Dielectric and conductivity measurements as proxy method to monitor contamination in sandstone

V. Saltas\textsuperscript{a,∗}, F. Vallianatos\textsuperscript{a}, P. Soupios\textsuperscript{a}, J.P. Makris\textsuperscript{b}, D. Triantis\textsuperscript{c}

\textsuperscript{a} Department of Natural Resources and Environment, Technological Educational Institute of Crete, Greece
\textsuperscript{b} Department of Electronics, Technological Educational Institute of Crete, Greece
\textsuperscript{c} Department of Electronics, Technological Educational Institute of Athens, Greece

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Abstract

The present work investigates whether dielectric spectroscopy can be used to detect contamination, which may leach in a natural porous material, due to the spreading of contaminants. For this purpose, dielectric and conductivity measurements, in the frequency range from 10 mHz to 1 MHz, were carried out in sandstone samples, partially filled or saturated with solutions of leachates, at different concentrations. The experimental results suggest the dominant role of free water to the measured electrical conductivity and dielectric permittivity in contaminated samples with high water content. On the other hand, various relaxation mechanisms were observed in dried samples at different leachate concentrations. Experimental data were fitted using the Havriliak–Negami dielectric relaxation function, superimposed with a conductivity term. The determined parameters of the fitting function may serve to distinguish between different amounts of leachate in sandstone samples.

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1. Introduction

Last decade a constantly growing interest is discerned in the development of effective methods for the detection of subsurface contamination and monitoring environmental pollution. Indicatively, light or dense non-aqueous phase liquids (LNAPL and DNAPL) comprise serious pollution problems at landfill and buried waste areas, since they are difficult to identify and remedyle. Conventional methods of contaminated groundwater and soil characterization involve repeated and careful sampling and laboratory chemical analyses, which are expensive and time-consuming processes. Furthermore, the risk of samples contamination either during sampling, transportation or analysis is always substantial. On the other hand, if the sampling is continuous in time, aiming to monitor the diffusion of pollutants and spreading of contamination, a cost effective method must be used, which should indicate, in a first approximation, the chemical changes of the measured samples, correlated with the possible pollution.

Dielectric spectroscopy has been proposed by many researchers as a promising tool and experiments have been conducted to evaluate the efficiency of this technique to identify subsoil contamination and its sensitivity to different kinds and concentrations of organic or inorganic pollutants [1–7]. The pioneering work has been performed by Olhoeft [1] who measured distinct electrical signatures of certain pollutants in montomorillonite. Recently, Kaya and Fang measured dielectric permittivity and conductivity in soils, artificially contaminated with ionic solutions or organic solvents, at various ion concentrations or moisture content and interesting findings were obtained, concerning the role of ionic strength and organic liquids [3]. Shang et al. have developed artificial neural network models in order to distinguish heavy metal contamination in soil specimens, based on complex permittivity measurements [6].

The results of the above studies indicate that permittivity measurements even alone, could be helpful in detecting low concentrations of contaminants in soils, but acquiring dielectric data
in a wide frequency range, able to reveal the dielectric relaxation losses that occur in many organic or inorganic pollutants, could lead to establish a more reliable detection and identification tool.

Our work was intended to investigate whether dielectric spectroscopy is efficaciously applicable for detecting contamination, which may appear in a natural porous material, due to the spreading of the pollutants. Towards this direction, a local (Crete Island, Greece) sandstone was selected as a representative silicate porous material with a high porosity and leachate collected from a municipal landfill was used to contaminate the sandstone samples.

The electrical properties of leachate polluted sandy soils have been investigated by Yoon and Park and significant variations of their measured resistivity values have been observed before and after introducing leachates containing heavy metals [8]. Dielectric properties of porous materials, such as sandstone, have been widely investigated during the last decades, and various models have been proposed by several researchers [9–15]. Dielectric permittivity and conductivity prove to be extremely sensitive to ambient conditions like temperature and pressure, the chemical composition of the solid and liquid phases, the water content of the specimen and micro-structural factors like porosity [10,12,16–19].

