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NEW OBSERVATIONS ON CHEMICAL AND STRUCTURAL TRANSFORMATIONS IN GREEN RIVER OIL SHALES

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ABSTRACT

The temperature-dependent electrical, mechanical, and thermal behavior of Green River oil shales of varying oil yields in the range ~20—400 l ton^{-1} have been studied by a variety of complementary techniques including thermosonimetry, a.c. electrical conductivity measurements, dielectric spectroscopy in the microwave frequency domain, and differential scanning calorimetry. A close correlation exists in the data obtained by the above techniques although there are significant differences in the sensitivity of the selected measurement probes to various processes taking place in the material. At least four distinct chemical or physical processes are identified in the temperature range from ambient to ~500°C for Green River oil shales. Possible origin(s) for these processes and the effects that they manifest in the thermophysical behavior of these materials are discussed in the light of data obtained by the various techniques.

INTRODUCTION

An understanding of the electrical, mechanical, and thermal behavior of technologically important materials such as Green River oil shales is important both from a fundamental and practical point of view. The extreme sensitivity of electrical methods of analysis to chemical and structural transformations in these materials was highlighted in previous papers from this laboratory [1—5]. Knowledge of the thermal behavior is critical to efficient process design and to maximize product yields from the energy-rich organic constituents of these shales. From an application viewpoint, the practical potential of electrical methods has been demonstrated in a wide variety of geological problems related to remote probing, processing, and prospecting of underground resources [6—8]. It is conceivable that such methods utilizing propagation of electromagnetic radiation will have direct relevance to oil shale technology in the near future. The ultimate success of this sort of an

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approach will hinge on the completeness of knowledge as regards the thermal and electrical properties of oil shales and the interplay of factors related to these properties. It is the purpose of this paper to seek a correlation between the trends observed in the electrical and thermal behavior of Green River oil shales as a function of temperature. A wide variety of techniques such as a.c. electrical conductivity, thermosonimetry (TS), microwave dielectric spectroscopy and differential scanning calorimetry (DSC) was employed for this purpose, the choice of each technique being dictated by the specific nature of information that it was capable of yielding. As in a previous study [9], the use of several techniques of a complementary nature was of particular help in data interpretation on these complex materials.

In a previous study [10], a large anomaly in the temperature-dependent electrical resistivity behavior of Green River oil shales at 25—350°C was tentatively assigned to the gradual release of pore water from the oil shale matrix. This anomaly is re-examined in the light of new data obtained on the DSC, microwave dielectric, and TS behavior of these materials in the same temperature range. The presence of a structural transformation in the shales at ~380°C, which was indicated by electrical and mechanical measurements in a previous research [11], is confirmed by the TS data obtained in the present investigation. It may also be mentioned that the TS technique, which was developed by one of the authors [12—14], affords a convenient means of separating effects arising from chemical and mechanical transformations in the material.

EXPERIMENTAL

Mine-fresh oil shale was obtained from the Paraho Oil Shale Development Corporation, Rifle, Colorado. Organic contents of the samples were determined by a pulsed NMR technique [15] and by specific gravity measurements [16]. Right circular cylindrical cores of varying dimensions were drilled from the massive shale blocks in directions perpendicular to the shale bedding planes. Care was taken to ensure a fairly even distribution of the organic and mineral matter in the cored samples. Crack-free samples were carefully dried in vacuum to remove free moisture. DSC measurements were carried out on oil shale particles obtained by crushing appropriate cores to pass ~200 mesh.

All measurements were carried out in a flowing stream of pre-purified inert gas (dry N_2 or He) to avoid spurious effects arising from the oxidation of the organic constituents in the shale. Electrical conductivity measurements were carried out using the automated Dynamic Dielectric Analysis (DDA) technique described elsewhere [1—3,10]. A description of the principles of operation, experimental set-up, and other relevant details of the TS technique can be found in refs. 12—14. Microwave dielectric spectroscopy was carried out by an automated technique described in a previous paper [17]. DSC measurements were performed on a DuPont 990 Thermal Analysis system fitted with the DSC accessory module. A nominal heating rate of 10°C min^{-1} was employed for the DSC and TS measurements.

