Environ Geol (2007) 51: 821–833
DOI 10.1007/s00254-006-0362-6

ORIGINAL ARTICLE

Myounghak Oh
Yongsung Kim
Junboum Park

Factors affecting the complex permittivity spectrum of soil at a low frequency range of 1 kHz–10 MHz

Received: 13 April 2006
Accepted: 25 May 2006

M. Oh
Coastal Engineering Research Department, Korea Ocean Research and Development Institute, Sa2-dong, Sangnok-gu, Ansan, Gyeonggi-do 426-744, South Korea

Y. Kim · J. Park (✉)
Department of Civil, Urban and Geosystem Engineering, Seoul National University, San 56-1, Shillim-dong, Gwanak-gu, Seoul 151-742, South Korea
E-mail: junbpark@snu.ac.kr
Tel.: +82-2-8808356
Fax: +82-2-8756933

Abstract To establish the factors affecting the permittivity spectrum of soil in the low frequency range, the complex permittivities of soils were measured at the frequency range of 1 kHz–10 MHz. The effects of frequency, water content, soil types and heavy metal contamination on the dielectric response were evaluated and their theoretical mechanisms were discussed. Measurement distortions such as electrode polarization in the low frequency measurements were identified. The permittivity of the soil was analyzed at frequencies above 100 kHz, which was experimentally determined to be the limiting lower frequency. The real permittivities of the soils were strongly related to the volumetric water content, since it is determined by the polarizability of the free water. The effective imaginary permittivities of soils increased with volumetric water content due to the increase in conduction losses. The spatial polarization and conduction loss were found to be the main mechanism in the real and effective imaginary permittivity, respectively. Since such mechanisms are influenced by the specific surface area of the soil particles, the presence of particles with high specific surface area in the soil matrix was found to affect the permittivity of soil. Contamination of saturated soil by cationic species resulted in decreases in the real permittivity due to the decreased orientation polarization of water molecules caused by hydration of ions, but increases in the effective imaginary permittivity due to ionic conduction.

Keywords Complex permittivity · Polarization · Volumetric water content · Heavy metal contamination

Introduction

Detection and monitoring subsurface contamination are essential processes for preventing potential environmental risks. Conventional approaches of investigating the subsurface contamination involve sampling of soil, pore fluid and/or soil gas followed by laboratory analysis (Okoye et al. 1995; Kaya and Fang 1997; Lee et al. 2003; Oh et al. 2003). Since such methods often require iterative and laborious work, many researchers have tried to develop non-destructive and cost-effective in situ methods. Detection and monitoring by means of measuring the electrical properties of soils is advantageous in that it can be performed quickly with little data processing needed to obtain accurate and repeatable results (Rinaldi and Cuestas 2002; Yoon et al. 2002). In particular, the measurement of the dielectric properties of soil may provide a solution, reducing the number of samples to be collected when used in conjunction to the conventional method of sampling and analysis. It would be advantageous to have an alternative technique that could be used to identify whether changes in the pore fluid chemistry have occurred; especially, this monitoring could be conducted inexpensively (Rowe et al. 2002). The method of measuring permittivity, which represents the dielectric properties of a material, is based on the idea that the measured permittivity reflects the physical and chemical properties of the material (Rowe et al. 2001).

The permittivity of soil–water mixtures in the megahertz range has been studied (e.g., Campbell 1990; Santamarina and Fam 1997; Gardner et al. 1998; Robinson et al. 1999). They suggested that monitoring the permittivity of soil-contaminant mixtures might be a promising method of contaminant detection (e.g., Darayan et al. 1998; Rowe et al. 2001, 2002; Francisca and Rinaldi 2003). However, the electrolytes used in the previous research were not the contaminant commonly found in the subsurface. Although heavy metals are some of the most common contaminants found in the subsurface, few data are available on their electrical properties. Furthermore, there have been only a few studies for geoenvironmental applications on permittivity measured at low frequencies. Probably, the main reason is the presence of measurement distortions such as electrode polarization (Rinaldi and Redolfi 1996). Permittivity is a frequency-dependent parameter, and low frequency permittivity measurements are advantageous in that: (1) in situ testing and permittivity monitoring can be carried out with little influence of cable impedance; (2) low frequency test devices are comparatively less expensive; and (3) tests can be performed with very simple capacitive cells (Rinaldi and Redolfi 1996). For successful application of permittivity measured at the low frequency range in the geoenvironmental field, factors affecting the permittivity including electrode polarization, frequency and soil properties and their polarization mechanisms should be identified. In addition, carefully collected permittivity database for soil and contaminants must be established at the low frequency range.

This study focuses on the factors affecting the dielectric response of soil–water mixtures in the low frequency range. In this paper, the complex permittivities of soils were measured at the frequency range of 1 kHz–10 MHz by means of using LCR meters. Device calibration and measurement procedures are described. The effects of measurement frequency, soil types, water content and contamination of pore water on the dielectric response were evaluated by analyzing the complex permittivity of specimen at low frequencies.

Complex permittivity and polarization

When a capacitor containing material is connected to a sinusoidal voltage source, all materials including soils have a loss current component which is in phase with the applied voltage (von Hippel 1954). The partially out-of-phase response of the materials due to the existence of the loss currents can be well described in terms of the complex permittivity (ε^*). The relative complex permittivity, which is normalized with respect to the permittivity of free space, can be represented by Eq. 1 (von Hippel 1954). In common usage, the word "relative" is frequently dropped (ASTM D150).

$$\kappa^* = \frac{\varepsilon}{\varepsilon_0} = \kappa' - i\kappa'' \tag{1}$$

In Eq. 1, ε_0 is the permittivity of the free space ($= 8.85 \times 10^{-12}$ F/m) and i denotes an imaginary number.

The real part of the complex permittivity (κ') is commonly called the permittivity or dielectric constant of a material and represents the capacitive behavior or polarizability of the material. The imaginary part (κ'') is called the loss factor and represents the energy losses due to polarization and conduction (Kaya and Fang 1997; Shang et al. 2000). In the permittivity measurement, losses due to polarization and conduction are measured together (Santamarina et al. 2001). Hence, the effective imaginary permittivity $\left(\kappa''_{\text{eff}}\right)$ becomes Eq. 2.

$$\kappa''_{\text{eff}} = \kappa'' + \frac{\sigma}{\varepsilon_0 \omega} \tag{2}$$

where σ is zero-frequency current (DC) conductivity, ω is the angular frequency ($= 2\pi f$) and f is the frequency.

When an electric field is applied to a medium, some charges are bound, yet these positive and negative charges can move locally relative to each other, which results in a polarized medium. The polarizability of the medium is represented by permittivity. In other words, permittivity is a measure of the extent to which the electrical charge distributed in a material can be polarized by the application of an electric field. The spectral response of permittivity with frequency captures the various polarization mechanisms (Kingery 1963; Santamarina and Fam 1997). In single-phase and homogeneous materials, there are three types of polarization mechanisms: (1) electronic polarization due to the displacement of an electronic cloud around an atom, (2) ionic polarization due to the relative displacement of atoms in a molecule and (3) orientational polarization involving the rotation of dipolar or polarized molecules (Kingery 1963; Santamarina and Fam 1997; Santamarina et al. 2001). Polarization mechanisms display one of two characteristic spectra such as resonance or relaxation at characteristic frequencies. Electronic polarization manifests as a resonance at ultraviolet frequencies (10^{14}–10^{16} Hz). Ionic polarization manifests as a resonance at infrared frequencies (10^{11}–10^{12} Hz). Orientational polarization is evident as a relaxation at microwave frequencies (10^{9}–10^{11} Hz) (Santamarina et al. 2001). The contribution of a given polarization mechanism remains at frequencies lower than its characteristic frequency. Therefore, polarizations from different mechanisms accumulate towards lower frequencies, which implies that the polarizability of single-phase materials at low frequencies is the sum of electronic, ionic and orientational polarizations (von Hippel 1954; Carrier and Soga 1998; Santamarina et al. 2001; Lee et al. 2003).

