

지반의 중금속 오염도 조사를 위한 흙의 유전상수 측정기법의 적용성 평가 Applicability of Permittivity Measurement Method for Investigating the Heavy Metal Contamination of Subsurface

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개요 : 지반오염조사에 대한 유전상수 측정기법의 적용성을 평가하기 위하여 중금속 오염도에 따른 흙의 유전특성 변화를 분석하였다. 유전상수의 실수부와 허수부 모두 체적함수비에 따른 증가경향을 나타내었으며, 특히 MHz 범위에서 유전상수 실수부는 쌍극자모멘트에 비례하기 때문에 흙의 유전상수는 체적함수비에 따른 선형적인 증가경향을 나타내었다. 중금속 용액은 50kHz 이하의 저주파영역에서 전극분극효과에 의해 농도 증가에 따라 유전상수 실수부가 증가하는 경향을 나타내었으나, 고주파 영역에서는 이온의 수화작용에 의한 물분자의 배향분극 발현 감소로 인하여 유전상수 실수부가 감소하였다. 유전상수 허수부의 경우에는 모든 주파수 영역에서 중금속 농도 증가에 따른 전도손실에 의하여 증가하는 경향을 나타내었다. 흙과 중금속 혼합시료의 경우 함수비가 큰 시료에서는 중금속 용액 자체의 유전특성이 그대로 발현되었으나, 함수비가 작은 시료에서는 공간전하분극의 영향이 우세하여 유전상수 실수부가 10-20%정도 증가하는 경향을 나타내었다. 유전상수 허수부의 경우에는 중금속 농도 증가에 따른 뚜렷한 증가경향을 확인할 수 있었다. 본 연구의 결과에 의하면 중금속의 오염감지에 대해서는 유전상수 실수부보다는 허수부의 적용성이 높은 것으로 나타났으며, 현장에서의 정확한 오염도 평가를 위해서는 함수비에 대한 평가가 선행되어야 할 것으로 판단된다.

주요어 : 지반오염, 유전상수, 체적함수비, 중금속

1. Introduction

Detecting and monitoring subsurface contamination are essential processes for preventing potential environmental risks. In conventional approaches, representative samples of soil and pore fluid are collected in the field and analyzed for contaminants in the laboratory. However, the conventional sampling method has the following shortcomings: (1) soil sampling is extremely time consuming and expensive; (2) samples can be contaminated during collection, transportation and analysis in the laboratory, which might cause errors in the final results (Okoye et al. 1995; Kaya

and Fang 1997); and (3) samples require expensive laboratory analyses (Wilson et al. 1995). With regard to the disadvantages mentioned above, a lot of studies have tried to develop an in-situ, simple and cost-effective detecting method. In-situ monitoring using an electrical method has been proposed as a potential alternative (Kaya and Fang 1997; Rowe et al. 2001; Fukue et al. 2001; Lindsay et al. 2002). This method is based on the concept that the electrical properties reflect the physical and chemical properties of subsurface materials, with contamination of the subsurface being likely to change the electrical properties. Detection and monitoring by measuring the electrical properties is advantageous, as this is fast, with little data processing required to obtain accurate and repeatable results (Rinaldi and Cuestas 2002). Some researchers have proposed the potential availability of the permittivity in estimating subsurface contamination through laboratory experiments (Kaya and Fang 1997; Santamarina and Fam 1997; Darayan et al. 1998; Francisca and Rinaldi 2003). Although heavy metals are some of the most common contaminants in the subsurface, few data are available on their electrical properties.

In this study, laboratory experiments were performed to examine the effects of heavy metal contamination on the permittivity of soil. From the test results, the measured electrical properties were evaluated to see if they had sufficient sensitivity to identify subsurface contamination.

