.e., the normalized dielectric permittivity values are lower for 0.02 M NaCl than for 0.01 M NaCl for the kaolin-water system at a given frequency. Thus,

the surface interactions contribute to the dielectric permittivity of the clay-water mixture and the contribution is inversely proportional to the ion concentration.

Furthermore, to establish the effect of the ion concentration on the dielectric permittivity of the clay-water mixtures at the same solid concentration, the dielectric permittivity of kaolin and bentonite was normalized (Figures 5 and 6). Note that the effect of the surface interaction on dielectric permittivity is frequency dependent, and dielectric permittivity decreases with an increase in ion concentration. Moreover, the dielectric permittivity of the clay-water mixture is clay-type dependent.



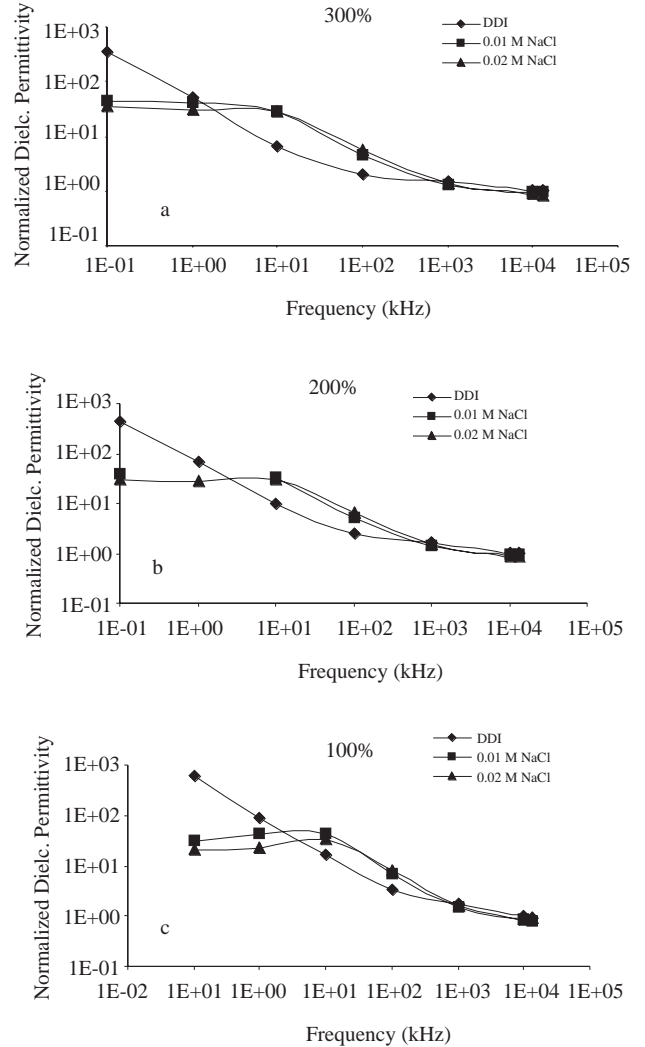
**Figure 3.** Normalized dielectric permittivity of kaolinite (dielectric permittivity of kaolinite-water is divided by that of pore water) as various NaCl concentrations.



**Figure 4.** Normalized dielectric permittivity of bentonite (dielectric permittivity of bentonite-water is divided by that of pore water) at various NaCl concentrations.

In Figures 3-6, note that polarization is high where the pore water is DDI, and decreases with an increase in the ion concentration in the system. As the ion concentration in the system increases, the diffuse double layer diminishes. When the pore water is DDI, the ions at the interface polarize and contribute to the dielectric permittivity of the mixture. However, when the ion concentration increases because of the charges accumulated at the interfaces and because of molecular rotation, polarization decreases. Molecular rotation occurs when an external electrical field is applied. Not all hydrated molecules can rotate in the direction of the externally applied electrical field, and therefore only rotated molecules can contribute to the dielectric permittivity of the mixture. These results are in agreement with Sen (1981) and Kaya and Fang (1997). Kaya et al. (1997) discussed the physical mechanism and contributions from these phenomena to the dielectric permittivity of soil-water mixtures: high dielectric permeability of a clay-water mixture is related to the polarization of molecular rotations and the accumulation of charges at the interfaces. Because the mineralogical compo-

sition and the surfaces of the particles in kaolin and bentonite are different, the polarizations of the ions at the interfaces of these particles are different also. Furthermore, dielectric permittivity can be utilized to determine changes occurring in the physico-state of the clay-water mixtures.

