ASSAYING GREEN RIVER OIL SHALE WITH MICROWAVE RADIATION

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Abstract

Microwave radiation may be an alternate means of assaying the organic content of Green River oil shale. Preliminary results show a strong correlation between the dissipation of microwave energy in shale and its richness, as determined by Fischer assay, in the frequency range investigated (0.3 to 1.0 GHz). The loss tangent, an index of a material's ability to absorb electromagnetic radiation energy and a function of the complex dielectric constant, increases by a factor of six as shale richness increases from 0.034 to .261 m^3 metric ton of shale (10 to 76 gal/short ton).

There is an indication also that radiation of oil shale with high-power microwave energy may aid in the recovery of oil and gas by the decomposition of kerogen.

Introduction

The potential oil yield of western shales is presently determined by Fischer assay--a pyrolytic method that measures the quantity of oil evolved during a heating process. Its success is largely due to the accuracy and reliability of the oil yield determinations which are within 1.7 l/metric ton (0.5 GPT) for lean and intermediate richness shales. A period of at least two hours, however, is necessary to assay a single specimen. This time includes sample crushing and drying as well as the actual retorting.

A new assaying technique with comparable accuracy has not yet been discovered. The search goes on, however, as there is a need in the industry to simplify and shorten the procedure for determining the oil yield of these western shales. Siggia and Uden (1974), in discussions at a National Science Foundation workshop on oil shale, cite the need for the "replacement of the modified Fischer assay procedure for oil yield determinations by a simpler, more reliable and more informative procedure."

Weak correlations between various physical and thermal properties and the organic content of shales have been found; the results are in the literature. J. W. Smith (1956) determined that specific gravity of shale from the Green River formation is related to Fischer assay oil yield. The relationship's accuracy is at best ±14 l/metric ton (±4 GPT). R. J. Shaw (1947) correlates specific heats with organic richness; Prats and O'Brien (1975) use thermal conductivities. Both, however, are weak for assaying purposes. F. P. Miknis and others (1974) have estimated potential oil yields with pulsed NMR* measurements. Instantaneous assays are possible, but standard errors are between 0.0069 and 0.0137 m^3/metric ton (2 and 4 GPT). R. L. Hanson and others (1975) have correlated acetylene production, during pulsed ruby laser pyrolysis, with Fischer assay results. Again, a strong relationship was not found. J. B. Sellers and others (1972) measured compressive strengths

*nuclear magnetic resonance

of different grade shales; only a general trend in the relationship is seen.

In preliminary work, we discovered that there is a significant dissipation of radiation energy in the microwave frequency range as it propagates through oil shale samples. This study correlates the relative amount of energy dissipated at 500 MHz with shale richness. The correlation is strong and accurate to 0.0058 m^3/metric ton (1.7 GPT) with the described procedure. The microwaves used for this analysis are of low power, on the order of 5 milliwatts. There exists a great potential for the application of high-power microwave radiation in the actual break-up of kerogen for the production of oil and combustible gases from shale.

Microwave Theory

The oscillating field of electromagnetic radiation induces an electric displacement of dipoles, generally out of phase with the field, in the irradiated medium. This never-ending effort of dipoles to stay aligned with the oscillating field, sometimes called dipole relaxation, will result in a maximum absorption of energy when the dipoles resonate between the extremes of completely random and perfect alignment. The energy is dissipated as heat. The microwave frequency range of 0.3 to 300 GHz encompasses the vibrational and rotational frequency range of typical organic bonds (R. P. Bauman 1962).

The precise structure of the polymeric macromolecule, kerogen, is unknown. However, polarity is clearly evident from structural studies of kerogen by Schmidt-Collerus and Prien (1976) and by T. F. Yen (1976). Furthermore, the numerous sulfur-, nitrogen-, and oxygen-hetero atoms present in kerogen (Robinson and others 1963) greatly augment the polarization characteristics of this substance. The polar nature of kerogen enhances dipole relaxation and, hence, the observed energy dissipation. Such high polymers usually exhibit "orientation polarization" where segments of the macromolecule change orientation rather than the entire molecule itself. This produces a distribution of relaxation time values (C. P. Smith 1955) and, consequently, energy loss is fairly constant over a wide range of frequencies.