RESULTS

Figures 1—4 present TS data obtained in the present study on three selected grades of Green River oil shale. Figure 1 shows the results for an oil shale sample with low organic content, 54 l ton^{-1}. The results presented in Figs. 2 and 3 correspond to medium grade and "rich" oil shale samples, respectively. Data obtained on a sample with very high organic content (392 l ton^{-1}) are shown in Fig. 4. The same general features (vide infra) were observed in the thermosonigrams for the other oil shale samples of varying grades in the range ~20—400 l ton^{-1} that were examined in the present study. The degree of reproducibility that is to be expected from the TS measurements is illustrated by the data shown in Fig. 2(a) and (b) on two oil shale samples of identical grade (150 l ton^{-1}). In the TS data presented in Figs. 1—3, the ordinates refer to the TS activity defined as the number of counts of electrical oscillations detected by the piezo-electric cell per degree centigrade [12]. The corresponding temperatures given on the abscissae refer to the reference temperature as measured in a "dummy" cavity placed adjacent to the test sample.

Four regions of TS activity may be distinguished in the data presented in Figs. 1—4. Overlapping of the temperature regimes of the processes contributing to the TS activity in the intermediate region 300—470°, gives rise to loss of resolution as evidenced by the data in Figs. 1, 2, and 4. On the other hand, this intermediate region is fairly well resolved for the 273 l ton^{-1} sample (Fig. 3). In only a few cases could such a degree of resolution be obtained, most samples showing a tendency to exhibit activity that was "smeared" over a broad temperature region extending from ~300 to ~470°C.

Postponing, for the moment, a discussion of the chemical and/or physical processes that give rise to the TS-activity, we now present the results of some electrical measurements on Green River oil shales. Figure 5 is a semi-log plot

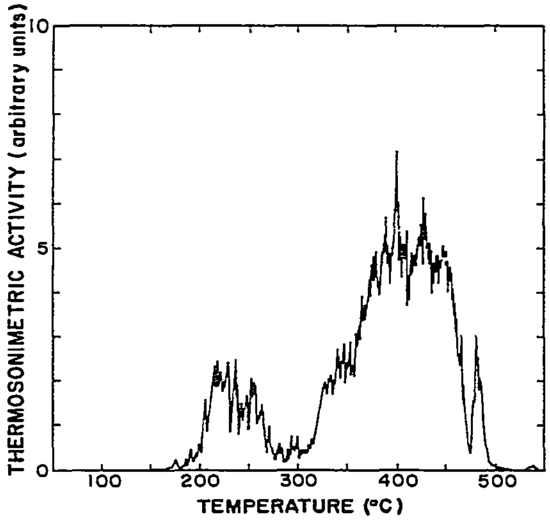


Fig. 1. Thermosonigram for a Green River oil shale sample assaying 54 l ton^{-1}.

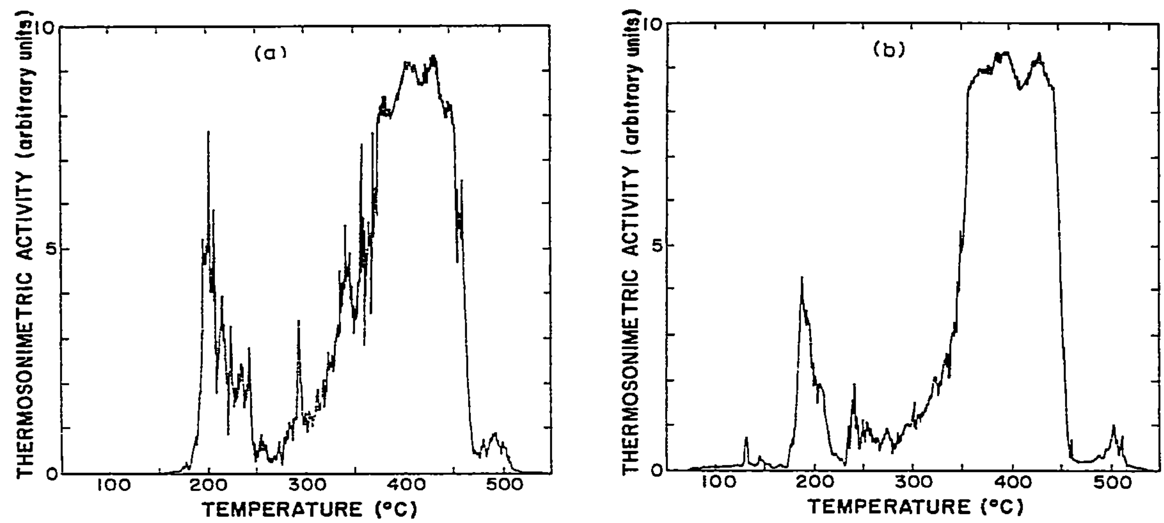
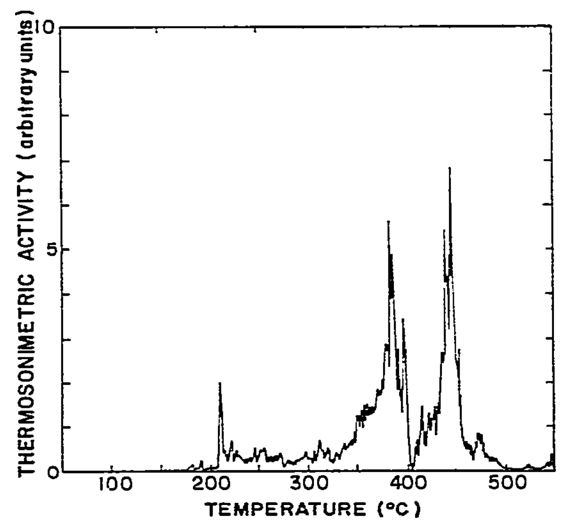