In multi-phase materials, the predominant polarization mechanism is spatial polarization, which is also known as interfacial polarization or Maxwell–Wagner polarization. This mechanism results from the differences in the polarizability and conductivity among each component composing the material (Santamarina and Fam 1997). In such a condition, charges accumulate at the interfaces to maintain the same current density throughout the contiguous layers (Santamarina et al. 2001). Accumulation of charges at the component interface appears as an increase in the capacitance of the material. Spatial polarization manifests as a relaxation spectra of real permittivity at radio frequencies because the accumulation of charges under an alternating current field is strictly time dependent. Compared with other polarization mechanisms in single-component materials, this polarization mechanism has a very large spatial scale.

Experimental description

Test material

Jumunjin sand and weathered granite soil were used to investigate the permittivity of soil in this study. Jumunjin sand is a commercially available silica sand in Korea. Weathered granite soil is a typical field soil commonly found in the Korean peninsula. The test soil was collected from the vicinity of the Seoul National University, Korea, and thus is hereafter termed "SNU soil" to clarify sample designation. Additionally, to examine the effects of clay particles on the electrical properties of soil, kaolinite and bentonite were also used in this study. The basic physical properties of the test soils are summarized in Table 1.

Mercury (Hg) and lead (Pb) were used in this study as the cationic heavy metals due to their importance as environmental contaminants. Besides heavy metals, aluminum (Al) with different valence and atomic weight were included as cationic species. The index properties of cationic species used in this study are summarized in Table 2.

Test method

Low frequency (Hz to low MHz) permittivities were measured in capacitor-type cells to subject the material to an alternating electric field. The capacitor-type cell was carefully designed to measure the permittivity of the soil–water mixture in this study. Basically, the cell is comprised of a pair of parallel plate electrodes which sandwich the material under measurement to form a capacitor. The two brass electrodes installed in the acrylic mold containing the soil under study were 70 mm in diameter and 20 mm apart.

The soils were air-dried, sieved through a No. 10 sieve, and then oven dried at 105°C for 24 h. The soils were then thoroughly mixed with tap water at different water contents before being placed into the acrylic mold. To achieve the desired dry density, soil was compacted in the acrylic mold taking the sample homogeneity into consideration.

The capacitance and resistance of the materials were measured using the HP4285A LCR meter (Hewlett-Packard, USA) in the range of 100 kHz–10 MHz and the Agilent 4263B LCR meter (Agilent Technologies

Table 2 Index properties of cationic species used in this study

	Mercury (Hg)	Lead (Pb)	Aluminum (Al)
Atomic number	80	82	13
Atomic weight	200.59	207.2	26.98
Ionic valence	+1	+2	+3
Atomic radius (Å)	1.50	1.75	1.43
Ionic radius (Å)	1.27	1.20	0.51

Source: Oxtoby and Nachtrieb (1996)

Table 1 Index properties of the test soils

	Jumunjin sand	SNU soil	Kaolinite	Bentonite
Specific gravity	2.64	2.60	2.59	2.60
Specific surface area (m^2/g)		3.95	7.39	40.78
Liquid limit	–	–	44.4	393
Plasticity Index	NP	NP	23.3	351
Sand fraction (% by wt.) (0.075–4.75 mm)	100	92.5	0	0
Silt/clay fraction (% by wt.) (< 0.075 mm)	0	7.5	100	100
Unified Soil Classification System	SP	SW	CL	CL

NP Non-plastic

Japan, Ltd.) in the range of 1 kHz–100 kHz. The electrodes of a capacitor-type cell are connected to a bridge-type measuring system. As shown in Fig. 1, a two-terminal electrode system acts as both current and potential terminals: high current H_c, high potential H_p, low current L_c and low potential L_p connectors. The electrical properties of the specimens were determined by measuring the potential difference between the H_p and L_p terminals, while the current was applied across the H_c and L_c electrodes. A sinusoidal excitation was imposed and measurements were repeated at different frequencies. The real and effective imaginary permittivity were obtained using the following equations (Agilent Technologies 2000):

$$\kappa' = \frac{C_s}{C_0} = \frac{C_s}{\varepsilon_0 \times (A/d)} \tag{3}$$

$$\kappa''_{\mathrm{eff}} = \frac{1}{\omega \varepsilon_0 R \times (A/d)} \tag{4}$$

where A is the area of the electrodes, d is the distance between the electrodes, R is the measured resistance, ω is the angular frequency ($= 2\pi f$) and f is the frequency.

Calibration

In permittivity measurements, residual impedance and stray admittance develop in series and parallel with the specimen under test as shown in Fig. 1. To remove such unwanted parameters apparent in the wire and clip leads, standard short and open circuit calibrations were performed. This is a common technique by which compensation is made by measuring the stray admittance (Y_o) and residual impedance (Z_s).

In addition to the residual impedance and stray admittance, edge capacitance, which develops at the fringe of the specimen, must also be compensated when parallel plate electrodes are implemented. Due to the development of such undesirable electric current flow, the measured capacitance is larger than the actual capacitance of the material. When the two parallel plate electrodes have an identical diameter which is smaller than that of the test specimen, the edge capacitance can be computed by using the following equation (ASTM D150 1994):

$$C_e = (0.0019\kappa' - 0.00252 \ln d + 0.0068)\pi(2r + d) \tag{5}$$

where C_e is the edge capacitance [pF], r is the radius of the circular electrode (mm), and d is the thickness of the specimen (mm).

Therefore, the capacitance of a specimen (C_s) can be obtained by subtracting the edge capacitance (C_e) from the measured capacitance (C_m).

Finally, measurements in the capacitor-type cell were calibrated using materials of known permittivity. Air, carbon tetrachloride (CCl_4), methanol and deionized water were selected as materials that exhibit real permittivity values of 1, 2.17, 31 and 79 (von Hippel 1954), respectively, at a constant temperature of 20°C at frequencies used in this study.

Electrode polarization effect

The current in the electrodes, cables and in the measurement device involves electron flow, while the current in the materials takes the form of ionic flow. Given the incompatibility among charges, charge accumulation occurs at the electrode–specimen interface (Santamarina et al. 2001). The accumulation of charge resembles a double layer, which is called electrode polarization. In two-terminal electrode systems, electrode polarization occurs at frequencies below a few tens of kilohertz as discussed by Dias (1972). Electrode polarization causes an increase in the measured real permittivity values, and its effect is magnified with decreasing frequency. Such an increase in real permittivity due to electrode polarization is not representative of material properties (Santamarina et al. 2001).