Another interesting and successful application of dipole relaxation has been reported by R. W. Parsons (1975). He used a microwave attenuation technique to measure water saturations in Berea sandstone slabs. Water is quite polar and, therefore, "lossy" at microwave frequencies.

The complex permittivity, or dielectric constant ε^*, is a measure of the ability of a material to store radiation energy. The imaginary term of this constant is an index of the amount of energy actually absorbed. The relative permittivity is usually of importance and is defined as

$$\varepsilon_r = \varepsilon^*/\varepsilon_o = \varepsilon' - j\varepsilon'' , \qquad (1)$$

where ε_o is the permittivity of free space and equals 8.85×10^{-12} farads/meter and $j = \sqrt{-1}$. It is often useful to define the relative dielectric constant as:

$$\varepsilon_r = \varepsilon'(1-j\tan\delta), \qquad (2)$$

where $\tan\delta = \varepsilon''/\varepsilon'$.

Here, the loss tangent, tan δ, is the ratio of power lost in heat per cycle to power stored per cycle. It is a measure of the "lossy" characteristics of the dielectric material.

Assaying Apparatus and Procedure

Mine-run shale samples from both the Anvil Points and Colony mines in Colorado were assayed with the modified Fischer retort, described by Stanfield and Frost (1949).

Permittivity measurements were taken with a General Radio, Type 874-LB slotted line, fitted with a 200-ohm crystal detector and an adjustable stub attenuator. The microwaves were generated with a Hewlett-Packard Model 612A UHF signal generator, externally modulated by an HP Model 200-CD oscillator. A Hewlett Packard Model 415B standing wave indicator was used to measure voltage standing wave ratios (VSWR) and to locate wave troughs in the slotted line

tube. The VSWR is the ratio of maximum voltage to minimum voltage in the transmission line. Figure 1 shows the arrangement of the apparatus. Since the measurement of permittivity by this technique is standard procedure, further details are not included here. Sucher and Fox (1963) describe the various techniques available quite well. The necessary data, however, include null position shifts and standing wave ratios. This data is taken with the sample backed, first, by a "short circuit" and, then, by an "open circuit" (see figure 1). A homemade, variable position short facilitated the measurements with the short, one-quarter wavelength behind the sample. An Ames gauge insured accurate length measurements in the slotted line.

A technique for preparing the shale samples to proper dimensions was also developed. The sample holder, attached at the right end of the slotted line, was designed for a sample filling the annular space, as shown in figure 2. Thickness, d, should be no greater than $\lambda_m/4$; λ_m being the wavelength in the sample. A 1.588 cm O.D. (5/8 in.) diamond coring drill was used to core shale specimens perpendicular to the bedding. The cylindrical samples were then drilled through the center with a size "C" (0.6147 cm, 0.2420 in.) carbon steel drill bit. A jig was used to guide the bit and to hold the cylinders securely. This minimized breakage of lean shales. Moisture-free samples were used for all measurements.

Mathematical manipulation to compute the dielectric constant from raw data involves complex variables but is easily handled by a computer program. Inpedances are first calculated by the following relationship:

$$Z = \frac{(1/\rho - 1/\rho_o) - j\tan(2\pi\ell/\lambda_o)}{1 - j(1/\rho - 1/\rho_o)\tan(2\pi\ell/\lambda_o)}, \qquad (3)$$

where ρ = measured VSWR with the slotted line containing a sample (open or short circuit)

ρ_o = measured VSWR without a sample

ℓ = null position shift (open or short circuit)

λ_o = measurement frequency.

The complex permittivity is then calculated from

$$\varepsilon^* = \pm \frac{j\lambda_o \text{ arc tanh } \left(\frac{Z_{sc}}{Z_{oc}}\right)^{1/2}}{2\pi d (Z_{sc} Z_{oc})^{1/2}}, \qquad (4)$$

where d = sample length.

