

EFFECT OF PORE WATER AND ADSORBED MOISTURE ON THE DIELECTRIC PROPERTIES OF GREEN RIVER OIL SHALE

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ABSTRACT

Moisture and pore water are found to have appreciable effects on the dielectric parameters of Green River oil shale. A regular decrease in the relative dielectric constant, ϵ' , and dielectric loss, ϵ'' , with decreasing amount of adsorbed moisture and pore water, is observed at 24°C for oil shale samples ranging in oil yields from ~6–~100 gallons per ton. The weak dependence of ϵ' and ϵ'' on shale richness at frequencies in the range 50 Hz–1 MHz effectively rules out the application of dielectric techniques as an assay tool. The results are discussed in terms of interfacial polarization effects arising from the presence of adsorbed moisture and pore water in the oil shale matrix.

INTRODUCTION

An important factor to be considered in the design of dielectric heating and fracture techniques that have been recently proposed^{1, 2} for large-scale processing of Green River oil shales, is the possible effect of pore water and adsorbed moisture contained in the shale deposits. In particular, information regarding the influence of pore water on the dielectric properties of oil shales is significantly lacking in the current literature. Electrical methods of analysis are also potential candidates in the choice of a rapid method for determining the organic content of shale deposits. The extreme sensitivity of electrical properties to moisture and sample geometry (grain boundaries, impurities, bedding plane orientation, etc.) could, however, prove to be a hindrance to the successful application of these techniques as a routine well-logging tool. The objectives of the present study are thus two-fold: (a) to investigate the effect of pore water on the dielectric parameters of Green River oil shale, and (b) to assess the feasibility of dielectric techniques for assaying oil shale deposits.

EXPERIMENTAL

Dielectric parameters consisting of the relative dielectric constant ϵ' and dielectric loss ϵ'' were monitored as a function of frequency (50 Hz–1 MHz) at room

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temperature, using the Dynamic Dielectric Analysis (DDA) technique described elsewhere³⁻⁵. Measurements were carried out on Green River oil shale samples assaying between 6.1–100 gallons per ton. Details of the preparation and handling of samples for the electrical measurements can be found in a previous paper⁶.

Right circular cylindrical samples (23 mm diameter, 6.25 mm thick) were used in the present study; these samples were cored from massive shale blocks in directions both perpendicular and parallel to the shale bedding planes. Proper electrical contact between the sample surface and electrodes was ensured by appropriate loading of electrode contact plates.

Removal of pore water and adsorbed moisture from the shale matrix was facilitated by the recommended procedure⁷ of heating the test samples in an air-free oven at $\sim 110^\circ\text{C}$ and subsequent storage in vacuum desiccators. Each drying cycle consisted of pre-heating these samples at 110°C for 24 h and then cooling back to room temperature for the dielectric measurement.

RESULTS

Figure 1 shows the dielectric loss, ϵ'' , as a function of the number of heating cycles for several grades of oil shale ranging from 6.1 to 64.7 gallons per ton. ϵ'' is seen to exhibit an initial sharp decrease with the number of heating cycles for all the oil shale samples examined in the present study. The relative constancy of ϵ''

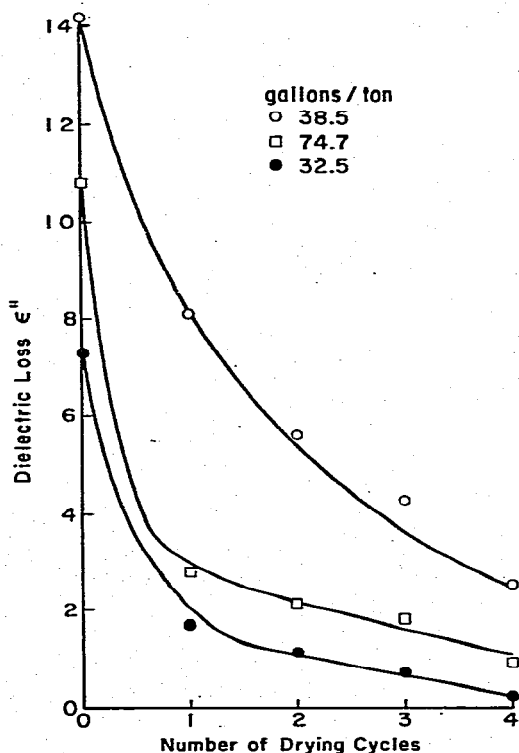


Fig. 1. Variation of dielectric loss, ϵ'' , with number of heating cycles for several grades of oil shale (electric field perpendicular to shale bedding planes).

