Dielectric permittivity of clay adsorbed water: Effect of salinity

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Summary

The propagation of ground penetrating RADAR waves through complex earth materials in general and clay minerals in particular remain only poorly understood. Most ground penetrating radar (GPR) studies, however, are conducted through clay-containing materials; and this laboratory study focuses on radar wave behavior through clays in close proximity with salt. This is examined by laboratory measurements of the 'dielectric constant' of mixtures of clay and sodium chloride as a function of frequency (0.01 - 3GHz) and salt concentration. The main idea is to investigate the effect of adsorbed water salinity on the conductivity and permittivity: the main factors influencing the speed and attenuation of radar waves. The conductivity and the dielectric permittivity are found to both increase with salt content. The increase in the dielectric permittivity (and resultant decrease in radar wave speed) likely results from increasing charge density and consequent interfacial polarization. The dispersion caused by the interfacial polarization (accumulation of charges at the interface between two phases or two media with different dielectric properties) seems to extend to the upper RADAR band (up to ~500MHz). The results suggest that waves travelling in such a media will suffer attenuation even in the high frequency radar band and therefore the acquired GPR data might not be useful in clayey salt. Furthermore the result suggests increase in the electrical conductivity which is believed to be a measure of the hydraulic conductivity and therefore questioning the idea of using either salt deposits or clay as a geological repositories for chemo-toxic and nuclear wastes.

Introduction

The dielectric permittivity of pure dry salt is relatively low (~6) and independent of frequency (Annan et al., 1988) which allows the GPR waves to travel with little attenuation in clean halite or sylvite formations. Clay minerals on the other hand are known to have a relatively high and frequency dependent permittivity. The dispersion in clays is attributed to its fine particle size and therefore large reactive surface area (due to an excess of negative charge) which can adsorb a significant amount of water. Bulk water posses a large dielectric permittivity and that is why a small amount of water can be detected in any rock or soil matrix that has a low dielectric permittivity. Adsorbed water however displays a different trend than the bulk water because of its restricted mobility, which affects its physical properties including the overall effective dielectric permittivity.

Adsorbed water-permittivity relations have been studied in the past mainly by direct measurements on clay or clayey soils [(Hoekstra and Doyle, 1971); (Wang and Schmugge, 1980); (Lockhart, 1980); (Kenyon, 1984); (Myers, 1991); (Kaviratna et al., 1996); (Saarenketo, 1998); (Ishida et al., 2000); (Logsdon and Laird, 2002); (West et al., 2003); (Lasne et al., 2008); (Arcone et al., 2008)]. These studies focused primarily on clayey soils and only rarely on such soils saturated with water of different salinities. The transition moisture (defined as the water

content which causes a jump in the dielectric properties of some soil) was found to be high in clayey soils than in clean sandy soils. This was attributed to the ability of clay particles to adsorb more water than the sand because of their high surface area and negative surface charge that is neutralized by positive charge being the positive side of the water molecule dipoles in this case. Soil adsorption then became a rich area of research for geoscientist as they start to create models for dielectric of water saturated systems (Topp et al., 1980). Adsorbed water physical properties are known to be different from that of free water. The surface forces limit the mobility of the water molecules leading to a higher viscosity and lower diffusion coefficient. Consequently other properties that are related to the mobility of these molecules such as evaporation dielectric constant and relaxation frequency are altered. Dissolved salt are also known to alter the physical properties water. The interesting aspect in the free water versus adsorbed water studies is that there seems to be a completely opposite behaviour in some conditions. For example while temperature decreases the dielectric constant of free water it increases that of adsorbed water (Or, 1999) .The explanation is that the increase in the temperature causes some of the adsorbed water to become free and therefore the overall dielectric constant of the system increases. Salinity is known to decrease the dielectric constant of free water but increase the conductivity and the imaginary permittivity. Reported in this paper is a systematic study of the effect of changing the salinity of clay adsorbed water on its dielectric permittivity. The study has been conducted in support of GPR surveys conducted in potash mines which aim to locate the potash ore and to avoid the clayey salt which present a hazard to drilling. The successful interpretation of these surveys requires understanding of the relationships between dielectric permittivity, free (brine inclusions) and adsorbed (to the clay minerals) water content.