Results of Microwave Study

The richness of Green River oil shales, as determined by Fischer assay, correlates strongly with the shale's loss tangent and the imaginary term of the relative dielectric constant at 500 MHz. This assumes the

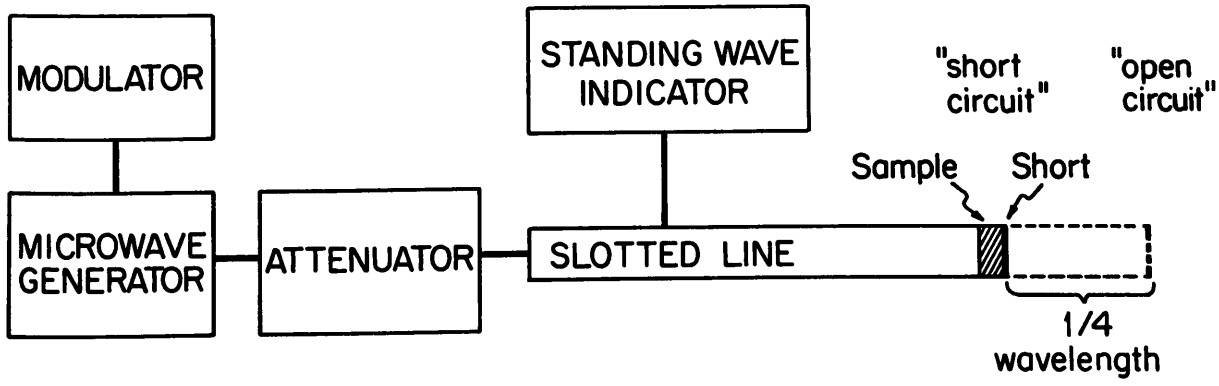

Figure 1. Permittivity measurement apparatus.

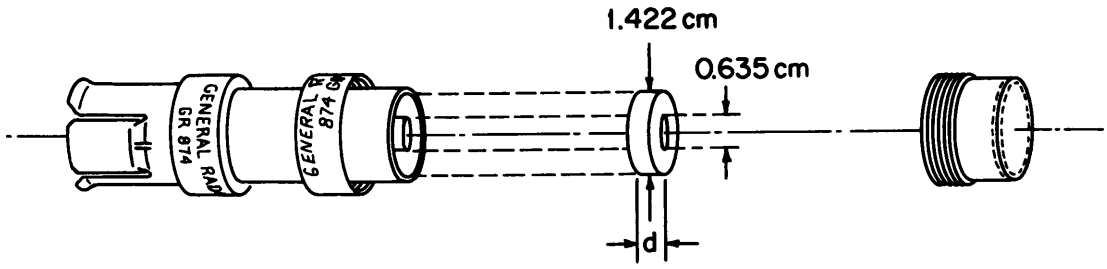

Figure 2. - Slotted line sample holder assembly.

sample is maintained at room temperature, about 24°C. Figure 3 shows the latter relationship. Repeated permittivity measurements, with 0.113 m^3/metric ton (33 GPT) samples, produced standard deviations of 0.0049 for the loss tangent, tan δ, and 0.0020 for the imaginary term of the dielectric constant, ε''. This corresponds to an accuracy of approximately $\pm$0.0058 m^3/metric ton shale ($\pm$1.7 GPT). The magnitude of the relative complex dielectric constant of the available oil shale varied between 3.5 and 4.7.

Discussion

Shale samples, between 0.034 and 0.261 m^3/metric ton (10 and 76 GPT) richness, were studied. The sensitivity of the relationship, with respect to shale richness, is partially responsible for the accuracy of this new assaying technique. The loss tangent, for example, increases by a factor of six as shale richness increases from 0.034 to 0.261 m^3/metric ton (10 to 76 GPT). Such sensitivity has not been found with other physical and thermal properties, described previously.