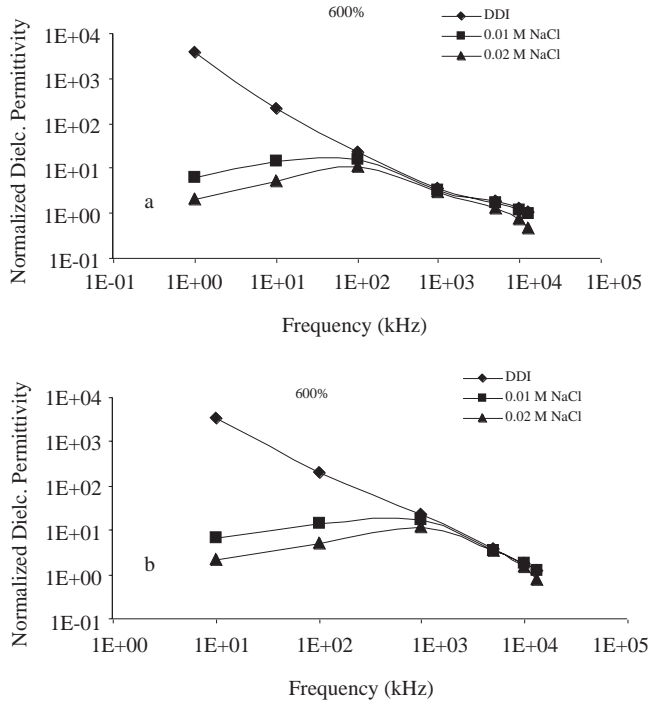


**Figure 5.** Normalized dielectric permittivity of kaolinite (dielectric permittivity of kaolinite-water is divided by that of pore water) at a constant solid concentration with different NaCl concentrations.

**Electrical conductivity**

Figures 7 and 8 show the electrical conductivity of kaolin and bentonite at various ionic concentrations as a function of frequency. As the ionic concen-

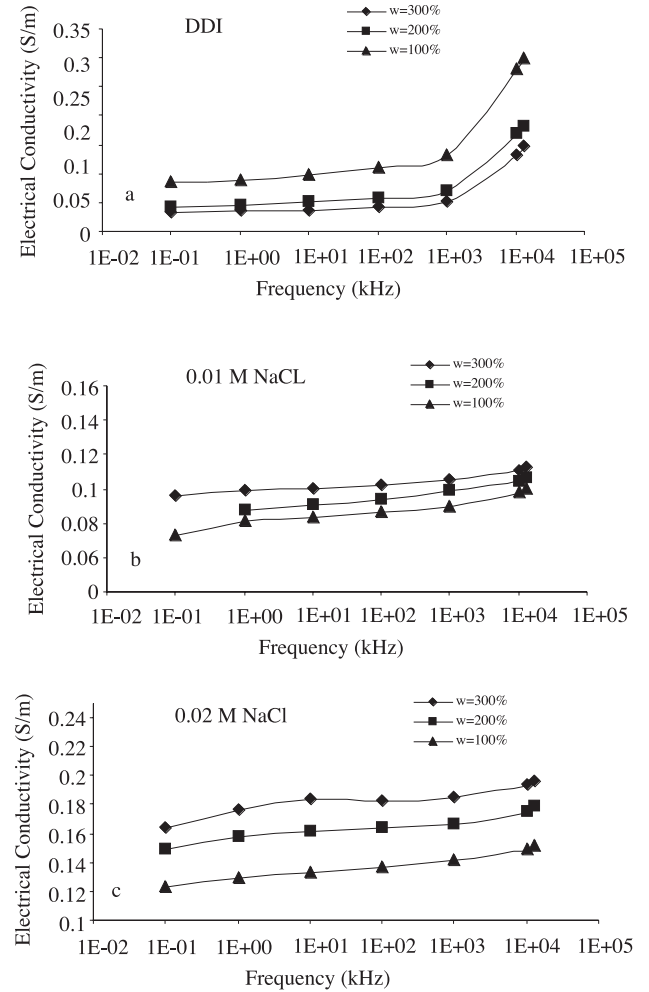
tration increases, so does the electrical conductivity. Kaolin and bentonite show different electrical conductivity behavior at low and high frequencies. At high frequencies (MHz range), the electrical conductivity of the bentonite increases. However, this does not occur for kaolin, except where the pore water is DDI.