This paper presents experiments carried out over a wide frequency range and at various leachate concentrations, at room temperature. Due to the sample’s high porosity, the pollutants may migrate to the pores of the material probably resulting to detectable divergences of the dielectric dispersion against the uncontaminated samples. The recorded spectra were fitted by the Havriliak–Negami (HN) empirical dielectric relaxation function [20], in an attempt to correlate the determined fitting parameters with the amount of leachate in the contaminated sandstone samples.

2. Experimental set-up

2.1. Dielectric spectroscopy technique

Dielectric spectroscopy is based on the interaction of an applied alternating electric field with the material under test. Dielectric permittivity, which is a measure of the specimen’s response to the applied field, is a frequency dependent complex function that provides information on the characteristics of the material. Its real part ($\varepsilon'$) represents the polarisability of the material, while the imaginary part ($\varepsilon''$) represents the energy losses due to polarization and ionic conduction. There are four main types of polarization mechanisms, namely electronic, atomic, orientation and interfacial or space charge polarization [21]. Each of these mechanisms dominates a certain frequency range with a characteristic resonant frequency or relaxation frequency.

In the present study, dielectric and conductivity measurements were carried out by means of a high-resolution broadband spectrometer (Novocontrol Alpha-N Analyzer) connected with a sample holder, model BDS 1200, supplied by Novocontrol. The frequency range of the applied ac electric field was between $10^{-2}$ and $10^6$ Hz. Good electromagnetic shielding was implemented to the whole sample holder in order to diminish noise problems that are common, especially at low frequencies. The specimen was mounted in a sample cell between two parallel electrodes forming a sample capacitor. The dielectric sample placed in the capacitor can be considered as an equivalent electrical circuit comprised of a capacitance, $C(\omega)$, in parallel with a resistance, $R(\omega)$. These values are the output of the dielectric analyzer and are associated to the real and imaginary part of the complex dielectric permittivity ($\varepsilon^*$) through the relations:

$$\varepsilon'(\omega) = \frac{C(\omega)d}{\varepsilon_0 \pi \tau^2} \quad (1)$$

and

$$\varepsilon''(\omega) = \frac{R^{-1}(\omega)d}{\omega \varepsilon_0 \pi \tau^2} \quad (2)$$

where $d$ is the distance between the electrodes, $r$ their radius, $\omega = 2\pi f$ and $\varepsilon_0$ the permittivity of the vacuum.

In the case of liquids or water-saturated porous media, the existence of free ions results in dc-conductivity. This conductivity manifests itself in the imaginary part of the relative dielectric constant:

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \left\{\left(\frac{\sigma_0}{\varepsilon_0}\right)^N + \varepsilon''\right\} \quad (3)$$

where $\sigma_0$ is the specific dc-conductivity and the exponential factor, $N$, in most cases, equals to 1. The specific conductivity $\sigma^*$ is related to the dielectric constant by the equation:

$$\sigma^* = \sigma' - i\sigma'' = i\omega\varepsilon_0(\varepsilon^* - 1) \quad (4)$$

The experimental data were fitted by the Havriliak–Negami (HN) dielectric relaxation function, superimposed by a conductivity term, as shown below [20].

$$\varepsilon(\omega) = \varepsilon' - i\varepsilon'' = -i\left(\frac{\sigma_0}{\varepsilon_0}\right)^N + \frac{\Delta\varepsilon}{(1 + i\omega\tau)^\beta} + \varepsilon_\infty \quad (5)$$

where $\tau$ is a characteristic relaxation time, $\varepsilon_\infty$ gives the value of $\varepsilon'$ at infinite frequency and $\Delta\varepsilon$ (relaxation strength) is the difference between $\varepsilon'$ at zero frequency and $\varepsilon'$ at infinite frequency. Parameters $\alpha$ and $\beta$, which are constrained to lie between 0 and 1, provide the slope of the left and right increase respectively, of the $\varepsilon''$ peak in a log–log plot for the HN function. For not too low values of $\alpha$ and $\beta$, $1/2\pi\tau$ corresponds approximately to the frequency of the maximum peak in $\varepsilon''$ [21]. Fig. 1 depicts an indicative example of the two terms of the dielectric fitting function, which was applied to a dataset of a pure sandstone sample, used in the present work.