Theory

A given material's complex dielectric constant ε^* has both real (ε') and imaginary (ε'') components:

$$\varepsilon^* = \varepsilon' + \varepsilon''$$ Equation (1)

The imaginary component ε'' includes both relaxation (ε''_r) and electrical conductivity (σ) contributions. The relaxation contribution to the imaginary component is caused by the different relaxation processes associated with the different polarization mechanism. In the frequency range used in this study (0.01 to 3GHz) the lag of the dipolar molecules behind the applied electromagnet field (εr) together with the ionic conductivity cause energy loss that is represented by the imaginary permittivity ε''

$$\varepsilon'' = \varepsilon''_r + \sigma / 2\pi f \varepsilon_o$$ Equation (2)

Where ε_o is the permittivity of vacuum. The dipolar relaxation of rocks is caused by the free water molecules. If there is no free water then the imaginary permittivity (or the energy loss) is caused by the ionic conductivity and therefore equation 2 becomes

$$\varepsilon'' = \sigma / 2\pi f \varepsilon_o$$ Equation (3)

Method

Clay's are notoriously difficult to characterize. The 'clay' used in this study refer to a dry powder obtained courtesy of Plainsman's Clay, Medicine Hat. X ray diffraction, used to identify its mineralogy, reveals that this powder is a mixture of muscovite, kaolinite and quartz. The clay is assumed to contain some amount of adsorbed water because it was handled in room condition

(humidity, temperature and atmospheric pressure). The assumption is valid because clay tends to readily adsorb water in humid conditions in order to neutralize the negative charge on its surface (Chatlley, 1927). The clay powder was mixed with sodium chloride powder and densified by hydrostatic compression to 250 MPa for more than 12 hours. The dielectric permittivity of these samples was then measured using an open ended coaxial line sensor (Agilent 85070B) in conjunction with a vector network analyser (Agilent 4991A).

Examples

The dielectric constant and the effective conductivity functions of frequency for different concentration clay-salt mixtures is shown in Figure 1. The dielectric constant decreases with frequency in all of the samples except for the pure NaCl. This radar wave velocity dispersion is greater in samples with a salt content ≤ 10% (by mass). The dispersion continues to affect the measured value up to ~500MHz. We believe that this dispersion effect is a contribution from the interfacial polarization which is defined as the build up of charges at the interface. Both free and bound charges likely contribute to this mechanism. When the amount of salt in clay is increased (≥10%) more adsorbed water is involved in the salt dissociation possibly leaving a single layer of water. As more salt is added, the undissociated salt particles precipitate in salt grain form which has a dielectric permittivity that is higher than that of clay particles at high frequency (>0.5GHz), and therefore the high frequency permittivity of the samples that contains salt is always higher than that of clay. The electrical conductivity increase with frequency and salinity of the adsorbed water up to the point where the adsorbed water become saturated (~10%salt by weight).

Conclusions

Salt that is added to dry clay dissociate into cations and anions increasing both of the dielectric constant and the electrical conductivity. The dissociation occurs because of the existence of adsorbed water. The salinity of the adsorbed water increases both of the dielectric constant and the electrical conductivity. In bulk (free) water salinity increase the conductivity but causes a decrease in the dielectric constant.
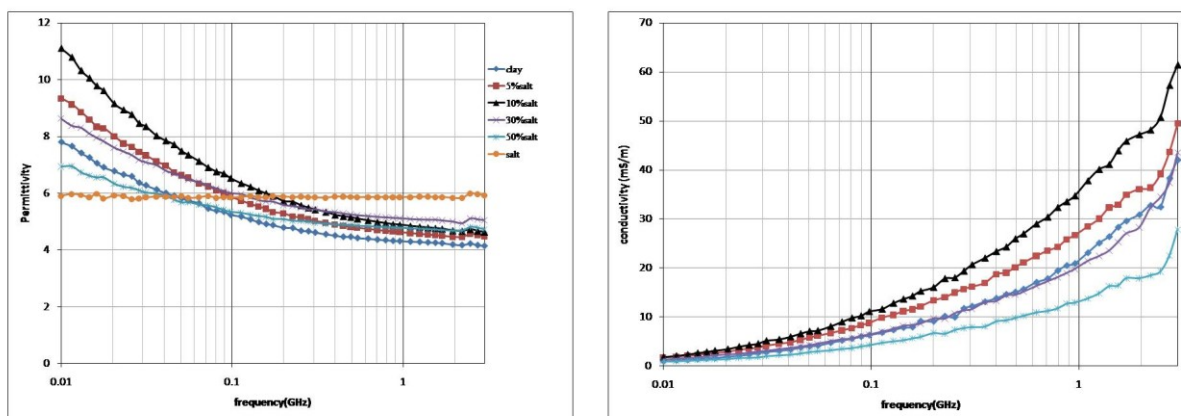

Figure 1. The dispersion in the real dielectric permittivity (left) and the electrical conductivity (right) of clay samples that contain salt. The salt concentration is given by weight. The conductivity was calculated from the measured imaginary permittivity.

Acknowledgements

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