Fig 2. Comparison of thermosonimetric (TS) behavior of two oil shale samples of identical grade (a) and (b) are TS data obtained on two different samples assaying ~150 l ton^{-1}.

of a.c. resistivity (ρ) as a function of reciprocal temperature expressed in thermal energy units. Note the broad minima in the resistivity curves followed by a sharp "spike" at temperatures around 380°C. This effect is particularly pronounced at higher measurement frequencies. The ρ values thereafter show a monotonic decrease with temperature, the values at temperatures >470°C reaching up to five orders of magnitude lower relative to that at room temperature (not shown in the figure). These effects are characteristic of oil shale samples of all grades that were examined in the present study. Figure 6 is a contour diagram showing the simultaneous variation



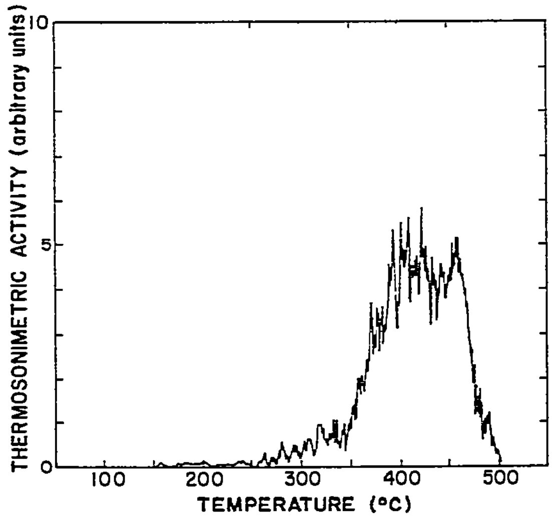
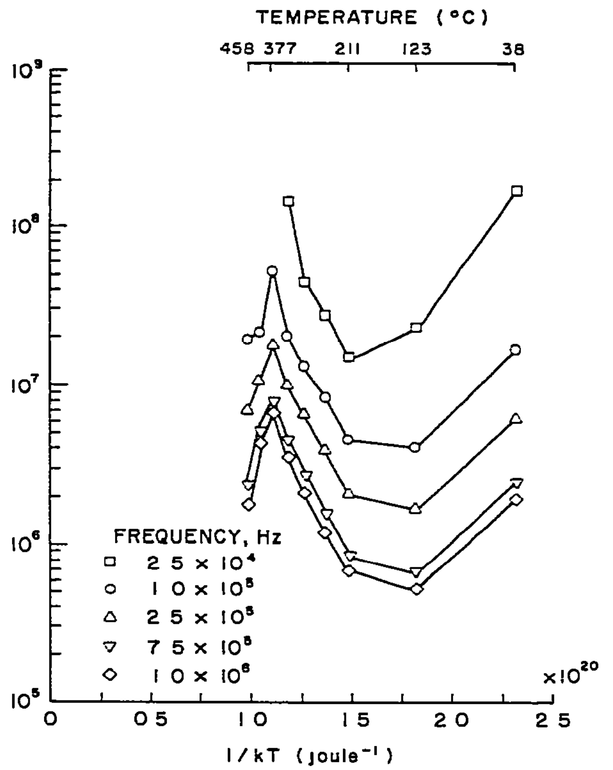


Fig. 3. Thermosonigram obtained on a rich Green River oil shale sample (~260 l ton^{-1}).