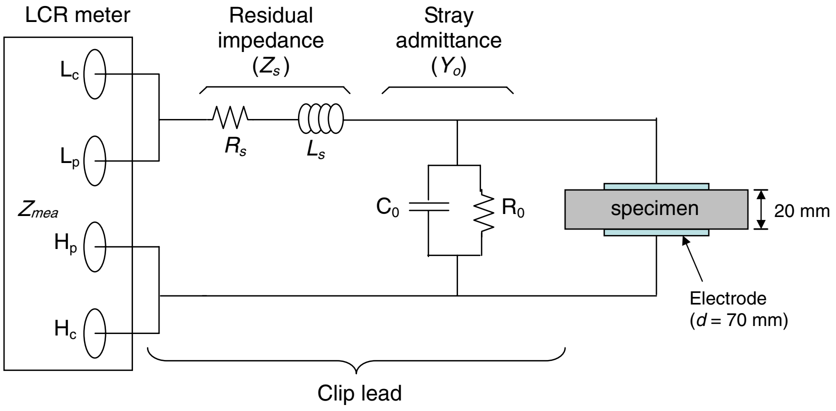


Fig. 1 Schematic diagram of two-terminal electrode system and equivalent circuit of residual and stray parameters (modified after Klein and Santamarina 1997; Agilent Technologies 2000)

Figure 2 shows results from two-terminal electrode measurements performed on deionized water, tap water and potassium chloride (KCl) solutions. The electrical conductivity of tap water, and 0.1 and 1 mM potassium chloride solutions were 201.7, 17.15 and 161.2 μS/cm, respectively. Electrode polarization, which increases the measured real permittivity values with decreasing frequency, was observed at lower frequencies. In solutions which have ionic constituents, measurement errors can occur due to the formation of an electrical double layer between the electrode surface and the solution. The minimum frequency at which electrode polarization does not significantly affect the real permittivity measurements is known as the limiting lower frequency. The limiting lower frequency is proportional to the ionic conductivity of the material; therefore, highly conductive materials are affected by electrode polarization at higher frequencies than less conductive materials. As shown in Fig. 2, the permittivity values at frequencies less than approximately 100 kHz, which is the estimated limiting lower frequency, were affected by electrode polarization.

Several methods have been suggested to eliminate or minimize the effect of electrode polarization: use of reversible electrodes (Scott et al. 1967), measurements at two different specimen lengths (Hill et al. 1969), an insulating layer method (Gross and McGehee 1988) and substitution techniques (Hill et al. 1969). However, based on the analysis of these methods applied to equivalent circuit models, Santamarina et al. (2001) reported that these methods are mostly ineffective and unreliable when applied to equivalent circuit models because they contribute to the uncertainty in the results. Therefore, permittivity was analyzed at frequencies above 100 kHz to exclude electrode polarization effect in this study.

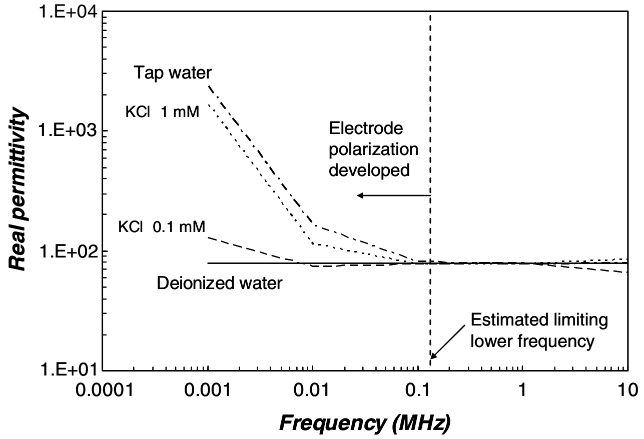


Fig. 2 Spectral responses and electrode polarization effect in the real permittivity measurement

Results and analysis

Influence of measurement frequency

Single-component, homogeneous materials have almost constant permittivity values at frequencies below approximately 1 GHz. Their values are equal to the sum of the permittivity values from three different types of polarization mechanisms: electronic, ionic and orientational polarization. Table 3 shows the real permittivities of some representative materials. The measured real permittivity values of the selected materials were within 1% deviation to the reference values. In addition, the real permittivity values of the selected materials showed no significant spectral features at frequencies used in this study since the measured frequencies were lower than the molecular relaxation frequency.

However, the permittivity of soil–water mixtures was influenced by the frequency of the applied electric field. Figure 3 shows the spectral responses of the real and effective imaginary permittivities, and alternating current (AC) conductivity for test soils at a constant porosity.

The real permittivity of soils tended to decrease with increasing frequency; this is commonly known as the relaxation behavior (Mitchell and Arulanandan 1968; Campbell 1990; Santamarina and Fam 1997; Klein and Santamarina 1997). The decrease in the real permittivity of wet soil suggests a relaxation extending across the kHz region up to almost 10 MHz. This can be inter-

Table 3 Real permittivity values of selected materials

Materials		Real permittivity measured in this study			Reference values
		100 kHz	1 MHz	10 MHz	
Deionized water		78.4	78.0	79.2	79[a]
Carbon tetrachloride		2.26	2.27	2.19	2.16–2.23[b]
Methanol		30.8	31.6	31.6	31[a]
Oven dried soil	Jumunjin sand	3.75	3.52	2.77	3–5[c]
	SNU soil	4.27	3.92	3.00	

[a] Source: von Hippel (1954)
[b] Source: von Hippel (1954), Rinaldi and Redolfi (1996)
[c] Source: von Hippel (1954), Selig and Mansukhani (1975)

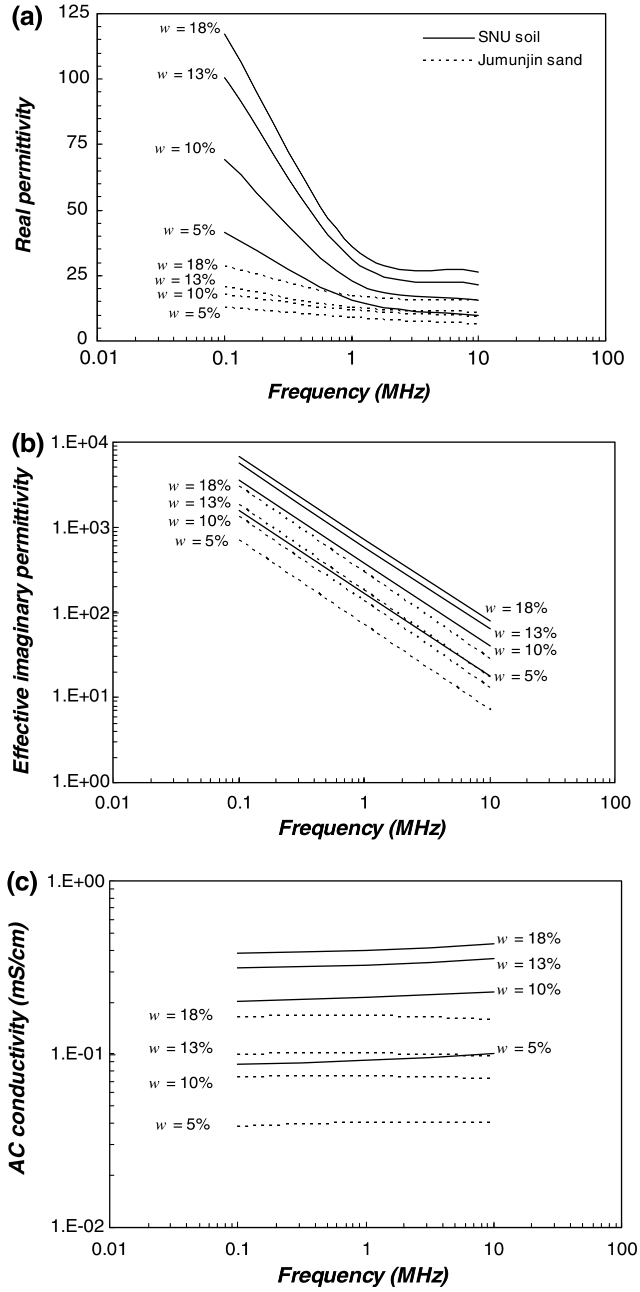


Fig. 3 Spectral responses with measurement frequency of complex permittivity and conductivity for test soils with different gravimetric water content (porosity of Jumunjin sand and SNU soil are 0.45 and 0.40, respectively): **a** real permittivity, **b** effective imaginary permittivity and **c** AC conductivity