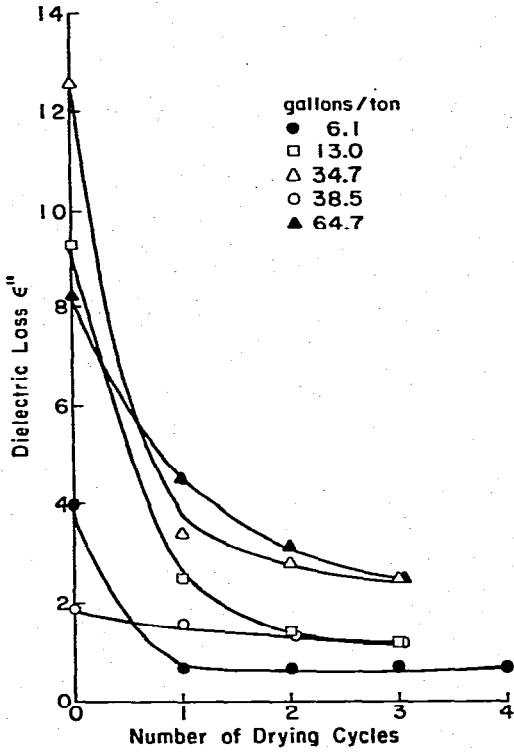


Fig. 2. Variation of ϵ'' with number of heating cycles for electric field parallel to shale bedding planes.

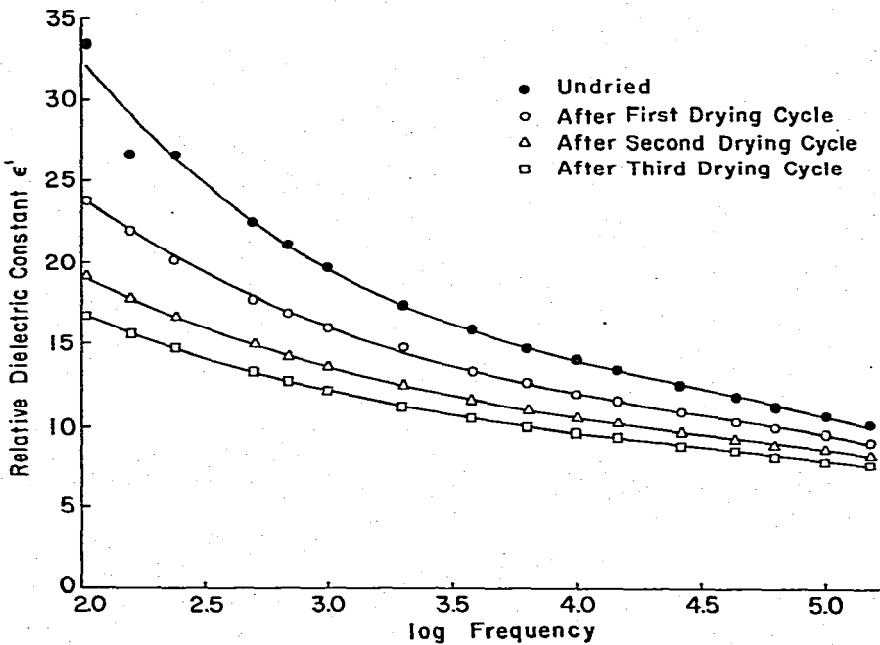


Fig. 3. Dispersive behavior of relative dielectric constant, ϵ' , as a function of heating cycle for a 59 gallons per ton oil shale sample.

