

PULSED NMR EXAMINATION OF OIL SHALES--ESTIMATION OF POTENTIAL OIL YIELDS

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INTRODUCTION

For the past 4 years the Laramie Energy Research Center has been investigating the application of nuclear magnetic resonance (NMR) as a method of rapidly and reliably predicting potential oil yields of oil shales. With the present interest in the government's oil-shale test-lease program, the need for a rapid and reliable oil-shale assay method is more urgent. The potential of wide-line NMR for this purpose has already been demonstrated by Decora, McDonald, and Cook.¹ Another type of NMR, pulsed or transient NMR, is being explored as a method for rapidly providing this information. The pulsed NMR method is more rapid than the wide-line NMR method because no time is spent sweeping the field or frequency to record the signal. Other advantages of pulsed NMR over wide-line NMR are the elimination of line-broadening effects, no need for signal integration, greater sensitivity in a given measuring time, and ease of spectrometer operation. In addition, direct measurements of the spin-spin, T_2 , and spin-lattice, T_1 , relaxation times by pulsed NMR can provide other useful information about oil shales.

In this paper we present the results of some pulsed NMR assays on oil-shale samples. Two groups of oil-shale samples from two different cores were analyzed by pulsed NMR in a routine assay-type operation. Statistical analyses are presented to show that the NMR data linearly correlate with the Fischer assay oil-yield data.

EXPERIMENTAL PROCEDURES

Oil Shales Studied

Two oil-shale cores were studied. The first came from a proposed test-lease core and had been recently Fischer assayed. A total of 141 samples, designated as Group I samples, was selected from this core to represent the entire depth (1,300 to 2,700 feet) and oil-yield ranges (0-70 gal/ton) of the cored interval.

The second core was cut below the B groove of the Mahogany zone. The total length of the core was 1,100 feet and the oil-yield range was 0 to 60 gallons per ton. The first 300 samples from this core, designated as Group II samples, were analyzed by pulsed NMR parallel with the Fischer assay oil-yield determination on the same core sections.

Sample Preparation

To prepare Group I samples for the first study, the sample remaining after Fischer assay was riffled to reduce the sample size to about 75 to 100 grams. This sample was then crushed to a fine powder on a disc grinder, and a representative portion (0.5 g) of the powdered sample was taken for the NMR measurements.

Group II samples for the second study were of the same particle size (8 mesh) as was used in the Fischer assay method. No further crushing was done to the samples prior to the NMR

measurements. The samples were, however, riffled to a smaller sample size from which a representative portion (2.5-4.5 g) was taken for the NMR measurements. The riffling of these samples was an attempt to minimize errors in the NMR method, which could arise from nonrepresentative sampling.

Instrumentation

Pulsed NMR measurements on the Group I samples were made on a Bruker 322S variable frequency pulsed spectrometer housed at the Marathon Oil Co. Research Center in Denver, Colo. These measurements of the free induction decay (FID) amplitude following a 90° pulse were made at a resonant frequency of 60 MHz, a pulse length of 2.5 μsec, a pulse repetition rate of 1 sec and using diode detection. About 30 FID amplitude measurements (requiring about 30 sec) were made for each oil-shale sample, and the average values of these measurements were used to determine the relationship with Fischer assay oil yields by regression analyses. The FID amplitudes were corrected to unit sample weight prior to the regression analyses.

FID amplitudes for the Group II shales were measured on a similar instrument housed at the Laramie Energy Research Center. A resonant frequency of 20 MHz, a pulse length of 6 μsec, a pulse repetition rate of 1 sec, and phase sensitive detection were used for these measurements. Because the Group II samples were coarser than the Group I samples, a larger sample tube (15 mm diameter) was used. As was done for the Group I samples, about 30 FID amplitude measurements were made for each Group II sample from which an average value was obtained and corrected to unit weight prior to the regression analyses.

Linear Regression Analyses

Linear first-order regression analyses were first performed on the FID amplitudes and Fischer assay oil yields for standard samples chosen from both groups. There were 30 standard samples chosen from Group I and 36 from Group II. Based on the slopes and intercepts of the best least-squares data fits, oil yields were calculated for the remainder of the samples in both groups. Regression analyses were then performed on the oil yields calculated from NMR measurements and oil yields determined by Fischer assay. The index of determination (square of the correlation coefficient, r) is the parameter we use to judge the "goodness of fit" in the regression analyses. A value of 1.00 for this parameter implies a perfect fit of data points to a straight line.