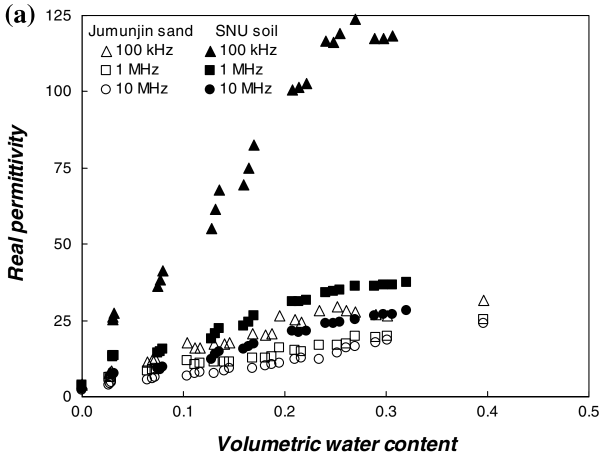
preted as a result from the development of spatial polarization which manifests as a relaxation response at low frequencies, even though the individual components of soil samples have a constant permittivity value within this frequency range. This polarization mechanism in soils develops at the interface between the pore fluid and the soil particle or air due to ionic migration. When the ionic charge carriers are impeded in their motion because they become trapped at such interfaces, space charge and macroscopic field distortions result. Such distortions appear as increases in the capacitance of the sample. In addition, such relaxation behavior of the soils studied was more evident in specimens with higher gravimetric water contents. Campbell (1990) reported that the decreases in real permittivity with respect to frequency depend on the water content. Soils with a higher gravimetric water content at a constant porosity have greater areas of soil–fluid interfaces. Increasing the soil–fluid interfaces of soils could magnify the spatial polarization at low frequencies.

As illustrated in Fig. 3b, the effective imaginary permittivities of both Jumunjin sand and SNU soil decreased as the frequency increased. The effective imaginary permittivity is a parameter which represents the losses due to both polarization and conduction and is inherently a frequency-dependent parameter as shown in Eq. 4. Although all materials experience the two types of losses mentioned above, Rinaldi and Francisca (1999) reported that loss from conduction has a greater effect than that from polarization on the effective imaginary permittivity. Their finding was based on the analysis of the contribution of conductivity and polarization loss of water molecules in the impedance plane. Linear decreases in the effective imaginary permittivity with increasing frequency on the log–log scale signify that the effect of electric conduction is dominant in the total energy loss at frequencies used in this study, and the contribution of polarization losses is not considerable. In addition, although AC conductivity includes DC conductivity and the dynamic effects of polarization which are affected by frequency (Santamarina et al. 2001), variations in AC conductivity with frequency are negligible (Fig. 3c). These results imply that polarization effects were not significant at frequencies used in this study. Therefore, the decreases in effective imaginary permittivity with frequency can be interpreted as follows: the higher the frequency, the lower the effect of conduction loss.

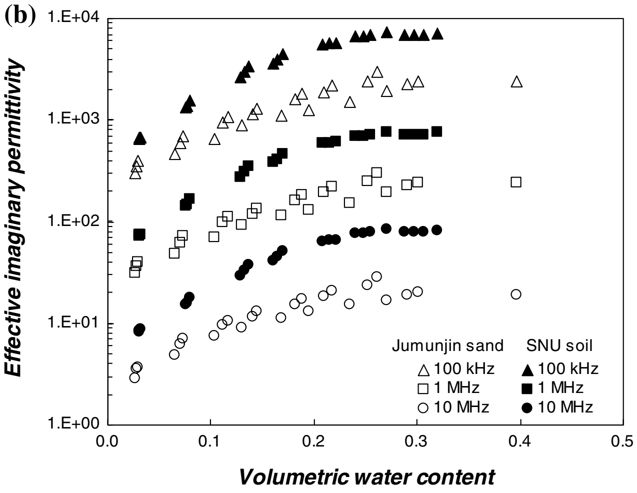
Influence of water content

Permittivity of a given soil can be conveniently expressed in terms of the volumetric water content since it is proportional to the number of dipole moments per unit volume (Topp et al. 1980; Santamarina et al. 2001; Lee et al. 2003). The volumetric water content (θ_v) is the ratio of the volume of pore water to the total volume of soil.

The real and effective imaginary permittivities of test soils as a function of volumetric water content at 100 kHz, 1 MHz and 10 MHz frequencies are shown in



Real permittivity



Effective imaginary permittivity

Fig. 4 Relationship between complex permittivity and volumetric water content for the Jumunjin sand and SNU soil at the frequency of 100 kHz, 1 MHz and 10 MHz: **a** real permittivity and **b** effective imaginary permittivity

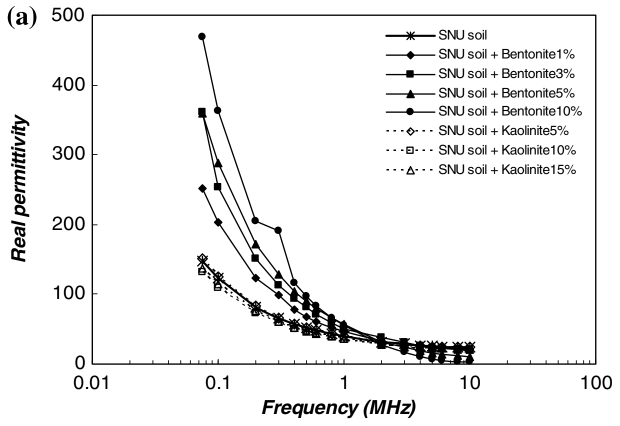
Fig. 4. As illustrated in Fig. 4a, the real permittivity of the soil increased with increasing volumetric water content and decreasing frequency. The real permittivity of soil is determined primarily by the polarizability of the free water. When an external electric field is applied to a soil sample, water molecules (permanent electric dipole) tend to orient themselves such that the positive and negative poles face the electrodes of opposite charge. Also, the negative electron cloud around the oxygen nucleus is deformed or polarized under the electric field. Thus, an induced dipole is formed which contributes to the overall moment in addition to the moment from permanent dipoles. An increase in the volumetric water content means an increase in the number of the permanent electric dipoles which are responsible for orientational polarization. Therefore, the real permittivity of the soil is significantly affected by the amount of water, which acts as permanent dipoles. In Fig. 4b, the effective imaginary permittivity of the soil increases with increasing volumetric water content and decreasing frequency. Increases in the effective imaginary permittivity of soils with volumetric water content can be explained by the increase in conduction loss. This is evidenced by the AC conductivity data (Fig. 3c). A higher volumetric water content enhances the connectivity of pore fluids which act as electric current pathways, consequently leading to a greater amount of conduction losses.