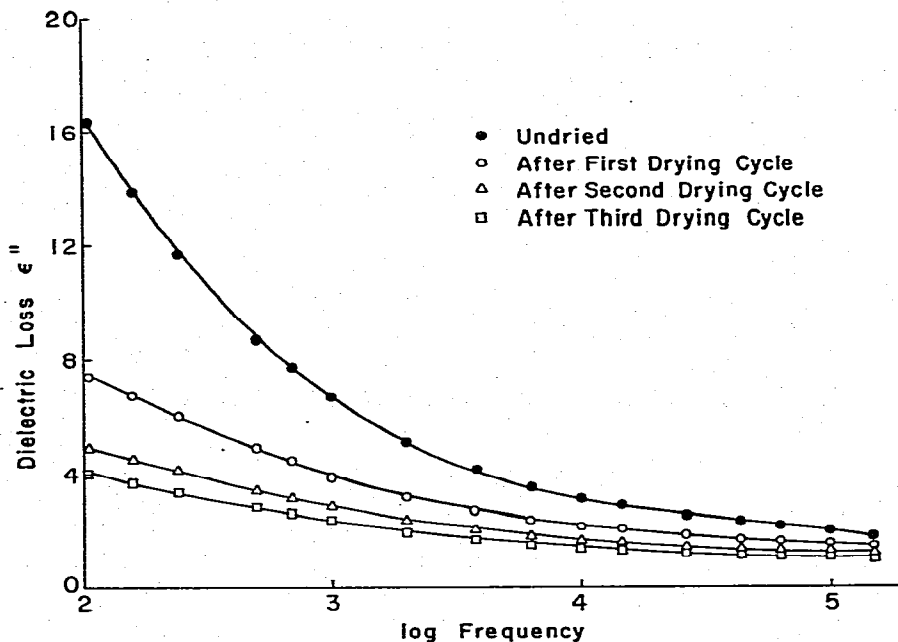


Fig. 4. Variation of ϵ'' with frequency and number of heating cycles for the sample shown in Fig. 3.

after approximately the third heating cycle is to be noted. Similar trends are observed in the case of the oil shale samples cored in a direction parallel to their bedding planes (Fig. 2). The failure of ϵ'' to reach limiting values even after the fourth heating cycle, however, distinguishes the dielectric behavior for the electric field parallel to the shale bedding planes, from the perpendicular situation shown in Fig. 1.

Figure 3 shows dispersive behavior of the relative dielectric constant ϵ' for a 59 gallons per ton oil shale sample (cored perpendicularly to the shale bedding planes) as a function of the heating cycle. A regular decrease in the ϵ' values with each subsequent heating cycle is evident. The ϵ' values were also seen to level-off after the third heating cycle. Similar trends are observed for the other oil shale samples of varying grades examined in the present study. Oil shale samples cored in a direction parallel to their bedding planes also exhibit essentially similar behavior.

Figure 4 shows the corresponding plots for the variation of ϵ'' with frequency and heating cycle for the sample discussed above. Again a regular decrease of ϵ'' with heating cycle is evident and is consistent with the trends shown in Figs. 1 and 2.

Figure 5 shows the dependence of ϵ' on the amount of organic matter for shales assaying from 6.1 to ~ 99 gallons per ton. Figure 5(a) depicts the data for the undried samples and Fig. 5(b), (c) and (d) shows the results for the samples subjected to one, two and three heating cycles, respectively. The significant decrease in the scatter of ϵ' values with heating cycle and the absence of noticeable trends in the dependence of ϵ' on grade are to be noted. (The curves were fitted to the experimental data points by regression analyses.) Similar results are obtained for the dependence of ϵ'' on shale richness.

The dielectric data shown in Fig. 5 were obtained at a frequency of 100 Hz.

