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ELECTRICAL CONDUCTION MECHANISMS IN GREEN RIVER OIL SHALE

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ABSTRACT

Results on the dielectric behavior of Green River oil shale in alternating current fields are reported. Oil shale samples with oil yields in the range 10–40 gallons per ton have been obtained by coring of the rock perpendicular to the bedding planes. Trends in the variation of AC conductivity, dielectric constant and loss factor are studied with frequency and temperature as the variable parameters. Measurements have been carried out in the range of frequencies 1 Hz–1 MHz and temperatures 25–500 °C. Increases in the conductivity of several orders of magnitude are observed for the samples heated from room temperature to 500 °C. The abnormally high values of dielectric constant and loss factor point toward the importance of Maxwell–Wagner interfacial polarization in electrical conduction mechanisms in oil shale. Striking variations in the conductivity–temperature curves are found before and after decomposition of the organic matter in the shale. The results of the present study indicate that measurement of electrical conductivity could be utilized to monitor the progress of retort fronts in oil shale beds.

INTRODUCTION

Characterization of the thermophysical properties of oil shale and related fossil fuel materials has assumed increasing importance in recent years in view of their attractiveness as viable energy sources. Thermoanalytical methods such as Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA), have been applied to varying degrees of success for the study of oil shale; these studies have ranged from routine identification of the various constituent minerals to investigations on the kinetic and mechanistic aspects of the thermal degradation of the organic matter in the shale[1–7]. Knowledge of the thermal behavior of oil shale, however, must be regarded as being far from conclusive. Heterogeneity of composition, the complex nature of chemical reactions and the sensitivity of the hydrocarbons present in oil shale to atmospheric effects, have all contributed to inconsistencies in the literature data. These problems are accentuated by the limitations inherent in techniques like DTA and TGA, namely that the information attainable by the application of these thermoanalytical methods reflects only the gross macroscopic nature of the reactions taking place in the material. On the other hand, the extreme sensitivity of electrical methods of analysis[8,9] to physical and chemical changes provides information on a molecular level. In view of this, it is surprising to note that very few examples for the application of such techniques to the study of solid fuels exist in the current literature. Direct current measurements on shales and coals have been reported[10,11]; the data obtained in these studies is, however, limited on account of the fact that only ohmic conduction is monitored. The variety of information provided by polarization effects manifests itself in alternating current measurements and adds a new dimension to the thermophysical picture of the material of interest. This paper, therefore, reports results of an investigation on the dielectric behavior of Green River oil shale in alternating current fields. Trends in the variation of different parameters such as dielectric constant ε', loss factor ε'' and conductivity σ are studied with frequency and temperature as the variables.

EXPERIMENTAL

The experimental arrangement for the measurement of electrical conductivity is reported elsewhere[12,13].

Samples of Green River oil shale in the present investigation were obtained from Rifle, Colorado. Care was taken to select samples which were crack free. Right circular cylindrical specimens (7/8-in diameter, 1/4-in thick) were cored perpendicular to the bedding planes. Oil yield of the shale samples was calculated from measured densities using correlation tables[14]. Samples with oil yields in the range 10–40 gallons per ton were chosen for the present study.

Good electrical contact between the sample surface and the electrodes was ensured by appropriate loading of the electrode contact plates onto the sample. Silver paint was employed in a few instances to reduce contact resistance but subsequent investigation proved this effect to be negligible.

Measurements were carried out in the range of frequencies 1 Hz–1 MHz and temperatures 25–500 °C. A continuous range of frequencies was facilitated by the automatic recording technique developed in this laboratory[13]; consequently the electrical conduction behavior at a large number of frequencies could be conveniently studied. Conventional bridge measurement techniques[15], on the other hand, are time-consuming and laborious; the frequency range in these techniques is also severely limited by the need to use different types of bridges in the various frequency domains.

In view of the extreme sensitivity of oil shale hydrocarbons to atmospheric oxidation[3], all experiments were carried out in a rapidly flowing atmosphere of pre-purified nitrogen gas over the samples. The gas also serves to sweep out the thermal degradation products from the reaction zone.

RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of a 19.8 gallons per ton oil shale sample as a function of frequency and temperature. The conductivity is seen to exhibit

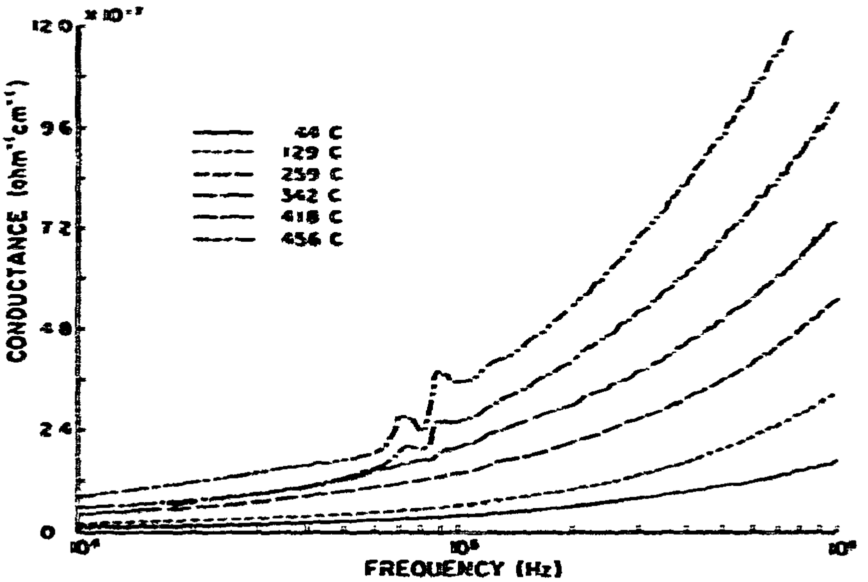

Fig. 1. Frequency and temperature dependence of the electrical conductivity of a 19.5 gallons per ton oil shale sample.

a smooth increase in its magnitude with frequency and temperature. The peaks in the conductivity curves at higher temperatures are interpreted to arise from polarization effects discussed below. Similar behavior is characteristic of other oil shale samples of varying grades. The trends observed in the present study for the dependence of the electrical conductivity on frequency are consistent with previously published work on the electrical properties of limestone, marl and dolomite[16], which shows that the lower the water content and/or the higher the resistivity of the material, the greater is the increase in the conductivity with increasing frequency. The water content of oil shale is variable; however, it seldom exceeds 6–10 %, which is well within the limits observed for sedimentary rocks exhibiting similar dielectric behavior. The temperature range in which the water is driven off from the oil shale matrix is quite broad ≈100–≈300 °C. The absence of well-defined endothermic dehydration peaks in the DTA[12] and the gradual weight loss observed in TGA of oil shale at these temperatures[5] suggest that the water molecules trapped in the oil shale matrix are probably zeolitic.

The increase in the electrical conductivity with temperature can be related to ohmic conduction which follows the well-known relationship[17].

$$\sigma_{(\mathrm{ohmic})} = \sigma_o \exp(-E_a/RT) \tag{1}$$

where E_a is the activation energy for the mobility of the current carriers and σ_o the pre-exponential factor related to the lattice vibration frequency. The ohmic contribution to the electrical conductivity of oil shale presumably arises from ionic conduction of the mineral constituents present in it. Conductivity in alternating current fields, however, is the sum of the ohmic and polarization components expressed as

$$\sigma_{(\mathrm{total})} = \sigma_{(\mathrm{ohmic})} + \sigma_{(\mathrm{pol})} = \sigma_o \exp(-E_a/RT) + 2\pi f \varepsilon'' \tag{2}$$

where ε'' is the loss factor, $\sigma_{(\mathrm{pol})}$ represents the contribution of polarization currents to the total conductivity $\sigma_{(\mathrm{total})}$ and ν is the operating frequency. The frequency and temperature dependence of the electrical conductivity in alternating current fields is therefore given by

$$\sigma_{(\mathrm{total})}(\nu,T) = \sigma_{(\mathrm{ohmic})}(T) + \sigma_{(\mathrm{pol})}(\nu,T) \tag{3}$$

The heterogeneous nature of oil shale and the presence of a variety of minerals in admixture with the organic matter are expected to give rise to strong Maxwell-Wagner interfacial polarization[11]. The contribution of the second term in eqn. (3) to the total conductivity of oil shale is therefore appreciable. This is reflected in the abnormally high values of ε' and ε'' observed in the present study. The frequency and temperature