In Fig. 4a, high values of real permittivity at low frequencies imply that the spatial polarization, which was formed in the mixture at low frequencies, still affects the permittivity of the soil. The effect of spatial polarization was more dominant in the SNU soil than in the Jumunjin sand. Especially, the real permittivity of the SNU soil at 100 kHz exceeds the permittivity of water. Development of spatial polarization at low frequencies indicated that permittivity versus volumetric water content varied according to the frequency bands studied. However, real permittivity is determined by the polarizability of the free water at higher frequencies, which is why the real permittivity of the wet soils increases continuously with volumetric water content.

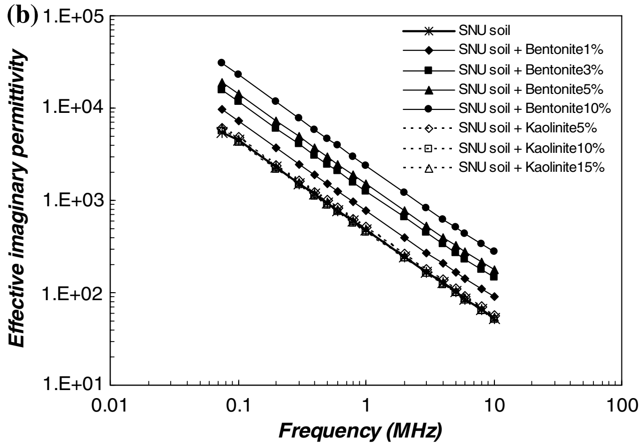
Influence of soil types

Figures 3 and 4 show that the SNU soil gave higher values of real permittivity than the Jumunjin sand, which may be a result from the differences in the fine grain. Sieve analysis revealed that the SNU soil was a well-graded soil with appoximately 7.5% fine grain content ($<$ 0.075 mm). Therefore, it is conceivable that the SNU soil is more likely to have a greater amount of soil–fluid interface. A greater area of soil–fluid interface increases the development of spatial polarization at low frequencies.

Introduction of clay into the soil matrix alters the permittivity of the soil. Figure 5 shows the complex permittivity of SNU soils mixed with bentonite and kaolinite, respectively. The real permittivity values of SNU soil–kaolinite mixtures were not varied, regardless of kaolinite content in the soil sample, while that of the bentonite-mixed SNU soils showed significant relaxation with the measurement frequency. The relaxation behavior was primarily due to spatial polarization and was related to the specific surface area. The real permittivity increased at frequencies below 2 MHz, but decreased at frequencies above 2 MHz with increasing bentonite content. The real permittivity at lower frequencies tended to increase because of spatial polarization which develops at the



real permittivity



Effective imaginary permittivity

Fig. 5 Complex permittivity of soil with different bentonite or kaolinite content (% by weight) at constant volumetric water content ($\theta_v = 0.23$): **a** real permittivity and **b** effective imaginary permittivity

component interfaces. Therefore, the permittivity of soils with high specific surface area can be considered to be strongly affected by electrical phenomena at the fluid–soil interface. However, as the frequency increases, the contribution of spatial polarization to the permittivity decreased. Therefore, it can be understood that polarizations other than spatial polarization (e.g. orientational polarization) are comparably more determining mechanisms of the permittivity of soil at relatively high frequencies.

Increasing the soil–water interface area is not the only reason for the change in the permittivity of soil with bentonite content. High bentonite contents or high specific surface areas in soils lead to increased amount of adsorbed water, and consequently decreased amount of free water. Such conditions of water molecules in soil also affect the permittivity of soil–water mixtures. The permittivity of tightly bound water near the mineral surface is assumed to be similar to that of ice (Dobson et al. 1985; Campbell 1990; Saarenketo 1998). Thus, the polarizability of adsorbed water is less than that of free water (Santamarina et al. 2001). Therefore, the reduction in real permittivity at frequencies above 2 MHz can be attributed to the decrease in the amount of free water, which governs orientational polarization.

Although the increase in effective imaginary permittivity from kaolinite content was almost negligible as shown in Fig. 5, the effective imaginary permittivity increased significantly with bentonite content in the soil specimen as shown in Fig. 5b. In clay particles, the ionic mobility in the diffuse part of the double layer is identical to that in the bulk electrolyte. Thus, ions in the counter-ion clouds near particle surfaces contribute to surface conduction in addition to the bulk fluid conduction in the pore space. Such development of surface conduction in soil–fluid mixtures is directly related to the specific surface area of the soil particle. Soils containing particles with low specific surface area have negligible amount of surface conduction, but soils containing clay particles with high specific surface area have dominant amount of surface conduction through the adsorbed water layer. The increase in imaginary permittivity with bentonite content can be interpreted as a result of increased conduction loss due to surface conduction of bentonite particles.

Effect of heavy metal contamination

Permittivity of cationic aqueous solution

The effect of cationic concentration on the complex permittivity was explored. The spectral responses of permittivity for solutions with cationic species including Hg, Pb and Al at the frequency range of 10 kHz–10 MHz are shown in Fig. 6. The increases of real permittivity at 10 kHz were caused by electrode polarization effects as mentioned earlier. At higher frequencies above 100 kHz where the effect of electrode polarization may be ignored, significant decreases in real permittivity were observed with increasing concentration for all cationic species as shown in Fig. 6. The decrease in real permittivity with concentration reflects the reduced mobility of water molecules involved in ion hydration. Ions dissolved in water may influence the molecular interaction between water and ionic species. Water molecules may be firmly bonded to the ions and behave like electrolyte molecules (Hill et al. 1969). The hydration of salts renders hydrated ions, which are surrounded by water molecules with hindered polarizability. Water involved with hydrating ions makes a lower contribution to global polarization than free water, resulting in lower real permittivities of electrolyte solutions at higher concentrations (Santamarina