THEORETICAL CONSIDERATIONS

The basis for the pulsed NMR assay method lies in the assumption that the organic hydrogen content of an oil shale is related to the shale's potential oil yield. The FID amplitude, following a 90° pulse, is proportional to the total number of resonant nuclei in the sample, just as is the area under the absorption curve in wide-line NMR. Because the resonant nuclei in this case are protons, the FID amplitude is proportional to the hydrogen content of the oil shale.

The basic NMR measurement is shown in figure 1(a). A sample introduced into a magnetic field, H_0 , achieves a net magnetization, M , proportional to the amount of hydrogen in the sample. If an rf pulse, H_1 , is applied at right angles to H_0 , M can be rotated from its equilibrium position and begins to precess about H_1 . If the intensity and duration of H_1 are properly chosen, M can be rotated into the xy plane at which time H_1 is turned off. The condition for a 90° rotation is

$$\pi/2 = \gamma H_1 \tau_p, \quad (1)$$

where γ is the magnetogyric ratio of the proton, H_1 is the strength of the pulse, and τ_p is the pulse

duration. Following the termination of H_1 , the individual magnetic moments begin to interact with each other and lose phase coherence as in figure 1(b). The net result is that the signal intensity decreases to zero in a characteristic time, T_2 , the spin-spin relaxation time.

In the pulsed NMR assay method, measurements are made on M_x immediately after the 90° pulse, to obtain the maximum signal from all the protons in the sample. These measurements may include signal contributions from inorganic protons (adsorbed water, mineral hydrogen, tightly bound hydroxyl groups, etc.) as well as the organic protons in the oil shale. To improve precision of the method effort is made to distinguish between the different types of protons in the sample. By the very nature of the pulsed NMR measurement it is difficult to make this distinction, except in the case of adsorbed water for which an example is shown on figure 2. Here the effect on the FID of drying the shale sample to remove water is illustrated. The signal that persists in the undried samples for times greater than about 50 μsec shows the effect of adsorbed water because upon drying, the signal is significantly reduced. This indicates that organic hydrogen relaxation times are shorter than those of adsorbed water and suggests that signal contributions due to adsorbed water can be corrected for by subtracting FID amplitude measurements at 50 μsec from those made at 20 μsec . The corrected FID amplitude was assumed to more closely represent the organic hydrogen content of the oil shale. This procedure was followed for the Group II shales but not the Group I shales.

Another parameter that may aid in minimizing signal contributions due to inorganic protons is the spin-lattice relaxation time, T_1 . This is the characteristic time during which equilibrium is restored along the applied field direction, after the application of a pulse. T_1 determines the frequency at which the 90° pulse sequence can be repeated and ultimately determines the rapidity of the pulsed assay method. Typically, one should wait at least 5 T_1 to allow for equilibrium to be restored before applying a second, third, etc., 90° pulse.² For oil shales the T_1 values for the organic material are quite short (10-300 msec) whereas some of the inorganic protons apparently have longer T_1 values. Evidence to illustrate this is presented in the next section of this paper.

RESULTS AND DISCUSSION

Pulse Repetition Rate

Shown on table 1 are the results of a preliminary study made to determine how T_1 values of inorganic and organic protons affect the pulsed assay method. Here, two FID amplitude measurements were made on 10 oil-shale samples containing substantial amounts (up to 53 percent) of nahcolite (NaHCO_3). The first NMR measurement was made with a pulse repetition rate of 1 sec, and the second was made with a repetition rate of 30 min. The results on table 1 show that the NMR measurements of 1 sec correlate better with the oil-yield determinations; whereas, those made at 30 min correlate better with the total hydrogen. The total hydrogen includes both organic and inorganic hydrogen and was determined by the combustion method. These results suggest that a fast repetition rate tends to minimize some effects due to inorganic protons.

Fischer Assay Repeatability

Previous work¹ related NMR signals to Fischer assay oil yields using single measurements. Repeatability measurements for each of these experimental methods was not determined. Because the reliability of the NMR assay method is dependent on that of the Fischer assay, a series of tests was made to determine the reliability of the Fischer assay oil yields. Seventy-five samples (three each of 25 Group I samples) were Fischer assayed, and average oil yields and standard deviations were calculated for each of the 25 samples. These results are presented in table 2. If one defines

the dispersion coefficient as the standard deviation divided by the average value, then the calculated "average" dispersion coefficient is 0.138 for the 25 samples and represents the uncertainty in Fischer assay oil yields.