2. Experimental Setup for Measuring Permittivity

2.1 Test Materials

Two kinds of soil including silica sand (Jumunjin sand) and local soil were used to investigate the permittivity of soil in this study. Local soil was collected from the vicinity of a dormitory at Seoul National University. The local soil used for experimental study will be termed as 'SNU soil'. SNU soil is weathered granite soil which is commonly found around the Korean peninsula. Jumunjin sand was classified as poorly graded sand(SP) and SNU soil was classified as well-graded sand(SW). The soils were air dried, sieved through sieve No. 10, and then oven dried at 105°C over 24 hours. Soil-water mixture was put into an acrylic mold and directly compacted to the designed dry density. Both gravimetric water content and total unit weight of soil samples were evaluated. Laboratory experiments were performed for the remolded soil samples with various gravimetric water content and unit weight. Because the electrical properties of material are affected by temperature, the measurements were performed at 19–21°C to minimize the effect of temperature variations.

Mercury(Hg), lead(Pb) and cadmium(Cd) were used in this study as cationic heavy metals due to their importance as environmental contaminants. When too much of these heavy metals are accumulated in the human body, heavy metal poisoning occurs. Generally, it has been reported that mercury and lead are neurotoxic metallic elements affecting the nervous system and cadmium damages filtering mechanisms of the kidney. Besides heavy metals, aluminum(Al) with different valence and atomic weight were included as a cationic species for comparison.

2.2 Permittivity Measurement

The two-electrode cell is commonly used to measure the electrical properties of material under the AC electric field. The measuring cell was designed for this study as shown in Figure 1(a). The two brass electrodes of capacitor-type cell are 70mm in diameter and are 20mm apart. Sample was placed between the two electrodes of the acrylic mold.

In this study, AC measurements were performed at frequency ranges between 1kHz and 10 MHz. Low frequency measurements turn into an advantage in the following aspects: (1) in-situ testing and monitoring can be performed with little influence of cable impedance; (2) low frequency test devices are comparatively less expensive; and (3) laboratory tests can be performed with very simple capacitive cells (Rinaldi and Redolfi 1996). The measurements were achieved using the Hewlett-Packard HP4285A Precision LCR meter (Hewlett-Packard, USA) in the range of 75 kHz to 10 MHz and the Agilent 4263B LCR meter (Agilent Technologies Japan, Ltd.) in the range of 1k Hz to 100 kHz. Both devices allow measurement of capacitance and resistance as a parallel resistor-capacitor(RC) circuit of the unknown material under test. In order to measure the electrical properties under the low frequency electric field, electrodes of cell are connected to a bridge-type measuring system. Kelvin clip lead (Agilent 16089A) was used to connect the cell to the measuring device. Both electrodes act as current and potential terminals: high current H_c , high potential H_p , low current L_c , and low potential L_p connectors. The configuration of the leads and the connection of the shields are shown in Figure 1(b). The permittivity of specimen was determined by measuring the potential difference between the high potential H_p and low potential L_p terminals, and the applied current across the high current H_c and low current L_c electrodes. A sinusoidal excitation is imposed and measurements were repeated at different frequencies.