2.2. Samples preparation

Samples of local (Crete Island, Greece) sandstone, with a porosity of 35%, were cut from a massive stone in a prismatic shape to fit between the electrodes of the sample cell. A leachate liquid sample was collected from a municipal landfill and was used to contaminate the sandstone samples. Leachate’s pH and electrical conductivity were measured 8.40 and 22.89 mS/cm,
respectively. The values of total $N$, COD and $P$ are 3320, 8889 and 24 mg/l, respectively. Pure sandstone samples were impregnated in solutions of leachates of different concentrations (1%, 5%, 10%, 20%, 40%, 70% and 100% v/v) for 24 h. Deionized water was used as a solvent. An uncontaminated sample remained for the same time in pure deionized water, in order to use it as reference. Afterwards, the samples dried in air for 3 days and dielectric measurements were carried out with 1-day intervals, in order to ascertain the influence of water content to the contaminated sandstone specimens. Finally, moisture was removed with mild heating of the samples at 40°C for 2 days and the dielectric measurements were repeated again.

3. Experimental results

Although all forms of dielectric representation contain the same information, various relaxation effects should be more or less dominant, depending on the frequency range (high or low) they appear and the type of representation. Thus, according to Eqs. (3) and (4), in the dielectric loss spectra, the $\sigma_0$ contribution is weighted by a $1/\omega$ factor, which masks the dielectric effects in the low frequency range. Similarly, in the conductivity spectra, the $\varepsilon''$ contributions are weighted by a factor $\omega$, and become dominant at high frequencies. So, the $\sigma'(\omega)$, $\varepsilon'(\omega)$, $\varepsilon''(\omega)$ formats have been used for the evaluation of the experimental data.

Fig. 2 represents the measured conductivity (real part) of the sandstone samples as a function of frequency, after (a) drying in air for 24 h and (b) final mild heating at 40°C. The solid line corresponds to the sandstone sample impregnated in pure deionized-water. The influence of water on the measured conductivity is very obvious in the whole frequency range, giving values between wet and dry samples that differ 5–6 orders of magnitude. Furthermore, considerable variations of conductivity are also observed in the spectra measured after 24 h, for different concentrations of leachates. Although water content should be the same in all the samples, higher leachate concentration leads to higher sample conductivity.

The results are quite different for dried samples, where at high frequencies we can hardly distinguish divergences in conductivity spectra between the contaminated samples. For both, pure and contaminated dried samples, at high frequencies (>10^2 Hz), the conductivity may be described with a power law function of frequency, as it is evident from the linear variation of $\sigma'(\omega)$ with frequency, in log-log representation. In this universal law, which has been suggested by Jonscher [11]:

$$\sigma'(\omega) - \sigma_0 \propto \omega^n$$  \hspace{1cm} (6)

the exponent $n$ lies between 0 and 1. In the present case we found that $n$ takes the value of 0.57 for the pure sample and of 0.54 ± 0.03 for the contaminated samples.

At low frequencies (below 10 Hz), an increase of concentration results in a considerable increase of conductivity. This variation in conductivity of the dry samples may be attributed to the different amount of contaminants, which settle to the pores of the material, as well as the different type of bound water in each case, which can not desorb at such a low temperature.

The dielectric and conductivity spectra measured after 48 and 72 h drying of the samples in air, are almost identical for the same leachate concentration, suggesting that the samples have reached an equilibrium state as far as the water content is concerned.

In principle, fluid-bearing sandstone is a multi-component fluid-solid system revealing significant complexity. It can be considered as a polycrystalline matrix with a system of pores, which may contain free and bound water, impurities and air. Each of these components contributes to the electrical properties of the material via different physical mechanisms. In addition, surface contributions due to solid–liquid interface and clustering
effects have to be taken into consideration for the determination of the electrical properties [9,10,22]. Previous investigations on partially filled or saturated with fluid sandstone exhibit polarization phenomena, which are probably due to the electrochemical interaction of moisture with the grains surface. A dispersion, which appears in the low frequency region, has been related to the humidity that coats the solid grains and provides diffusion paths, thus, suggesting a solid–liquid interfacial phenomenon rather than an electrode effect [15,23].