The method measures the concentration of kerogen directly, without interference from the mineral matter. This factor is also responsible for the accuracy of the assay in determining the potential oil yield of Green River oil shales. The absorption of radiation energy in the microwave frequency range by minerals in these shales is negligible. The carbonates, of which the inorganic matrix is predominantly made, contribute practically nothing, therefore, to the imaginary term of the dielectric constant. The same is true for other minerals present, such as nahcolite and dawsonite. Compositional variations in the mineral make-up should not significantly affect the outcome of shale assays using microwaves. It is

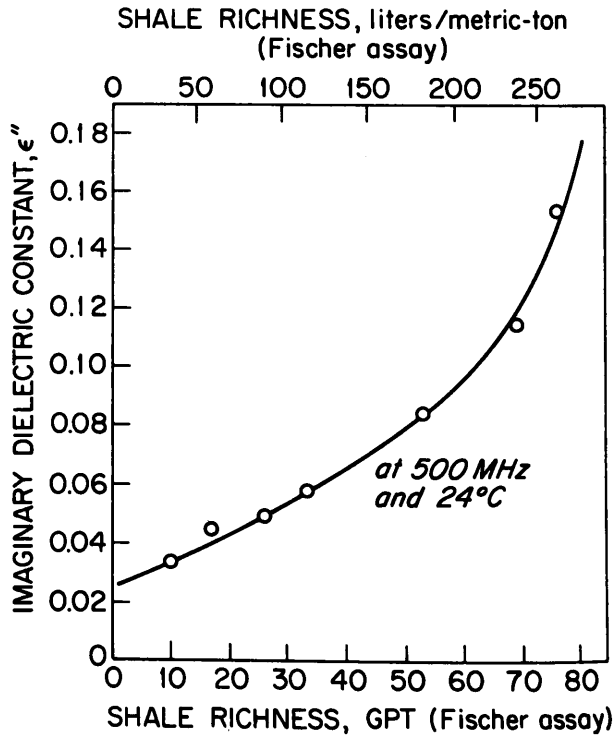

Figure 3. - Imaginary term of the relative complex dielectric constant, $\varepsilon^*/\varepsilon_o = \varepsilon' - j\varepsilon''$, vs. Fischer assay richness of Green River oil shale.

assumed, however, that kerogen and its structure are fairly uniform throughout the deposit.

The extension of the correlation to other shale deposits is feasible, provided the kerogen is similar in structure to that found in the Green River formation. This assaying technique is certainly applicable, however, to many other hydrocarbon deposits.

Permittivity measurements at frequencies of 300 and 1000 MHz produced similar relationships, but accuracy suffered. At the higher frequencies, the electrical short that terminated the transmission line was not sufficiently effective; at the lower frequencies, the slotted line was not long enough to obtain reliable data. Alternate equipment for obtaining the complex dielectric constant must be used for these other microwave frequencies.

Another parameter which will be incorporated in further studies is geometric orientation of the bedding planes with respect to the direction of the incident radiation. Pulverization of larger rocks, riffling, and subsequent compaction into the required doughnut shapes should be pursued. Problems in sampling severely stratified shale would then be eliminated. In this study, homogeneous samples were carefully chosen to eliminate effects of variation of kerogen content.

The ability of kerogen to absorb radiation energy in the microwave frequency range presents an interesting possibility for the future. High power applications of microwaves should decompose the organic matter in shale to oil and various gaseous products. The rotational and vibrational energy of irradiated kerogen is manifested as heat which will serve to sever bonds of the organic macromolecule. These higher energy fluxes in the radiation are necessary to compensate for heat losses by conduction while sufficient "quanta" of energy are collected by the bonds for breakage to occur. In-situ application of this phenomena might be possible if fragmented shale could be irradiated by microwaves transmitted from a centralized borehole.

Conclusions

1. The relationship between shale richness, as determined by Fischer assay, and the imaginary term of the dielectric constant is strong at a radiation frequency of 500 MHz and a temperature of 24°C.

2. The measurement of permittivity enables one to determine the concentration of kerogen in Green River oil shale directly. It, therefore, is an alternate and powerful assaying method. Extension of this technique to other hydrocarbon deposits is feasible.

3. High power microwave applications may aid in the recovery of oil and combustible gases in the future, perhaps on an in-situ basis.

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