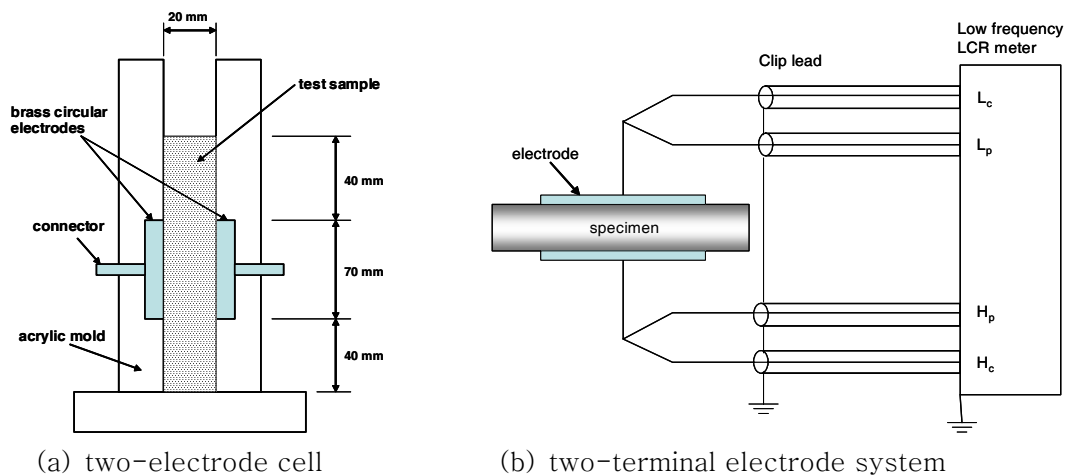


Figure 1. Schematic diagrams of permittivity measurements

3. Results and Discussion

3.1 Effect of water content on permittivity

It is reasonable to claim that permittivity is governed by volumetric water content, defined as the ratio of the volume of pore water to the total volume of soil, rather than gravimetric water content since the permittivity is proportional to the number of dipole moments per unit volume.

There are empirical relationships between water content and real permittivity based on the experiment at MHz ranges. Lundien(1971) presented an empirical formulation between real permittivity and moisture density(m_d), defined as the volume of water per unit volume of soil, as represented in Equation (1). Here, if unit weight of water is equal to 1g/cm^3 , moisture density has the same value as volumetric water content.

$$m_d = \frac{\kappa'}{80} - \frac{0.26}{\kappa' - 1} + 0.11 \quad (1)$$

Topp et al. (1980) reported the empirical formula for various soils at frequencies between 1MHz and 1GHz as represented in Equation (2) known as Topp's equation.

$$\kappa' = 3.03 + 9.3\theta_v + 146.0\theta_v^2 - 76.7\theta_v^3 \quad (2)$$

where, θ_v is volumetric water content.

Various empirical relationships between real permittivity and volumetric water content in the literature imply that volumetric water content is an effective parameter for describing the permittivity of soil. It is noted that these relationships were derived at frequencies above MHz range. The real permittivity of heterogeneous materials is governed by the permittivity of each component. The resultant permittivity of mixture can be evaluated through expressions known as mixture models. The three-phase mixture model can be used to indicate how soil components contribute to the real permittivity of bulk soil. For three-phase mixture of air, solid and water, one of the most useful and simple empirical models can be written as follows (Gardner et al. 1998; Robinson et al. 1999).

$$(\kappa')^a = f_a (\kappa'_a)^a + f_s (\kappa'_s)^a + f_w (\kappa'_w)^a \quad (3)$$

$$f_a + f_s + f_w = 1 \quad (4)$$

where, κ'_a , κ'_s , and κ'_w are the real permittivity of air, soil particle and water, respectively, f_a , f_s and f_w are their volume fractions and exponent a can take any value between 0 and 1.

The volume fractions of soil components can be expressed in terms of porosity and volumetric water content. Equation (3) can be rewritten as equation (5).

$$(\kappa')^a = (n - \theta_v)(\kappa'_a)^a + (1 - n)(\kappa'_s)^a + \theta_v(\kappa'_w)^a \quad (5)$$

If exponent a is set equal to 1/3, the expression becomes identical to the Looyenga model. Especially, with an index of 0.5, the equation is known as CRIM(Complex Refractive Index Method)(Gardner et al. 1998; Robinson et al. 1999; Francisca and Rinaldi 2003). The CRIM and the Looyenga models are most commonly accepted in literature. Similarly, the logarithmic model is a volumetric mixture formula with respect to the logarithms of the permittivities of phase components as represented in Equation (6).

$$\log(\kappa') = (n - \theta_v)\log(\kappa'_a) + (1 - n)\log(\kappa'_s) + \theta_v\log(\kappa'_w) \quad (6)$$