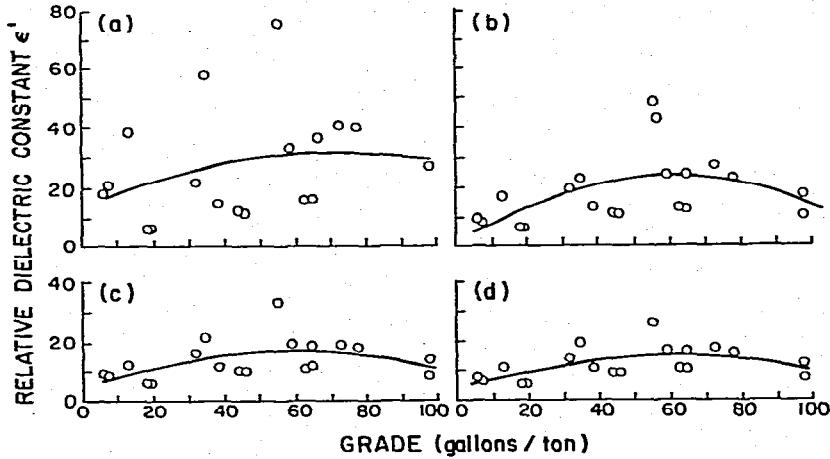


Fig. 5. Dependence of ϵ' (at 100 Hz) on the amount of organic matter in the shale. (a) Undried samples; (b) after one heating cycle; (c) after two heating cycles; (d) samples subjected to three heating cycles.

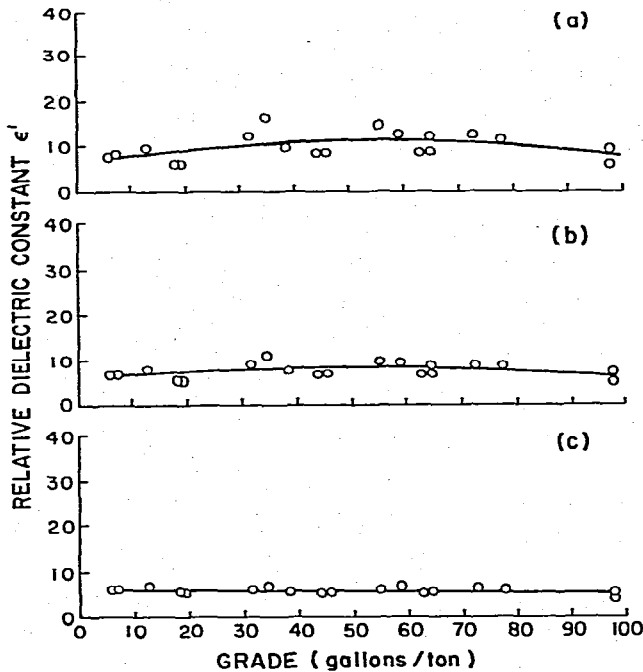


Fig. 6. Dependence of ϵ' (at 1 MHz) on shale richness. (a) Undried samples; (b) samples subjected to two heating cycles; (c) after four heating cycles.

Figure 6 shows the corresponding results at 1 MHz. The relatively small scatter in ϵ' values even for the undried samples (Fig. 6a) and the pronounced absence of any variation in ϵ' with shale grade for the samples subjected to four heating cycles (Fig. 6c) as seen by a comparison of Fig. 5(d) with Fig. 6(c) are to be noted.

DISCUSSION

The decrease in the values of the parameters ϵ' and ϵ'' with drying observed in the present study for Green River oil shale, is consistent with similar data reported in the literature for the electrical behavior of wet rocks⁸. The strong dispersion observed in ϵ' and ϵ'' for the undried oil shale samples and the pronounced decrease in the dispersive behavior with drying are to be noted (Figs. 3 and 4). Since the permittivity of water remains almost constant up to a frequency of 10^9 Hz⁹, the increase in ϵ' and ϵ'' at low frequencies (~ 1 kHz) for the undried oil shale samples may be attributed to interfacial polarization effects. The decrease in the scatter of ϵ' and ϵ'' values as a function of organic content with each drying cycle (Figs. 5 and 6) is also a direct manifestation of the interfacial polarization effect.