**Figure 6.** Normalized dielectric permittivity of bentonite (dielectric permittivity of bentonite-water is divided by that of pore water) at a constant solid concentration with different NaCl concentrations.

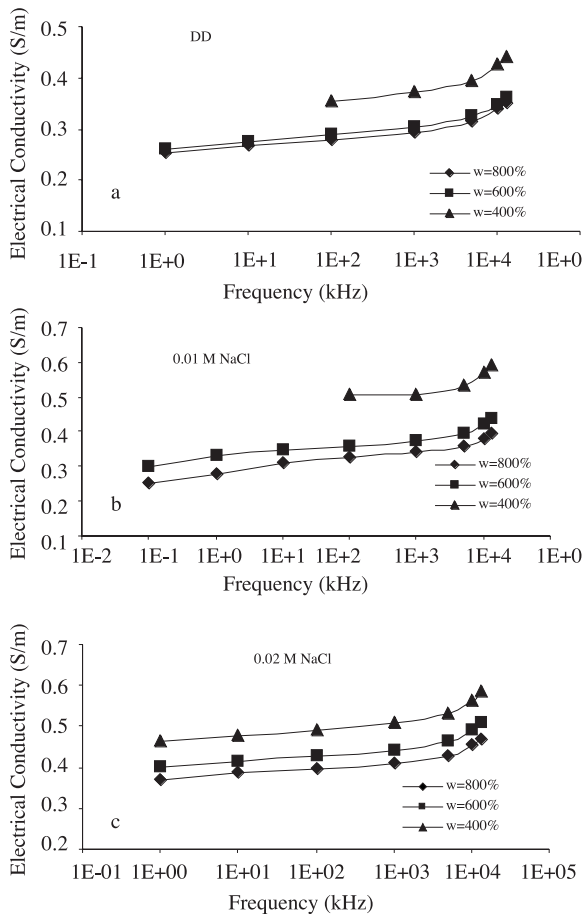
Because the electrical conductivity of the clay particles is negligible compared to that of pore water, the measured electrical conductivity should nearly equal that of water. If the measured electrical conductivity of the clay-water mixture is higher than that of the pore water, the difference is related to surface electrical conductivity (Rhoedes et al., 1976). The surface electrical conductivity is defined as the difference between the conductivity of the interface liquid and the conductivity of the interparticle solution (Shainberg and Levy, 1975). The major contributor to the electrical conductivity of the clay-water mixture is the excess of ions at the interface of the clay-water mixtures. By definition, the difference between the conductivity in the range of the double

layer and that of the bulk solution is equal to the surface electrical conductivity.



**Figure 7.** Electrical conductivity of kaolinite as a function of frequency.

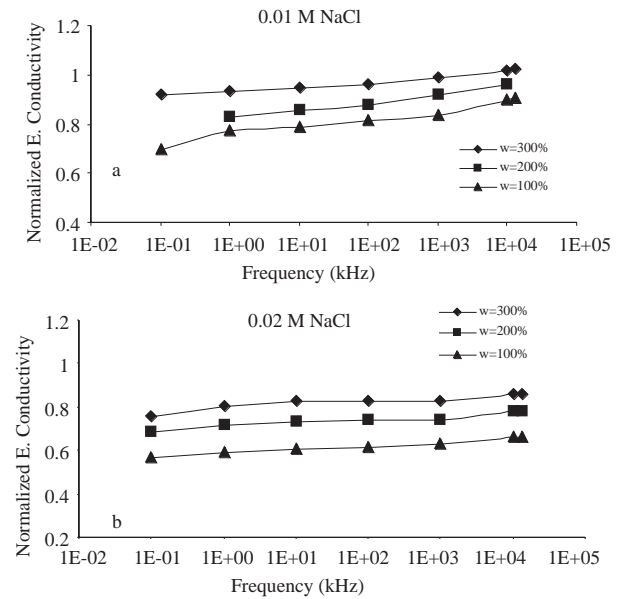
The way to determine the effect of the surface electrical conductivity on the measured electrical conductivity is to normalize the electrical conductivity (Figures 9 and 10). The normalized electrical conductivity of kaolin decreases as kaolin concentration increases in the clay-water mixture, as expected, because the electrical conductivity of the solid particles is much less than that of pore water. In contrast, the normalized electrical conductivity of bentonite increases as the solid concentration increases in the mixture. This suggests that the contributions of the surfaces to the measured electrical conductivity are different for kaolin and bentonite. To determine the