Plotted in Figure 2 are experimental data for the Jumunjin sand and the SNU soil obtained at 10MHz in this study and estimated real permittivity by three mixture models and two empirical equations. In the estimation of real permittivity using mixture models, measured values for dry soil, tap water and air at 10MHz were substituted as the real permittivity of each component in equations. Figure 2 shows that the real permittivity of the test soils were linearly related to the volumetric water content. This result indicates that the volumetric water content could be the most effective indicator for describing the real permittivity of a given soil. However, the real permittivity

calculated by mixture models and empirical formula were underestimated, especially for the SNU soil, since they did not consider the spatial polarization. The spatial polarization was the main mechanism in two or three phase mixtures such as soil. Although the spatial polarization tends to manifest at lower frequencies below MHz ranges and not significant at frequencies above a few MHz ranges, the real permittivity could be still affected by the spatial polarization at MHz frequencies. Therefore, the effect of spatial polarization on the real permittivity of soils should not be totally neglected even at MHz frequencies. Unfortunately, the relationship between soil properties and real permittivity based on the quantitative analysis of spatial polarization has not been suggested. In order to apply the mixing model for real permittivity over wide frequency ranges, modified mixing model considering the development of spatial polarization should be suggested.

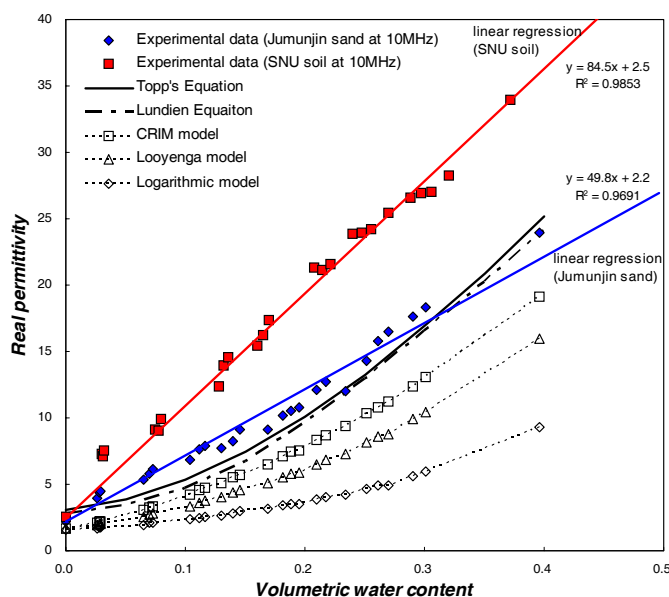
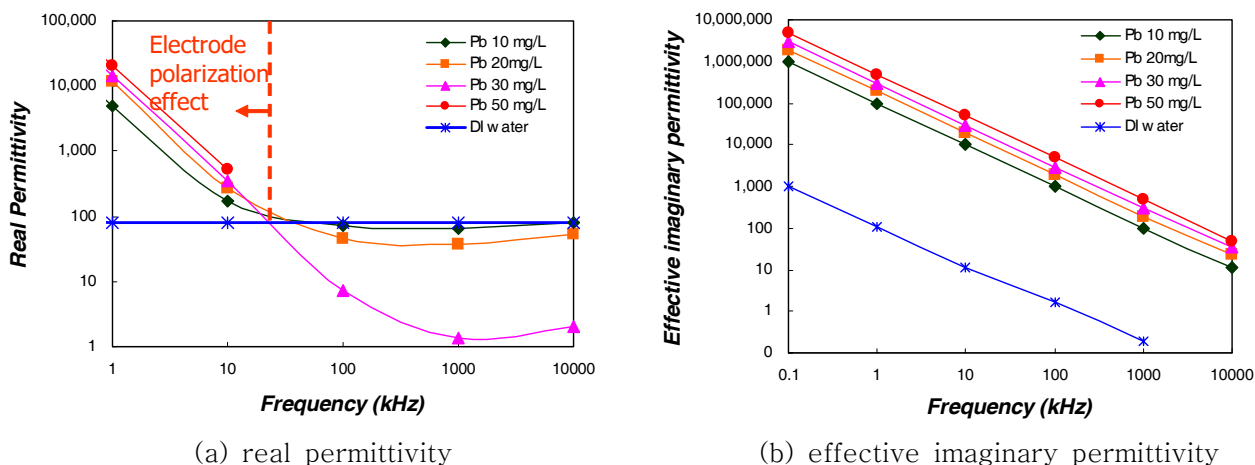