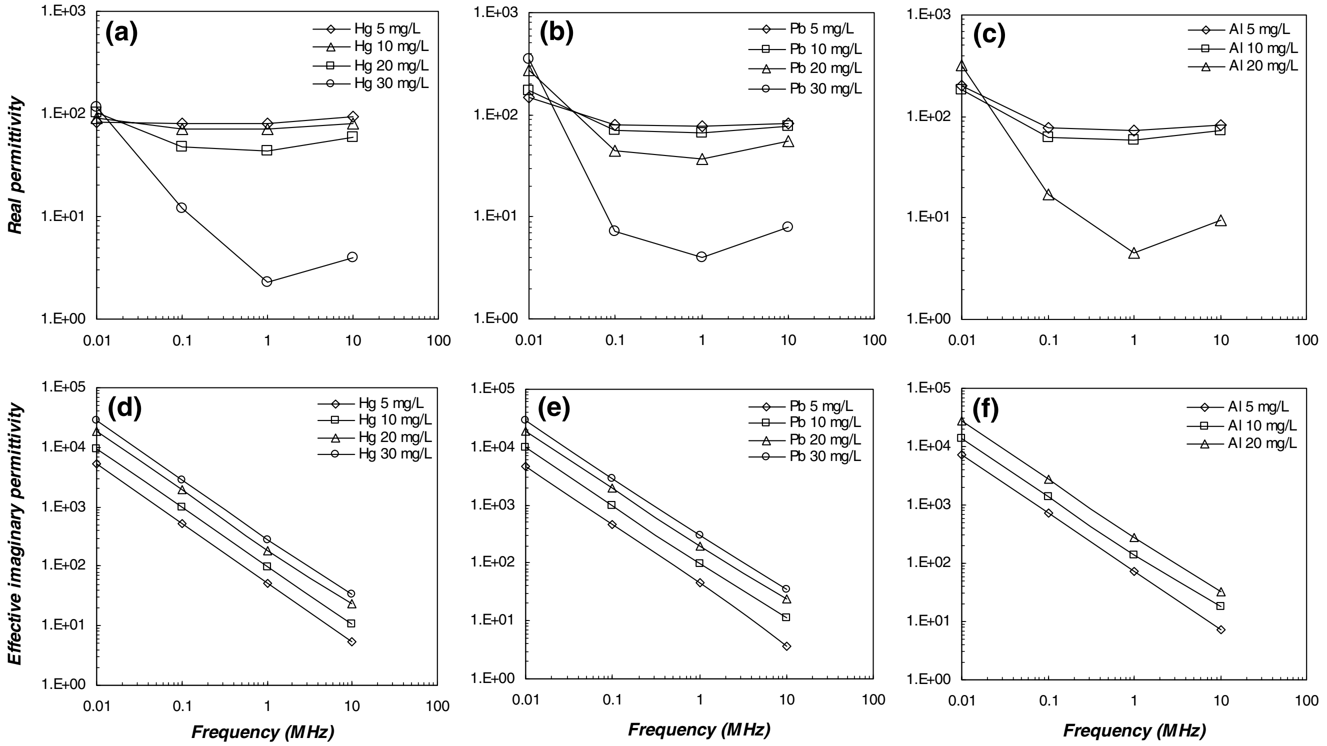


Fig. 6 Spectral responses for complex permittivity spectra of Hg, Pb and Al aqueous solutions

et al. 2001). The effective imaginary permittivity increases with the increase in electrolyte concentration. The effective imaginary permittivity data capture both conduction and orientational polarization losses. Above all, the increase in the effective imaginary permittivity of solutions with increasing ionic concentration is primarily due to higher DC conduction losses. Electric conduction is enhanced by free movement of cationic species since ionic constituents act as charge carriers.

Permittivity of soil mixed with cationic species aqueous solution

The spectral responses of complex permittivity for Jumunjin sand mixed with cationic aqueous solutions are presented in Figs. 7 and 8. In the case of real permittivity for saturated Jumunjin sand ($\theta_{\mathrm{v}} = 0.39$), addition of aqueous cations to a concentration of 50 mg/L in the pore solution caused significant decreases in the real permittivity. Such results are similar to those observed for cationic aqueous solutions. Identical interpretation may be applied in that hydration of cations is responsible for the reduced orientation polarization of water molecules in soils saturated by cationic solutions. For unsaturated Jumunjin sand ($\theta_{\mathrm{v}} = 0.13$), the real permittivity showed no distinctive behavior against cationic species concentration in the pore solution. It is implied that such result is due to the low volumetric content of the aqueous phase which experiences reduced orientation polarization from cation hydration.

While the decreases in the real permittivity was evident even at a low cationic concentration of 20 mg/L for cationic solutions, such tendency prevailed at a comparably high cationic concentration of 50 mg/L for saturated Jumunjin sand. It is noted that unlike cationic solutions which are single-phased, which of the effects has a very large spatial polarization must also be considered in understanding the spectral response of soils. Spatial polarization is a result of the differences in the polarizability among components, which produce charge accumulation in the interface between pore fluid and soil particles or air (Santamarina et al. 2001). Especially in unsaturated soils where air is present in the pore volume to create a greater area of phase interface than in saturated soils, spatial polarization is the mechanism that has a dominant control over the real permittivity.

Figures 7 and 8 also show that the cationic concentration increases the effective imaginary permittivity of Jumunjin sand over the entire frequency range studied. Such tendency of increase was more apparent in soils with greater volumetric water content. The effective imaginary permittivity increases with concentration reflecting the increase in electrical conductivity of the fluid since the effective imaginary permittivity is primarily due to conduction losses.

Figure 9 shows the changes in relative variation, defined as the ratio of permittivity of the contaminated soil

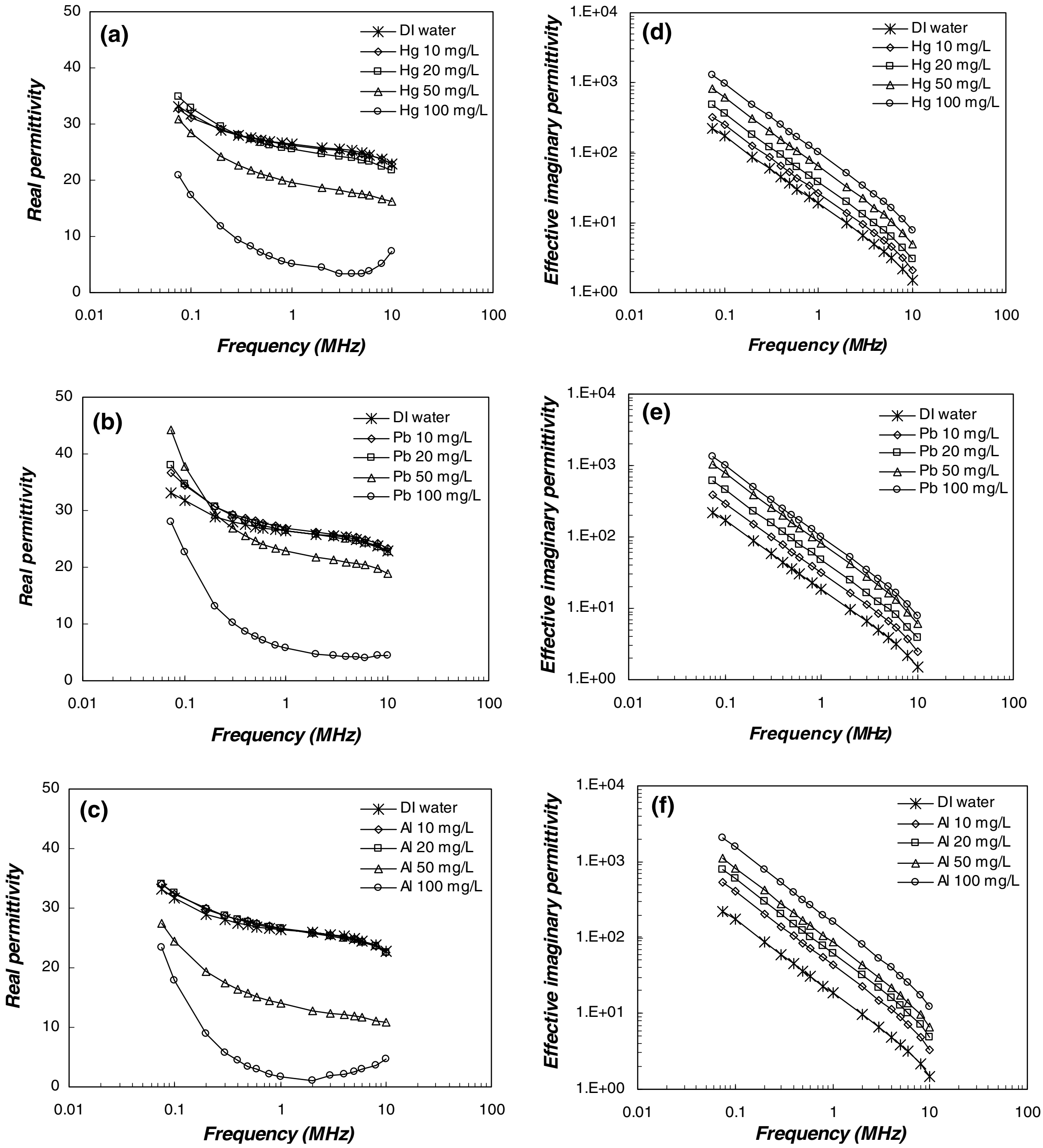


Fig. 7 Spectral responses of complex permittivity spectra for the saturated Jumunjin sand (θ_v = 0.39) mixed with cationic species aqueous solution