**Figure 8.** Electrical conductivity of bentonite as a function of frequency.

validity of this statement, the electrical conductivity was normalized at a constant solid concentration (Figures 11 and 12). Note that the normalized electrical conductivity values of bentonite are much higher than those of kaolin. Note also that normalized electrical conductivity values are  $<1$  for kaolin and  $>1$  for bentonite, which indicates that surface interaction, and thus surface electrical conductivity, does not occur in kaolin. However, for bentonite, most electrical conductivity occurs on the surface of the particles. Surface electrical conductivity is mainly a result of the polarization of the diffuse double layer. This occurs when the ion concentration is low, the thickness of the double layer is large, and the free ions outside the shear plane can move easily under an externally applied electrical field. However, as the concentration of the ions increases, the thickness of the diffuse double layer decreases because of the neutralization of the surface charges, which reduces the number of free ions. In turn, as the thickness

of the diffuse double layer shrinks, the contribution from the surface interaction to the surface electrical conductivity decreases, as indicated in Figure 12.

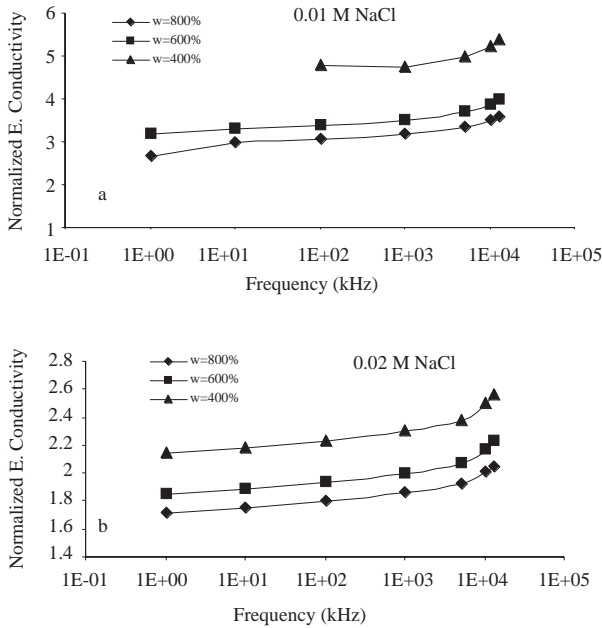


**Figure 9.** Normalized electrical conductivity of kaolinite (electrical conductivity of kaolinite-water is divided by that of pore water) with constant NaCl concentration with different solid concentrations.

## Practical Applications of Results

The present paper shows that the dielectric permittivity and electrical conductivity can be used to study the electrokinetic properties of clay minerals and to predict the interaction of ions with clay surfaces and the effect of this interaction on the measured electrical properties of clay-water mixtures. Conventional methodologies for the characterization of contaminated soil are expensive and time consuming (Fam and Santamarina, 1996; Soloyanis, 1996; Kayyal and Mohammed, 1997; Carrier and Soga, 1999). The advantage of this methodology is that, once the system is installed to measure the dielectric permittivity and electrical conductivity, spatial and temporal variations in the physicochemical state of fine-grained soils can be determined readily in a non-destructive manner. Consequently, this reduces the cost of data collection and the potential for contamination during sampling and testing. This system can be easily adapted to determine the performance of slurry walls constructed to confine contaminated

sites. Both sides of the slurry wall will have different dielectric permittivity and electrical conductivity as related to contaminant migration. Furthermore, both the dielectric permittivity and the electrical conductivity of pore fluids upstream and downstream can be measured, and the contamination source can be identified without elaborate testing procedures. Another potential application of this technique is in the assessment of growth of contaminant concentrations in the aqueous phase within specific locations in relatively intact barriers.



**Figure 10.** Normalized dielectric permittivity of bentonite (electrical conductivity of bentonite-water is divided by that of pore water) with constant NaCl concentration with different solid concentrations.