The real and imaginary parts of the complex permittivity of the sandstone samples, after (a) drying in air for 24 h and (b) final mild heating at 40 °C, are shown in Figs. 3 and 4, respectively. In the case of the measured samples after 24 h, enormous values have been recorded for $\varepsilon'$, and $\varepsilon''$ at low frequencies, which cannot only be explained by electrode polarization effects, because large values of $\varepsilon^*$ have been confirmed by the four-electrode method [10]. The limit of $\varepsilon'$ at high frequencies is the same for all the measured dried samples ($\varepsilon_\infty \sim 4$), indicative of sandstone samples. However, $\varepsilon_\infty$ varies between 12 and 40, for the sandstone samples partially filled or saturated with leachates, as they were measured after drying in air for 24 h (Fig. 3). Taking into account that the dielectric constant of pure water is about 80 in the MHz range, we may conclude that the contribution of free water is dominant at high water-contents. For porous rocks at frequencies below 10 MHz, there are several relaxation effects, which are related to different surface polarization processes with characteristic relaxation times range from $10^{-6}$ to $10^{-1}$ s [9]. These processes are, in order of increasing water, (i) orientational polarization of bound (adsorbed) water, (ii) polarization of liquid films or pockets, which allows the free migration of ions in the fluid, (iii) polarization of rough fractal surfaces and (iv) polarization of the “closed” or “open” electrical double layer (EDL), depending on the limited displacement of the excess surface charges or the free exchange of excess ions with the bulk electrolyte, respectively. In our case, dielectric spectra recorded after 24 h (see Fig. 3), are almost identical in shape and absolute values with those measured by Ruffet et al. in various sandstone samples partially filled with water or KCl solutions, at the same frequency range [10,24]. In these experiments, as in the spectra of Fig. 3, at low frequencies the real and imaginary parts of dielectric permittivity follow the power laws $\varepsilon' \propto \omega^\alpha$ and $\varepsilon'' \propto \omega^\beta$ with approximately equal exponents, $\alpha \approx -1$ and $\beta \approx -1$, which is a signature of constant loss angle or fractal behavior of the low frequency polarization of porous and fractured rocks. From the above findings, it is evident that, in order to diminish the influence of free water in sandstone and accent the role of leachate, only the spectra concerning the dried samples should be taken into consideration.

In the medium frequency range (1 Hz to 1 kHz) the evolution in $\varepsilon'$ of the contaminated dried samples deviates from that of the pure sample but it does not seem to be very sensitive to different concentrations of leachates. The situation is different at low frequencies (below 1 Hz) where $\varepsilon'$ increases considerably, especially at higher concentrations. This behaviour is also observed in the imaginary part of dielectric constant (see Fig. 4) and may be attributed to the increase of conductivity due to higher concentrations of leachates, in consistency with the curves of Fig. 2. Furthermore, various broad loss peaks are observed, which are shifted in frequency, depending on the leachate concentration.

Leachate samples can mainly be considered as an electrolytic solution with ions of different strengths and mobility. Apparently, at low frequencies, ions start to move resulting in an increase in the system conductivity, which contributes to $\varepsilon^*$ according to Eq. (3). Loss peaks are observed around 10 Hz (Fig. 4) for low concentrations of leachates, while at higher concentrations they are partially screened by the conduc-
ity contribution to dielectric losses. The influence of water in water-saturated sands has been also studied in the frequency range from $10^{-1}$ to $10^{6}$ Hz by Louven et al., and by Rusiniak, but no loss peaks were observed [14,18]. From the above findings we may conclude that these relaxation mechanisms could be attributed to the interaction of the leachates with bound water and solid surface. The explanation for the high relaxation times is that the bound water molecules are prevented from following a rapidly alternating electric field, because of their different binding forces with the solid surface and their interaction with the contaminants. These interactions may produce larger structures or clustering effects that will require a longer time to orient themselves in the direction of the applied electric field.