Fig. 4. Typical TS data on an oil shale sample with very high organic content (392 l ton^{-1})



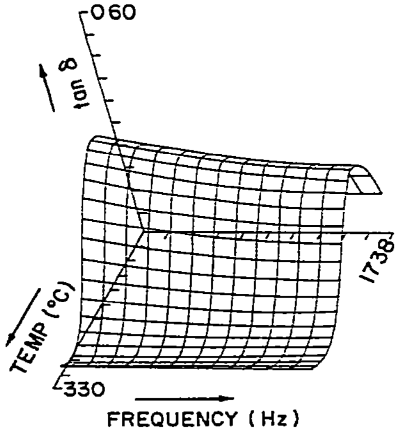


Fig. 5 Semi-log plot of a.c. resistivity vs reciprocal temperature for a 146 l ton^{-1} shale sample

Fig. 6 Contour diagram showing the simultaneous variation of the loss tangent (tan δ) with frequency and temperature in the microwave frequency domain

of the loss tangent (tan δ) with two variable parameters, namely temperature and frequency. These data pertain to the microwave frequency range, in contrast to the results presented at lower frequencies in Fig. 5. However, the same general features are evident in both frequency domains, particularly as regards the temperature dependence of the various dielectric parameters that were measured. Thus, the gradual increase in tan δ, or effectively in the a.c. conductivity at temperatures in the range 24—330°C (Fig. 6), cor-

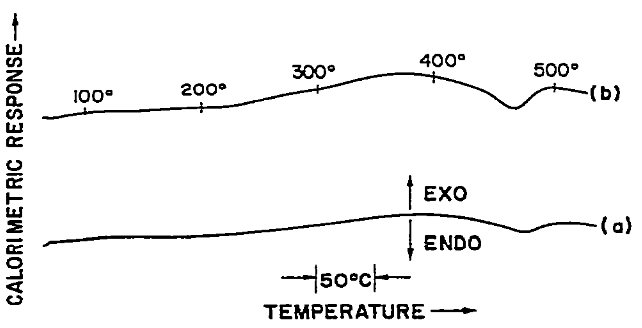


Fig. 7. DSC data on a 121 l ton^{-1} shale sample at two different calorimetric sensitivities. (a) 0.5 (mcal sec^{-1}) div.$^{-1}$, (b) 1.0 (mcal sec^{-1}) div.$^{-1}$.

responds to the aforementioned resistivity minima (Fig. 5). A subsequent increase in the tan δ values at temperatures corresponding to the decomposition of the organic matter (not shown in Fig. 6 for purposes of clarity) correlates well with the effects observed in the variation of ρ with temperatures above 470°C.

For comparison with the trends observed in the electrical and TS behavior, DSC experiments were carried out on Green River oil shale samples of varying organic content. Typical results are shown in Fig. 7 for a 121 l ton^{-1} sample at two different calorimetric sensitivities. Endothermic effects are observed in two temperature regions, i.e. 100—300°C and 400—500°C, intensity of the DSC peaks corresponding to these regions being roughly proportional to the amount of organic matter in the shale.

DISCUSSION

To aid in interpretation of data obtained by various types of measurements described above, we will designate four temperature regions, i.e. ambient to ~250°C, 300—380°C, 380—470°C, and 470—500°C, and denote the chemical and/or physical processes occurring in the above regimes by A, B, C and D, respectively. The various processes, speculation on the specific nature of each process, and the effects that they manifest in the TS, electrical and thermal (DSC) behavior of Green River oil shales are given below.

Process A

This process, which takes place over a very broad range of temperature (ambient —250°C) gives rise to the resistivity anomaly referred to above, the increase in tan δ values (Fig. 6), the weak endothermic peak extending from 100—300°C in the DSC thermograms, and a peak in the thermosonigrams at temperatures around 200°C (Figs. 2—4). Note the absence of this peak for the oil shale sample of low organic content (Fig. 1).

There are three chemical processes that could conceivably give rise to the effects mentioned above: (a) loss of pore water from the oil shale matrix, (b) decomposition of light hydrocarbon ends from the organic matter in the shale, and (c) effects arising from thermal alterations undergone by the oil shale minerals. In previous papers [10,11], the resistivity anomaly was tentatively assigned to process (a). Seeking an alternative interpretation of this process in terms of either (b) or (c), we take into account the following factors. Firstly, oil shale samples with low organic content do not show a peak at ~200°C (e.g. Fig. 1). This experimental observation seems to link process A with the organic matter in the shale which consequently points towards (b) rather than to (a) or (c). Secondly, in the thermal chromatographic studies reported by Yen and his co-workers [18], the authors observe a peak in the total gas yield at ~200°C which persists even in samples of kerogen concentrate freed of initial bitumen. Thirdly, the results obtained from microwave dielectric spectroscopy at temperatures corresponding to process A (e.g. Fig. 6) indicate that the observed effects are linked to either reaction (a) or (b) rather than to (c), in view of the fact that oil shale minerals are presumably transparent to the electromagnetic radiation at these frequencies [19]. Further confirmation on the nature of the gaseous species being evolved in this temperature range (whether H_2O or light hydrocarbons) will probably hinge on mass spectrometric studies.