Figure 2. Comparison of experimental data for the real permittivity of Jumunjin sand and SNU soil obtained at 10MHz and various empirical relations reported in the literature

3.2 Permittivity of heavy metals

The effect of cationic concentration on the complex permittivity was explored. However, it was difficult to identify the ion type using the measured complex permittivity. The spectral responses of permittivity of lead at frequency ranges from 10kHz to 10MHz are shown in Figure 3. Electrode polarization effects, which causes measured real permittivity values to increase as frequency decreases, were observed at lower frequencies below 50kHz. Above 50kHz, 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. The hydration of salts renders hydrated ions, which are surrounded by water molecules with hindered polarizability. Water involved with hydrating ions in electrolytes makes a lower contribution to global polarization than free water, resulting in a lower real permittivity of electrolyte solutions at higher concentrations (Santamarina 2001). The effective imaginary permittivity increases with the increase in electrolyte concentration. The effective imaginary

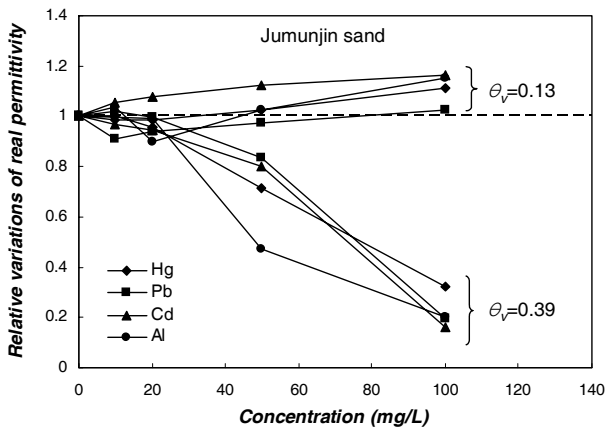
permittivity data capture conduction and orientational polarization losses. The addition of ionic constituents to water may be expected to a decrease in the molecular structure of water. Ions dissolved in water may bond, producing an ion pair or similar species with a significant dipole moment. In this way, the electrolyte dissolved in water contributes to polarization loss. Above all, the increase in effective imaginary permittivity for cationic species solutions with increasing concentration is primarily due to higher conduction losses. Electric conduction is enhanced by free movement of cationic species since ionic constituents act as charge carriers.



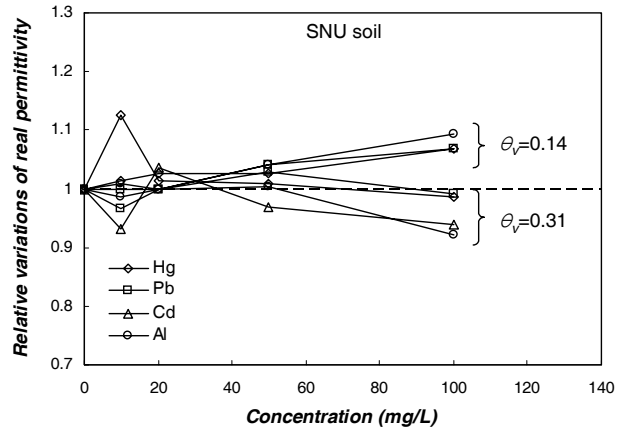
(a) real permittivity (b) effective imaginary permittivity
Figure 3. Spectral responses for complex permittivity of lead solution