As it has been mentioned in Section 2.1, dielectric curves are fitted well by a linear superposition of the contribution from the dc-conductivity and a dielectric relaxation process expressed by an asymmetric Havriliak–Negami function. However, we have to mention that, divergences of the experimental data from the fitting curves occur at low frequencies and for high leachate concentration. This could be attributed to electrode polarization effects, which are more dominant as the conductivity of the samples increases due to higher leachate concentration. The dc-conductivity $\sigma_0$, the parameters $\alpha$, $\beta$ and the relaxation time derived from the fitting of the experimental data for $\varepsilon''$ to the HN relation given in Eq. (5), are shown in Figs. 5–7 respectively. In this equation, the exponential factor $N$ varied close to unit, in order to achieve better fittings. The value of $\varepsilon_{\infty}$ was chosen equal to 4, which is the value of $\varepsilon'$ at high frequencies, according to Fig. 3.

As it is seen in Fig. 5, dc-conductivity $\sigma_0$, increases linearly over the whole concentration range. This linear behavior could be explained by the fact that the electrolytic conductivity of the leachate solutions has been found to increase also linearly with concentration. This linearity is directly reflected to the estimated dc-conductivity of the samples. Furthermore, it seems that mild heating of the contaminated samples did not cause any significant adsorption of contaminants except of the free water. These results are in agreement with those reported by Yoon and Park [8], where a decrease of resistivity with leachate proportion in leachate-contaminated soils has been observed.

The variation of $\alpha$ and $\beta$ parameters (Fig. 6), which are a width and an asymmetric parameter respectively, implies different distributions of relaxation processes with varying leachate concentration. This is a reasonable result since, leachate must be considered as a multi-component system, contributing to dielectric response with different mechanisms, related to chemical reactions, such as oxidation–reduction reactions, ion-exchange reactions and water–leachate interaction [1].

However, at moderate leachate concentrations, parameter $\beta$ varies close to unit, indicating a Cole–Cole relaxation process, rather than a more complicated mechanism. A rapid decrease in relaxation times is observed at the first stage of sandstone contamination (concentration <10%), while at higher concentrations, $\tau$ remains almost constant (Fig. 7).

From the above presented findings, we may conclude that the combination of the HN fitting parameters, which specify the shape of the dielectric response of the examined contaminated samples, may serve to distinguish between different amounts of leachate in sandstone samples.
4. Conclusions

In the present work dielectric and conductivity measurements in the frequency range $10^{-2}$ to $10^6$ Hz were carried out at room temperature in sandstone samples, partially filled or saturated with solutions of leachates, at different concentrations. From the thorough analysis of the experimental data, we may conclude that the role of free water is dominant suggesting a fractal behaviour at leachate-contaminated samples with high water contents. Desorption of free water with mild heating at $40^\circ$C, diminishes its influence and accents various relaxation mechanisms in dielectric spectra, associated with the interactions between bound water, leachate and solid surface of the sandstone.

Conductivity measurements in dried samples suggest a power law behaviour at frequencies above 10 Hz, which however cannot distinguish between different concentrations of leachate.

Spectral curve fitting for the dried sandstone samples, using a Havriliak–Negami relaxation process superimposed with a conductivity term, suggests that the estimation of the parameters $\sigma_0$, $\alpha$, $\beta$, and $\tau$ is well suited and applicable for the detection of leachate contamination in sandstones.

Specifically, relaxation time of pure sandstone is strongly influenced by small changes in leachate concentration, while it remains insensitive at higher concentrations. The above parameter, in conjunction with the dc-conductivity could be serving for a rough estimation of leachate over the whole concentration range.

Therefore, dielectric spectroscopy method could be a promising tool in the survey of existing contamination in the subsurface and well suited for monitoring of hazardous waste. However, further investigation is necessary, in order to verify the validity of the above analysis to the identification and quantification of leachate or other contaminants in various solid-fluid systems.

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