Process A cannot be physical (i.e. related to changes in mechanical properties) in nature in view of the fact that the mechanical properties do not show any discontinuity at temperatures ranging from ambient to ~250°C [11].

Process B

This process gives rise to a sharp discontinuity in the a.c. resistivity (Fig. 5), a peak in the thermosonigrams (Fig. 3), which is most often masked by subsequent TS activity (e.g. Figs. 1, 2, and 4), no effect in the DSC and a sharp discontinuity in the mechanical yield versus temperature curves [16]. Taking the above observations into account, it is reasonable to assign this process to a mechanical transition taking place in the shale. This interpretation is consistent with that given in previous studies [10,11], wherein it was proposed that these temperatures represent the gradual "loosening" of the kerogen molecules from the inorganic matrix with the abrupt degradation of mechanical strength at a critical point, which probably corresponds to the peak temperature, ~380°C in the $\ln \rho$ vs. $1/T$ curves (e.g. Fig. 5). It is interesting to note that, in favorable cases, the peak in the TS activity corresponds closely with this temperature (e.g. Fig. 3) although this transition is often masked by subsequent events occurring in the oil shale sample.

Process C

This process, which takes place in the approximate temperature range 380—470°C, gives rise to anomalously high conductivity values both at radio frequencies and in the microwave frequency range, intense activity in the thermosonigrams, and an endothermic effect in the DSC. The intensity of the DSC endotherm is also proportional to the organic content of the shale. These factors are consistent with a process involving massive thermal fragmentation of the kerogen macromolecular network in the shale. This process has also been fairly well characterized in the literature by a variety of techniques (vide infra).

Process D

This process gives rise to small peaks in TS activity in the region 480—500°C (Figs. 1—4), no discernible effects in the electrical characteristics, and an endothermic DSC effect often superimposed on the peak representing process C (see, for example, Figs. 6 and 7 in ref. 1). Two chemical processes could be visualized as giving rise to these effects, (a) transformation of pyrobitumen, which is formed as an intermediate in kerogen decomposition, to gas, oil, and carbon residue (see ref. 20 for details of this process) and/or (b) secondary reactions including radical species formed in process C. Further speculation on the nature of process D and unequivocal identification of various steps associated with this process must await future studies, preferably by mass spectrometry.

In summarizing the above discussion, one may conclude that process A is distinctly chemical in nature, process B has features predominantly associated with a physical rather than a chemical change, and processes C and D are accompanied by changes both in the chemical and physical nature of the oil shale sample. The data obtained in the present study serve to highlight the complexity of the thermophysical behavior of oil shales on being subjected to heat. In particular, the decomposition temperature range (400—500°C) that is widely regarded as being characteristic of oil shale kerogen (see works cited in ref. 20) is shown to be an over-simplification. There are distinct changes taking place in the oil shale matrix at temperatures right from the ambient value and at least four different processes have been identified in the present study. More importantly, these processes seem to be related mostly to the organic constituents of the shale. These observations assume added significance when one recognizes the "additional" energy input that will have to be taken into account for heat and material balance computations (e.g. in retorting procedures) as a result of the above-mentioned processes. Thus the cautionary remarks of increased heat requirements for retorting oil shales containing minerals such as analcime, nahcolite etc., that were expressed by Johnson et al. [21], remain true even in the absence of these minerals; although this additional heat input will be admittedly small in this case. In this regard, it is worth noting that none of the oil shale samples examined in the present study contained minerals that are known to decompose at temperatures below ~500° C.

One of the primary objectives of this research was to establish a correlation between the trends observed in the electrical, mechanical, and thermal behavior of Green River oil shales as a function of temperature. The remarkably good degree of correlation that is revealed in a comparison of the results obtained from TS, electrical, and DSC measurements is indeed gratifying. In a wider perspective, however, it is also instructive to note the different sensitivity of the above techniques to a particular process taking place in the material. For example, although the electrical techniques are extremely sensitive to process A (Figs. 5 and 6) the TS and DSC probes are much less responsive to this type of perturbation (Figs. 3 and 7). The lesson to be learnt here is that for studies on complex materials such as oil shales, the use of more than one technique and judicial selection of several complementary probes simplify considerably the task of meaningfully interpreting the data obtained therein.

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