TABLE 1. - Correlations between oil yields and total hydrogen for different pulse repetition rates

Regression	Pulse rate	Index of determination r^2
Oil yield (gal/ton) versus free induction decay amplitude	1 sec	0.97
Total hydrogen (wt pct) versus free induction decay amplitude	1 sec	.95
Oil yield (gal/ton) versus free induction decay amplitude	30 min	.90
Total hydrogen (wt pct) versus free induction decay amplitude	30 min	.98

TABLE 2. - Summary of data for Fischer assay repeatability test

Sample No. SBR71-	Average F.A., gal/ton	Standard deviation, S	Dispersion coefficient, K
10164	38.7	11.2	0.289
10178	35.2	3.1	.088
10335	15.5	1.3	.083
10446	18.2	1.1	.059
10648	14.2	6.7	.472
10262	24.7	5.7	.230
9522	21.7	6.6	.303
9993	9.4	.7	.074
10296	17.9	1.0	.056
10650	11.9	.5	.039
10352	30.7	.8	.025
10026	22.0	.6	.028
9947	8.8	.5	.061
10162	9.5	4.2	.436
10115	14.1	.3	.019
10531	22.1	1.3	.059
9587	21.4	.8	.038
10444	28.5	1.0	.033
10603	6.4	2.4	.381
10452	28.7	5.8	.202
10254	21.5	1.6	.073
10137	18.8	.26	.014
10564	21.9	6.9	.317
10217	29.0	.82	.028
10224	27.0	1.2	.045

Group I Oil-Shale Samples

Results of linear regression analyses made with the 30 standard samples chosen from Group I were used to calculate oil yields of the remaining 111 samples. The correlation between the measured Fischer assay oil yields and calculated oil yields is shown on figure 3. The value of 0.93 for the index of determination is remarkably good, considering the small sample size (0.5 g) used in the NMR measurements compared to the much larger size (100 g) typically used for Fischer assay. It appears that the procedure for preparing the NMR samples effectively duplicated the quality of the larger Fischer assay samples. Furthermore, these results were obtained for a single FID amplitude measurement, suggesting an insignificant adsorbed water contribution from these samples.

Group II Oil-Shale Samples

The Group II shales were run in a more routine assay type of operation than the Group I shales. In this case the oil-shale samples were run by NMR before, during, or after the Fischer assay of the same samples. Thus the reported Fischer assay oil yields were not known prior to making the NMR measurements. Thirty-six samples were processed at any given time by the NMR method. When Fischer assay data became available, linear regression analyses were made on the FID measurements and reported oil yields. The results for each run are shown on table 3. The poorer index of determination for run 1 was due to improper tuning of the pulsed spectrometer, and in subsequent runs this problem was remedied as evidenced by the better correlations in runs 2-9. These data also indicate that day-to-day tuning of the pulsed spectrometer on a standard sample can be accomplished readily and with good reliability.

TABLE 3. - Indexes of determination for the pulsed NMR assay method

Run	r^2 (Index of determination)
1	0.78
2	.91
3	.96
4	.94
5	.93
6	.97
7	.96
8	.98
9 ^{1/}	.92

^{1/} This run totaled 12 samples; all other runs contained 36 samples each.

The 36 samples of run 3 were chosen as "standards" to determine how well the pulsed NMR measurements could predict oil yields for the remaining samples. The correlation between the measured and calculated oil yields is shown on figure 4. Again a good correlation was obtained between the predicted and measured oil yields. The data for the 36 samples in run 1 were not included in the correlation on figure 4. It should be emphasized that the correlations on figures 3 and 4 assume complete reliability in the Fischer assay. No uncertainties in the Fischer assay data were incorporated in our regression analyses, although the data on table 2 show that the Fischer assay method is subject to errors. This could account for some of the scatter in figures 3 and 4. Another reason for the scatter in these figures is probably due to sample size and sampling procedures. The indices of determination, however, indicate that our sampling procedures tended to give NMR samples representative of the total samples.