**Conclusions**

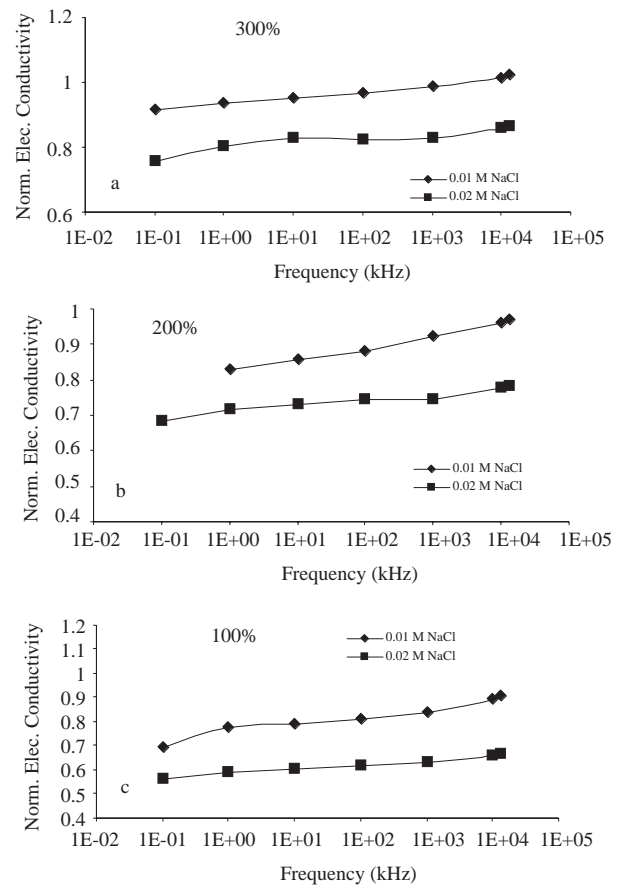
Based on the data presented, the following conclusions are made from this study:

1. Mainly that of pore water controls the dielectric permittivity of soil-pore water mixture. As the frequency at which measurements are taken increases, the dielectric permittivity of the soil-water mixture decreases.
2. As the ion concentration in the soil-water mixture increases, the dielectric permittivity of the mixture decreases at a high frequency range (MHz) whereas it increases at a low frequency range (kHz).
3. The electrical conductivity of the kaolinite-

water mixture is almost independent of frequency; however, that of the bentonite-water mixture is frequency dependent in such that bentonite-water mixture has higher electrical conductivity at a high frequency (MHz) than at a low frequency (kHz).

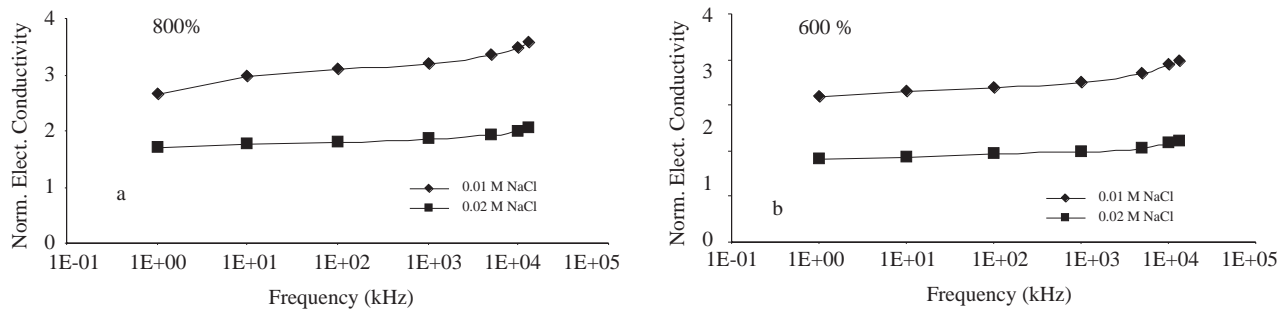
4. The electrical conductivity of kaolinite-water and bentonite-water increases with an increase in the ionic concentration in the mixture; however, the increase is soil mineral-type dependent. Surface electrical conductivity becomes dominant on the measured electrical conductivity of bentonite-water mixture.

5. The presented methodology can be used to determine spatial and temporal variations in the physicochemical state of subsurface contamination in a non-destructive manner.



**Figure 11.** Normalized electric conductivity of kaolinite (electrical conductivity of kaolinite-water is divided by that of pore water) at a constant solid concentration with different NaCl concentrations





**Figure 12.** Normalized dielectric conductivity of bentonite (electrical conductivity of bentonite-water is divided by that of pore water) at a constant solid concentration with different NaCl concentrations.

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