to that of uncontaminated soil, according to different ion types and their concentrations. It was observed that soil samples mixed with Al show the largest decrease in real permittivity with concentration. This can be interpreted in terms of hydration radius which is dependent on the polarizing power of the cationic species. Higher the polarizing power, which is equivalent to electrostatic charge over ionic radius, more layers of solvent are attracted to the cation in hydration. Of the three cationic species studied, Al has the greatest polarizing power and thus involves with a greater number of water molecules for hydration, consequently bringing about a greater decrease in the real permittivity. In the case of effective imaginary permittivity, it was observed that soil samples mixed with Al show the largest change with concentration, followed by Pb and Hg (refer to Fig. 9). Such differences observed may be attributed to the inverse of ionic radius (see Table 2). From a microscopic view-

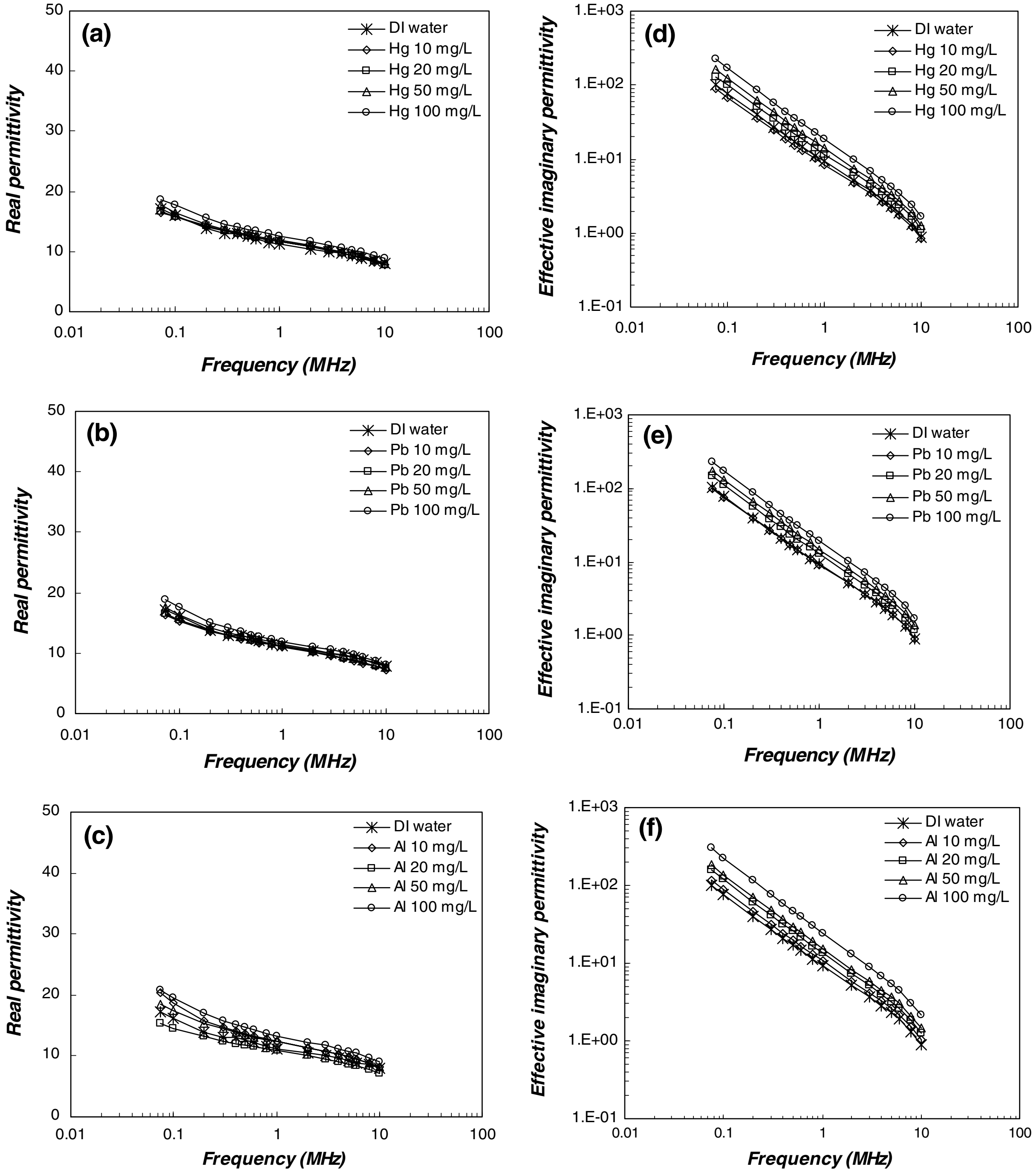


Fig. 8 Spectral responses of complex permittivity spectra for the unsaturated Jumunjin sand ($\theta_v = 0.13$) mixed with cationic species aqueous solution

point, ionic radius is inversely proportional to ionic mobility (Oxtoby and Nachtrieb 1996) and higher ionic mobility means higher electrical conductivity under the assumption that electrolyte is relatively homogeneous and thus the movement of ions is free.

Test results indicate that the variations in permittivity of soil due to cationic species may be applicable for a monitoring or detection system. Both real permittivity and effective imaginary permittivity are clearly more effective as a parameter indicating presence of cationic species when the target soil under study is fully saturated. Providing the background values on various soil types and water contents, it is highly probable that permittivity measurement method

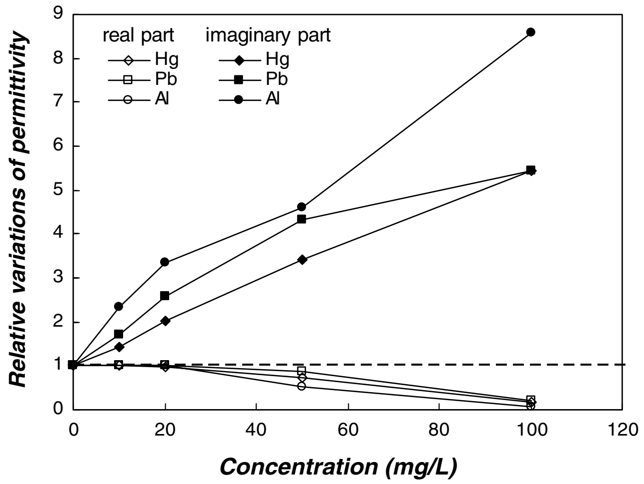


Fig. 9 Relative variations of complex permittivity measured at 1 MHz for the Jumunjin sand mixed with different cationic species aqueous solutions

can be used for detecting the cationic species in the subsurface.