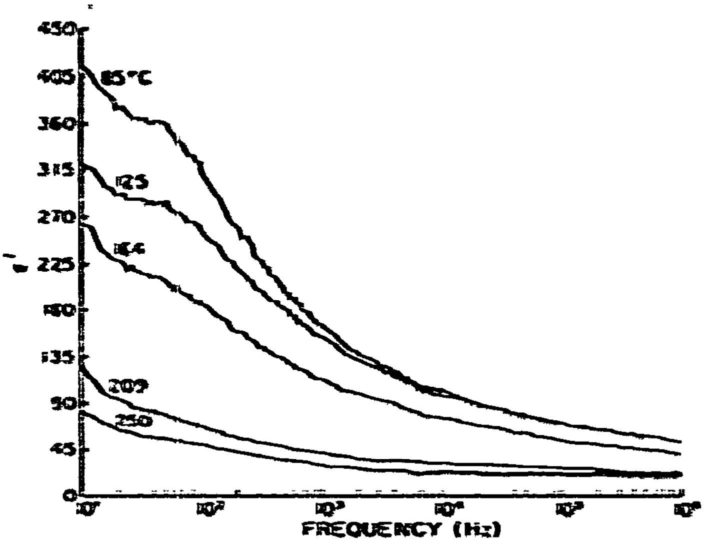

Fig. 2. Frequency and temperature dependence of the dielectric constant, ε' at low temperatures.

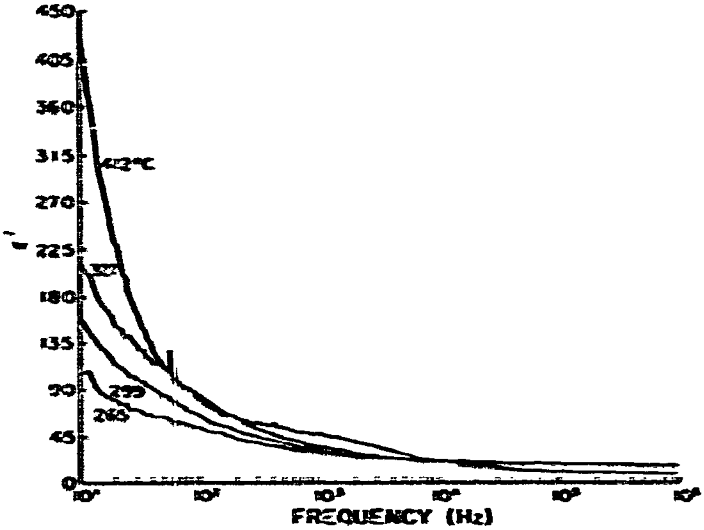

Fig. 3. Frequency dependence of ε' at elevated temperatures.

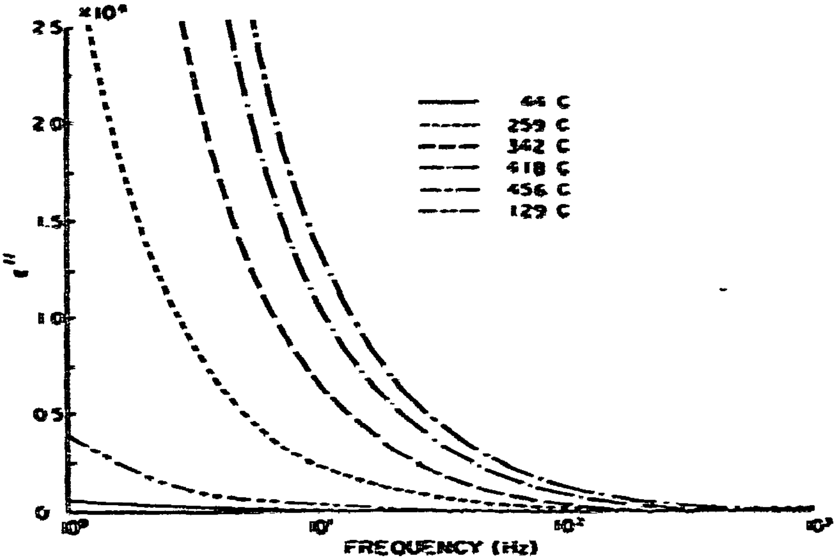

Fig. 4. Representative plot for the variation of loss factor ε'' with frequency at different temperatures.