The absence of a strong dependence of ϵ' and ϵ'' upon shale richness, as brought out by the results of the present study, clearly points towards the "interfering" effects of sample geometry and pore water/adsorbed moisture on the electrical properties of oil shales. The layered structure characteristic of oil shales and the random orientation of mineral grains and of the indigenous organic matter within each sedimentary varve coupled with the highly heterogeneous nature of these materials effectively preclude direct observation of any possible dependence of ϵ' and ϵ'' on the amount of organic matter in the shale. In this regard, it is interesting to compare these results with the data on Green River shales reported by Piwinskii and Duba¹⁰ in an earlier study, which seem to indicate a direct dependence of ϵ' and ϵ'' on the oil yield of these shales (at frequencies in the range 50 Hz–10 kHz). However, as Judzis¹¹ has pointed out recently, the results of Piwinskii and Duba¹⁰ are questionable in view of the lack of sufficient data points in their study (Piwinskii and Duba¹⁰ demonstrate the dependence of ϵ' and ϵ'' on organic matter only for three shale samples of varying grades). It is also significant to note the absence of any discernable relationship between ϵ' and shale richness at microwave frequencies (10^7 – 10^9 Hz) as found by Judzis¹¹ (cf. results shown at 1 MHz in Fig. 6). The author however finds a good correlation between the loss tangent ($\tan \delta = \epsilon''/\epsilon'$) and shale richness at 500 MHz and 24°C. In this frequency range, as Judzis points out, the inorganic phase of oil shale is probably transparent to the electromagnetic radiation.

The possibility of decomposition of the shale organic matter as a result of the pre-heating at 110°C is minimal as evidenced from the results of previous studies^{12, 13}. Hubbard and Robinson¹³ find that the low temperature decomposition of oil shale kerogen* is exceedingly slow; even at a temperature of 350°C, these authors find that more than a third of the initial kerogen is still undecomposed after heating for 24 h.

It is doubtful whether pre-heating of the shale samples at 110°C effectively

* The term "kerogen" was first applied by Crum-Brown¹⁴ in 1912 to denote specifically the insoluble organic matter in oil shale. The specificity of this definition has however been lost in recent years (for example, see ref. 15).

removes all the pore water from the shale matrix (for example, see Fig. 2). The water bonded to clays present in the shale possibly requires higher temperatures. However, the relative constancy in sample mass and the levelling-off of the ϵ' and ϵ'' values (for samples cored perpendicular to bedding planes) after three to four drying cycles, indicate that the fractional amount of this pore water is relatively small. The point to emphasize here is that the dielectric parameters, ϵ' and ϵ'' , are extremely sensitive to the presence of pore water and adsorbed moisture in the shale.

CONCLUSIONS

Moisture and pore water have appreciable effects on the dielectric parameters of Green River oil shale. These effects will have to be taken into account in the design of dielectric heating and fracture techniques.

The effects of pore water and moisture are relatively small at frequencies above ~ 100 kHz. This result coupled with the absence of appreciable interfacial polarization observed at these frequencies⁶ indicates that frequencies for operation of dielectric heating methods should preferably be selected at the higher end of the spectrum, viz. in the range 100 kHz and above. Penetration depths at higher frequencies are, however, small and therefore a compromise has to be sought between two conflicting requirements.

The impermeable nature of Green River oil shale makes it difficult for the pore water and adsorbed moisture to diffuse out of the shale matrix. This results in long pre-heating times (~ 90 h) for "complete" removal of pore water and adsorbed moisture.

The weak dependence of ϵ' and ϵ'' on shale organic content at frequencies in the range 50 Hz–1 MHz effectively rules out the application of dielectric techniques as an assay tool. The transparent behavior of oil shale minerals to electromagnetic radiation in the microwave frequency range could, however, facilitate possible determination of organic content at these frequencies.

ACKNOWLEDGEMENTS

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