Conclusions

In order to identify the factors affecting the dielectric response of soil–water mixtures in the low frequency range, complex permittivity of soils were measured in the frequency range of 1 kHz–10 MHz. From the results, the following conclusions have been derived:

1. Electrode polarization was observed at frequencies below ≈ 100 kHz. Electrode polarization is an inherent measurement distortion in a two-terminal electrode system. Therefore, in measurement of real permittivity at low frequencies, the effects of electrode polarization and the limiting lower frequency on real permittivity should be identified.
2. The real permittivities of the soils were strongly related to the volumetric water content since the real permittivity of the soil is determined by the polarizability of the free water. The effective imaginary permittivities of soils increased with volumetric water content due to the increase in conduction losses by pore water. These results indicate that the complex permittivity can indicate the volumetric water content and can be a promising tool for monitoring water content. For permittivity measurement to have a high applicability in the field, a sufficient amount of data is required to validate the relationship between complex permittivity and volumetric water content for various types of soils.
3. Presence of fine particles with high specific surface area magnifies spatial polarization at low frequencies (kHz ranges), but leads to reduction in the real permittivity from the decrease in free water at high frequencies (MHz range). The effective imaginary permittivity increased due to the development of surface conduction through the adsorbed water layer of soil particles. Since such mechanisms were influenced by the specific surface area of the soil particles, the presence of particles with high specific surface area in the soil matrix affect the permittivity of soil.
4. Presence of cationic species in the pore solution was a factor which brought about decreases in the real permittivity and increases in the effective imaginary permittivity. Such tendencies were found to be more evident in saturated. While reduced orientational polarization from hydration of ions was found to be responsible for the decreases in real permittivity, increases in the effective imaginary permittivity were due to losses from ionic conduction. Providing the background values on various soil types and water contents, permittivity measurement may be employed as a means of detecting cationic species in the subsurface.

Acknowledgements This work was supported by grant No. R01-2002-000-00136-0 from the Basic Research Program of the Korea Science and Engineering Foundation.

References

Agilent Technologies (2000) Impedance measurement handbook, 2nd edn. Agilent Technologies Co. Ltd

ASTM D150 (1994) Standard test methods for AC loss characteristics and permittivity (dielectric constant) of solid electrical insulation, ASTM D150–94, Philadelphia

Campbell JE (1990) Dielectric properties and influence of conductivity in soils at one to fifty megahertz. Soil Sci Soc Am J 54:332–341

Carrier M, Soga K (1998) Dielectric measurements of clay as a potential method of contaminant. In: Proceedings of the 3rd international congress on environmental geotechnics, Lisboa, Portugal, pp 491–496

Darayan S, Liu C, Shen LC, Shatthuck D (1998) Measurement of electrical properties of contaminated soil. Geophys Prospect 46:477–488

Dias CA (1972) Analytical model for a polarizable medium at radio and lower frequencies. J Geophys Res 77(26):4945–4956

Dobson MC, Ulaby FT, Hallikainen MT, El-Rayes MA (1985) Microwave dielectric behaviour of wet soil: Part II. Dielectric mixing models. IEEE Trans Geosci Remote Sens 23(1):35–46

Francisca FM, Rinaldi VA (2003) Complex dielectric permittivity of soil-organic mixtures (20 MHz–1.3 GHz). J Environ Eng 129(4):347–357

Gardner CMK, Dean TJ, Cooper JD (1998) Soil water content measurement with a high-frequency capacitance sensor. J Agric Eng Res 71:395–403

Gross GW, McGehee RM (1988) The layered-capacitor method for bridge measurements of conductive dielectrics. IEEE Trans Electr Insul 23:387–396

Hill NE, Vaughan WE, Price AH, Davies M. (1969) Dielectric properties and molecular behaviour. Van Nostrand Reinhold, London

von Hippel AR (ed) (1954) Dielectric materials and applications. The Technology Press of Massachusetts Institute of Technology

Kaya A, Fang HY (1997) Identification of contaminated soils by dielectric constant and electrical conductivity. J Environ Eng 123(2):169–177

Kingery WD (1963) Introduction to ceramics. Wiley, New York

Klein K, Santamarina JC (1997) Methods for broad-band dielectric permittivity measurements (soil–water mixtures, 5 Hz to 1.3 GHz). Geotech Test J 20(2):168–178

Lee JH, Oh MH, Park J, Lee SH, Ahn KH (2003) Dielectric dispersion characteristics of sand contaminated by heavy metal, landfill leachate and BTEX. J Hazard Mater B105:83–102

Mitchell JK, Arulanandan K (1968) Electrical dispersion in relation to soil structure. J Soil Mech Found Div 94(SM2):447–471

Oh MH, Lee JH, Yoon GL, Park J (2003) Pilot-scale field model tests for detecting landfill leachate intrusion into the subsurface using a grid-net electrical conductivity measurement system. Environ Geol 45:181–189

Okoye CN, Cotton TR, O'Meara D (1995) Application of resistivity cone penetration testing for qualitative delineation of creosote contamination in saturated soils. In: Proceedings of Geoenvironment 2000, Geotechnical Special Publication 46, ASCE, New York, pp 151–166

Oxtoby DW, Nachtrieb NH (1996) Principles of modern chemistry, 3rd edn. Saunders, Philadelphia

Rinaldi VA, Redolfi ER (1996) The dielectric constant of soil–NAPL mixtures at low frequencies (100 Hz–10 MHz). In: Proceedings of nonaqueous phase liquids (NAPLs) in the subsurface environment: assessment and remediation, ASCE, Washington D.C., pp 163–174

Rinaldi VA, Cuestas GA (2002) Ohmic conductivity of a compacted silty clay. J Geotech Geoenviron Eng 128(10):824–835

Rinaldi VA, Francisca FM (1999) Impedance analysis of soil dielectric dispersion. J Geotech Geoenviron Eng 125(2):111–121

Robinson DA, Gardner CMK, Cooper JD (1999) Measurement of relative permittivity in sandy soils using TDR, capacitance and theta probes: comparison, including the effects of bulk soil electrical conductivity. J Hydrol 223:198–211

Rowe RK, Shang JQ, Xie Y (2001) Complex permittivity measurement system for detecting soil contamination. Canad Geotech J 39:498–506

Rowe RK, Shang JQ, Xie Y (2002) Effect of permeating solutions on complex permittivity of compacted clay. Can Geotech J 39:1016–1025

Saarenketo T (1998) Electrical properties of water in clay and silty soils. J Appl Geophys 40:73–88

Santamarina JC, Fam M (1997) Dielectric permittivity of soils mixed with organic and inorganic fluids (0.2 GHz to 1.30 GHz). J Environ Eng Geophys 2(1):37–51

Santamarina JC, Klein KA, Fam MA (2001) Soils and waves. Wiley, New York

Scott JH, Caroll RD, Cunningham DR (1967) Dielectric constant and electrical conductivity measurements of moist rock: a new laboratory method. J Geophys Res 72:5101–5115

Selig ET, Mansukhani S (1975) Relationship of soil moisture to the dielectric property. J Geotech Eng Div 101(GT8):755–770

Shang JQ, Scholte JW, Rowe RK (2000) Multiple linear regression of complex permittivity of a till at frequency range from 200 MHz to 400 MHz. Subsurf Sens Technol Appl 1(3):337–356

Topp GC, Davis JL, Annan AP (1980) Electromagnetic determination of soil water content: measurements in coaxial transmission lines. Water Resour Res 16(3):574–582

Yoon GL, Oh MH, Park J (2002) Laboratory study of landfill leachate effect on resistivity in unsaturated soil using cone penetrometer. Environ Geol 43:18–28