dependence of these parameters is shown in Figs. 2, 3 and 4. The strong dispersion shown by ε' (Figs. 2 and 3) is indicative of an interfacial polarization mechanism[11]. Additional evidence is also provided by the occurrence of loss tangent (tanδ) peaks at low frequencies in oil shale[13]. It is significant that organic polymer systems with inorganic fillers exhibit analogous dielectric behavior[20]; this is reasonable in view of the fact that both oil shale and these materials represent heterogeneous systems with organic and inorganic compounds interspersed in them. Polarization at the interfacial boundaries in these systems is expected to predominate their dielectric behavior, especially at low frequencies and high temperatures[19]. Oil shales with low organic content (< 30 gallons per ton) can be regarded as a Maxwell-Wagner system of highly resistive organic particles dispersed uniformly in a fairly conductive mineral matrix; $\varepsilon_1' >> \sum_i \varepsilon_i', \sigma_1 < \sum_i \sigma_i$ where ε_1' is the dielectric constant of the organic fraction and $\sum_i \varepsilon_i$ is the composite dielectric constant representing the various mineral constituents*, σ_1 is the electrical conductivity of the organic matrix and $\sum_i \sigma_i$ is the total conductivity of all the mineral particles in the oil shale matrix. Richer shales with high organic content, on the other hand, can be represented by the organic matter as the continuous phase and the mineral particles as the disperse phase.

At low temperatures, the conductivity of the mineral matrix is probably the dominant factor in the total conductivity of oil shale, i.e., $\sigma_{(\text{ohmic})}(T) \gg \sigma_{(\text{pol})}(r,T)$ in eqn. (3). Examination of the conductivity curves in Fig. 1 shows that this is indeed the case; the dispersion exhibited by the electrical conductivity is seen to increase with temperature as the second term in eqn. (3) becomes more and more important.

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* It must be noted that the dielectric constant of the mineral matrix expressed as $\sum_i \varepsilon_i'$ is not strictly additive in many cases. Previous work on the dielectric properties of rocks and minerals[21] has shown that the presence of moisture can increase the dielectric constant by an amount greater than that predicted by simple mixing rules.

The initial decrease in ε' values with temperature shown in Fig. 2 is correlated with the loss of polar water molecules from the matrix. The subsequent increase in ε' with temperature seen in Fig. 3 presumably arises from the Maxwell–Wagner polarization effects discussed above. Changes in the orientational freedom of the various molecules and ions brought about by the decomposition of the organic matter are also likely to cause variation in the dielectric constant. An added factor in the extremely high values of ε' found at elevated temperatures (Fig. 3) could be the carbon which forms as a residue from the decomposition of the organic matter in the shale. The situation is similar to the high dielectric constants characteristic of carbon-filled rubber vulcanizates[22].

The extreme sensitivity of the electrical conductivity to the chemical reactions in oil shale is depicted in Figs. 5 and 6 which show semi-log plots of ρ vs. $1/kT$ (ρ is the resistivity and k the Boltzmann constant) at selected frequencies for two different grades. The curves exhibit a sharp minimum in the resistivity values in the 100–250 °C range followed by a peak in the temperature range corresponding to the decomposition of the organic matter. Similar behavior is characteristic of all the oil shale samples examined in the present study. The presence of such peaks in ρ vs. $1/T$ curves is indicative of changes in polarization behavior arising from the physical and chemical

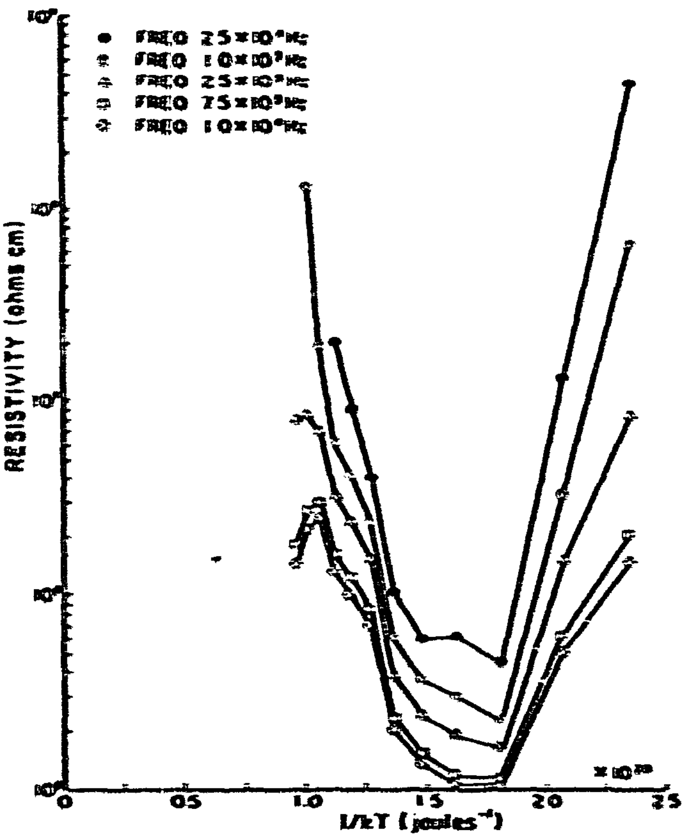

Fig. 5. Semi-log plot of resistivity (ρ) vs. reciprocal temperature ($1/kT$) for a 10.4 gallons per ton oil shale sample.