3.3 Permittivity of soil-heavy metal mixtures

In order to evaluate whether the complex permittivity was sensitive enough to detect subsurface contamination due to heavy metals, relative variations defined as the ratio of electrical properties of the contaminated soil to that of uncontaminated soil with their concentration, were shown in Figures 4 and 5. The important findings obtained from Figures 4 and 5 are as follows. Firstly, the measurement of real permittivity alone may lead to some degree of ambiguity in the results mainly due to spatial polarization at low volumetric water content. Because the extent of spatial polarization is difficult to quantify, in order to overcome the ambiguity in measuring only the real permittivity, an additional measurement and analysis for the effective imaginary permittivity is required to characterize subsurface contamination besides real permittivity. Secondly, the data show that it was difficult to identify ion type using complex permittivity data. Yet, the sensitivity of the effective imaginary permittivity to concentration was valuable for the development of electrical methods to detect heavy metals in subsurface. The clear increases of effective imaginary permittivity with concentration were observed although their increment against concentration was small in the case of low volumetric water content. Such changes in electrical properties might be applicable for a detection system using electrical method for contaminant releases into the subsurface. Additionally, the electrical properties of soil are primarily dependent on soil types and volumetric water content. Therefore, in order to utilize the electric measurement method for investigating subsurface contamination, pre-evaluation of soil types and volumetric water content of subsurface is required. Providing the background values based on soil types and volumetric water content, it is highly probable that electrical properties can be used for detecting the contaminant in soils.

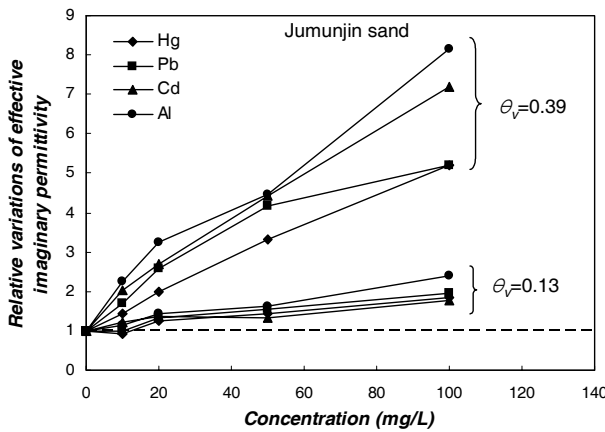


(a) Jumunjin sand

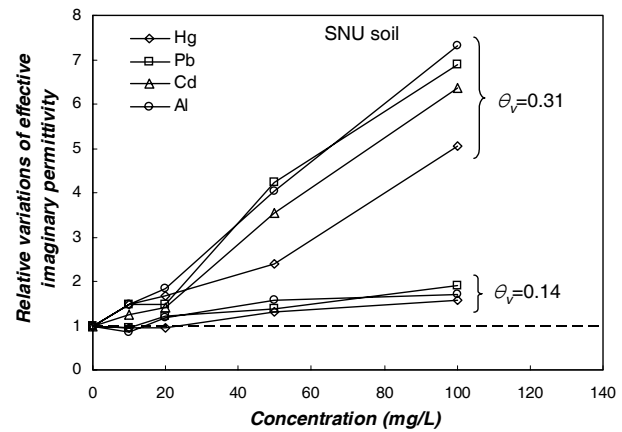


(b) SNU soil

Figure 4. Relative variations of real permittivity measured at 10MHz for mixtures of soils with cationic species aqueous solution



(a) Jumunjin sand



(b) SNU soil

Figure 5. Relative variations of effective imaginary permittivity measured at 10MHz for mixtures of soils with cationic species aqueous solution

4. Conclusions

The permittivity of unsaturated sand was strongly governed by the volumetric water content as this is proportional to the number of dipole moments per unit volume. The volumetric water content could be the most effective single parameter for assessing the permittivity of unsaturated soil. The linear relationship between the real permittivity of soil and the volumetric water content was derived at high frequencies (MHz ranges).

Ionic contaminants result in significant increases in the effective imaginary permittivity, due to ionic conduction, but significant decreases in the real permittivity arises due to the decreased orientational polarization of water molecules caused by hydration of ions. However, because the permittivity is primarily dependent on the volumetric water content of soil, pre-evaluation of the volumetric water content is required.