Time Savings

Thus far, data have been presented to show that pulsed NMR measurements can be used to predict potential oil yields of oil shales. We have not stressed an important advantage of the pulsed NMR assay method over the Fischer assay method--namely, the savings in time offered by the NMR method. To obtain a gallon-of-oil-per-ton-of-shale figure by the Fischer assay method for a single sample averages out to about 100 min per sample. This results from the number of measurements required by the Fischer assay method. Here one must weigh the sample retorts and collectors, retort the sample (60 min), reweigh the retorts and collectors, centrifuge (10 min) and measure the volume of oil and water produced, and finally determine the specific gravity (30 min) of the shale oil. In all these steps, there is chance for error, particularly when different people are doing the assays. The NMR measurements can be obtained directly in gallons-of-oil-per-ton-of-shale units with a suitable calibration line. To obtain an oil yield by NMR requires about 2 min per sample, including the time spent in riffing and weighing the sample. In the NMR method, a simple voltage measurement is made, and if coupled to a programmable calculator or minicomputer, an instantaneous assay can be obtained. Thus a factor of 50 in rapidity of assay is easily obtainable with NMR methods over the conventional Fischer assay.

CONCLUSIONS

The free induction decay amplitude measured on oil-shale samples by pulsed NMR linearly correlates with Fischer assay oil yields. This has been shown from analyses of 405 samples from two different oil-shale cores. In cores for which adsorbed water may be an important contributor to the NMR signal, it was necessary to make two NMR measurements of the free induction decay amplitude to correct for these interferences.

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Reference to specific equipment does not imply endorsement by the Bureau of Mines.

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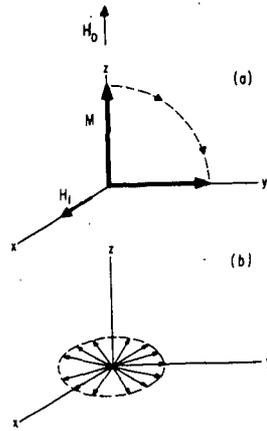


FIGURE 1.-A 90° Pulse Sequence.

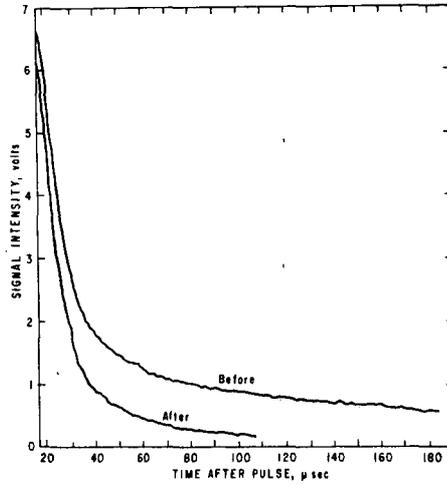


FIGURE 2.-Effects of Drying Oil Shale Samples on Free Induction Decay.

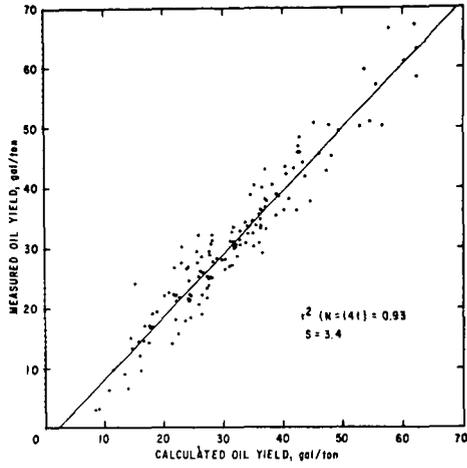


FIGURE 3.—Measured Oil Yields Vs. Calculated Oil Yields,
Group I.

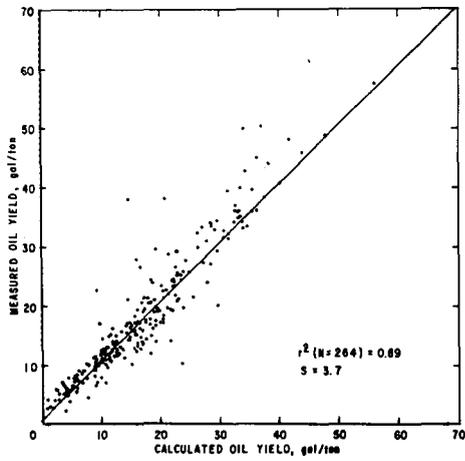


FIGURE 4.—Measured Oil Yields Vs. Calculated Oil Yields,
Group II.