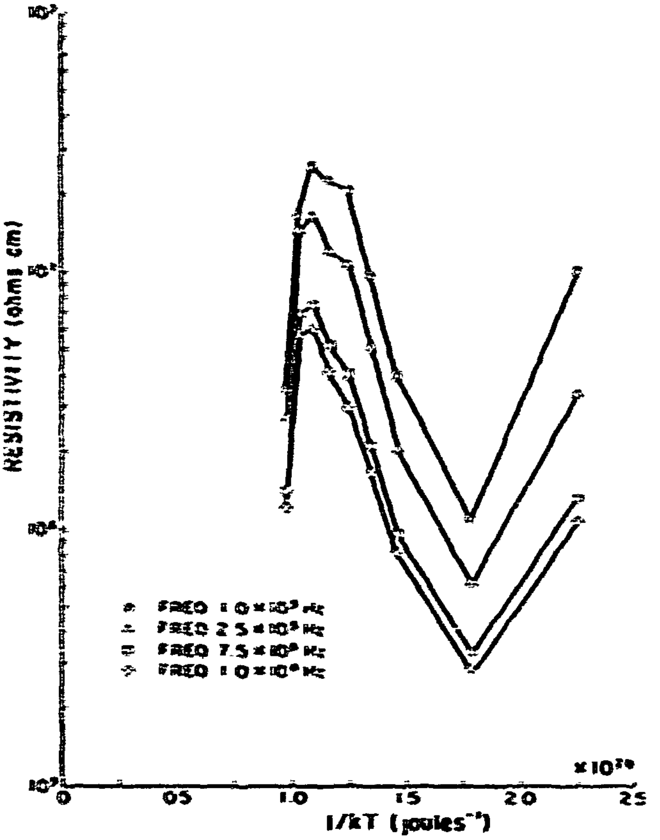

Fig. 6. ρ vs. 1/T plot for a 27.5 gallons per ton shale sample.

transformations in the material[9]. The resistivity curves for the same samples after decomposition of the organic matter are shown in Figs. 7 and 8; the difference in the shape of the curves is striking. The electrical conductivity of the "spent" shale arises from the mineral constituents present in the shale* and the carbon residue from the thermal degradation of the organic matter. The absence of any thermal reactions in the material is indicated by the non-occurrence of sharp maxima or minima in the conductivity curves. The small peaks in the conductivity curves at the lowest frequency in Figs. 7 and 8 arise from polarization effects superimposed on the ohmic contribution to the conductivity (cf. of Fig. 1).

It is possible to extract activation energies for mobility of the current carriers from the slope of the above plots (see eqn. 1). In materials as heterogeneous as oil shale, however, such values are of limited significance. The presence of a variety of mineral particles in the system and the complicating effect of the decomposition products arising from the organic matter, make it difficult to pinpoint the exact nature

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* All the minerals present in the oil shale samples examined in the present study are stable up to the temperatures corresponding to decomposition of the organic matter as indicated by DTA. Analcime (decomposition temperature ~350 °C) and nahcolite (decomposition temperature ~150 °C) two of the minerals commonly present in Green River oil shale were absent in the samples examined in the present study.