The clear increases of effective imaginary permittivity with concentration of ionic contaminants were observed. The sensitivity of effective imaginary permittivity to concentration is valuable in the application of electrical methods to the detection of heavy metals in the subsurface.

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References

1. Darayan, S., Liu, C., Shen, L. C. and Shatthuck, D.(1998), "Measurement of electrical properties of contaminated soil", *Geophysical Prospecting*, 46, pp.477-488.
2. Francisca, F. M. and Rinaldi, V. A.(2003), "Complex dielectric permittivity of soil-organic mixtures (20 MHz - 1.3 GHz)", *Journal of Environmental Engineering*, 129(4), pp.347-357.
3. Fukue, M., Minato, T., Matsumoto, M., Horibe, H. and Taya, N.(2001), "Use of a resistivity cone for detecting contaminated soil layers", *Engineering Geology*, 60, pp.361-369.
4. Gardner, C. M. K., Dean, T. J. and Cooper, J. D.(1998), "Soil water content measurement with a high-frequency capacitance sensor", *Journal of agricultural Engineering Research*, 71, pp.395-403.
6. Kaya, A and Fang, H. Y.(1997), "Identification of contaminated soils by dielectric constant and electrical conductivity", *Journal of Environmental Engineering*, 123(2), pp.169-177.
7. Lindsay, J. B., Shang, J. Q. and Rowe, R. K.(2002), "Using complex permittivity and artificial neural networks for contaminant prediction", *Journal of Environmental Engineering*, 128(8), pp.740-747.
8. Lundien, J. R.(1971), "Laboratory measurement of electromagnetic propagation constants in 1.0- to 1.5-GHz microwave special region", Report 5, Terrain Analysis by Electromagnetic Means, Technical Report No.3-693, U.S. Army Engineer Waterways Experiment Station.
9. Okoye, C. N., Cotton, T. R. and O'Meara, D.(1995), "Application of resistivity cone penetration testing for qualitative delineation of creosote contamination in saturated soils", *Proceedings of Geoenvironment 2000*, ASCE, New York, pp.151-166.
10. Rinaldi, V. A. and Cuestas, G. A.(2002), "Ohmic conductivity of a compacted silty clay", *Journal of Geotechnical and Geoenvironmental Engineering*, 128(10), pp.824-835.
11. Rinaldi, V. A. and Redolfi, E. R.(1996), "The dielectric constant of soil-NAPL mixtures at low frequencies (100 Hz - 10 MHz)", *Proceeding of Nonaqueous Phase Liquids (NAPLs) in the Subsurface Environment: Assessment and Remediation*, ASCE, Washington D.C., pp.163-174.
12. Robinson, D. A., Gardner, C. M. K. and Cooper, J. D.(1999), "Measurement of relative permittivity in sandy soils using TDR, capacitance and theta probes: comparison, including the effects of bulk soil electrical conductivity", *Journal of Hydrology*, 223, pp.198-211.
13. Rowe, R. K., Shang, J. Q. and Xie, Y.(2001), "Complex permittivity measurement system for detecting soil contamination", *Canadian Geotechnical Journal*, 39, pp.498-506.
14. Santamarina, J. C.(2001), *Soils and waves*, John Wiley & Sons.
15. Santamarina, J. C. and Fam, M.(1997), "Dielectric permittivity of soils mixed with organic and inorganic fluids (0.2 GHz to 1.30 GHz)", *Journal of Environmental and Engineering Geophysics*, 2(1), pp. 37-51.
16. Topp, G. C., Davis, J. L. and Annan, A. P.(1980), "Electromagnetic determination of soil water content: Measurements in coaxial transmission lines", *Water Resources Research*, 16(3), pp.574-582.
17. Wilson, L. G., Everett, L. G. and Cullen, S. J. (eds.)(1995), *Handbook of Vadose Zone Characterization & Monitoring*, CRC Press.