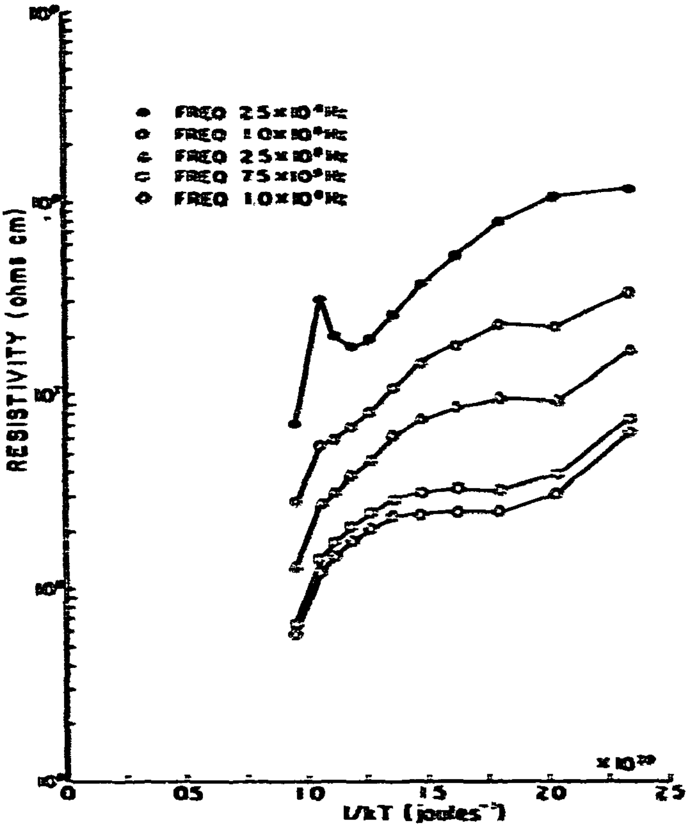

Fig. 7. Same plot as in Fig. 5 for the sample after complete decomposition of the organic matter.

of the current carriers. On the basis of the above results, a transition from an ionic conduction mechanism to semi-conducting behavior at elevated temperatures also cannot be ruled out.

CONCLUSIONS

The results of the present investigation show that:

(1) The electrical conductivity of Green River oil shale in alternating current fields, increases with increasing frequency and temperature. Increases in the conductivity of several orders of magnitude are commonly observed for the samples heated from room temperature to 500 °C.

(2) The abnormally high values of ε' and ε'' point toward the importance of Maxwell-Wagner interfacial polarization in electrical conduction mechanisms in oil shale. Interfacial polarization effects are more pronounced at low frequencies and high temperatures.

(3) The various dielectric parameters are extremely sensitive to the presence of water molecules in the oil shale matrix.

(4) The electrical conductivity is extremely sensitive to the physical and chemical changes in the material. The results of the present study indicate that measurement of

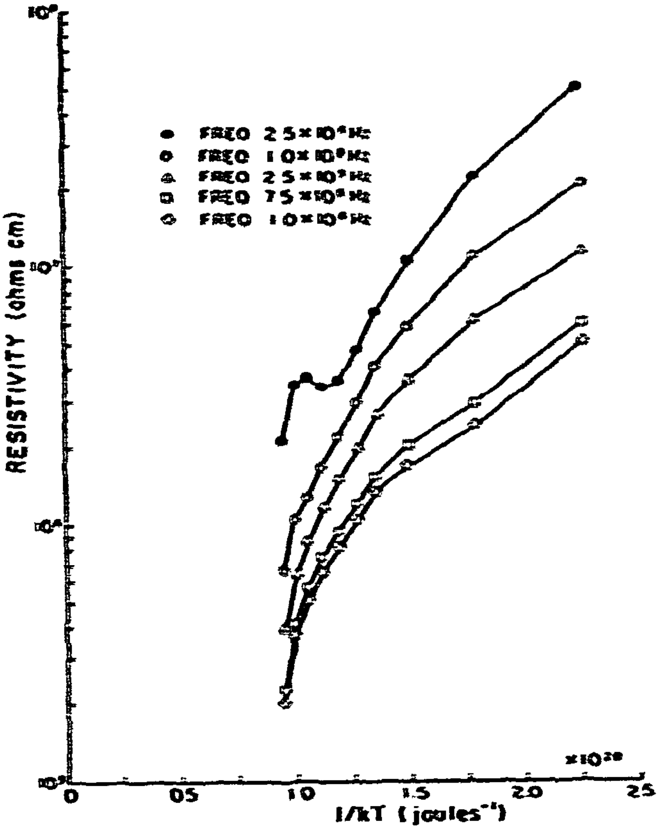

Fig. 8. Same plot as in Fig. 6 for the sample after complete decomposition of the organic matter.

this parameter could be utilized to monitor the progress of retort fronts in oil shale beds. Striking variations in ρ vs. $1/T$ curves are found before and after decomposition of the organic matter in oil shale.

(5) The trends observed in the results of the present study should be typically characteristic of analogous fossil fuel systems and in general, any system with organic and inorganic constituents interspersed in it.

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