

COMBINATION OF NMR AND ULTRACENTRIFUGE TECHNIQUES FOR EFFECTIVE CARBONATE RESERVOIR CHARACTERIZATION

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ABSTRACT

The combination of NMR and Ultracentrifuge techniques provides an easy and fast way of estimating the physical properties of rock/fluid systems such as wettability and irreducible saturation, capillary pressure and pore size distribution, fluid distribution in porous media and relative permeability curves. In this work, an extensive experimental program was conducted for the characterization of pores from some carbonate reservoirs and outcrops. During the experimental procedure, the difference between the mechanisms of rock/fluid and fluid/fluid interactions in restored state and natural state core was evaluated. As a result of our investigation it is established that the performance procedures provide the qualitative indication of adsorption of the heavy components of oil on the pore surface. Adsorption of the heavy fractions on a pore surface can take place not only in reservoirs containing heavy oil but also in light oil reservoirs with low concentrations of heavy fractions as indicated by the analysis of the recovered oil. Adsorption of the heavy components seems to take place predominantly in the largest pores which contain thinner films of irreducible water. This conclusion is made in view of similar work on cores with variable petrophysical properties. Modern laboratory systems and procedures, including NMR and Ultracentrifuge, provide the opportunity to estimate the changes of the thermodynamic conditions in a reservoir, at which additional adsorption of heavy hydrocarbon will not take place. Moreover, the procedures used in this work can be directed to increasing the hydrocarbon recovery efficiency.

INTRODUCTION

The characterization of carbonate reservoirs poses a number of problems associated with rock fluid interaction, wettability alteration and selective fluid adsorption that are hard to interpret with conventional core analysis tools^{1,2,3,4}. The development of novel tools for core and log analysis try to address some of these problems. Centrifuge technology allows for fast and accurate fluid production schemes at reservoir temperatures and immiscible conditions⁵. Such techniques give results of measurements on rocks of wide physical properties in small time frames. Another novel technology that holds promise in addressing the above problems, is Nuclear Magnetic Resonance (NMR) relaxometry.

Utilizing NMR technology in the laboratory and at well-bore scale provides the following NMR parameters which are associated with both reservoir rock and reservoir fluids⁶:

- Total amplitude of the NMR signal;
- Spectra of longitudinal and transverse relaxation times T_1 and T_2 ;
- Diffusion coefficient for a saturating fluid.

These NMR parameters, in the majority of cases, are determined by the presence of hydrogen atoms and their physical and chemical mobility within the limits of the medium under investigation. These parameters also depend on the physical and chemical properties of the fluids that saturate a porous medium, the fluid distribution, as well as the thermodynamic conditions in the porous media under study. NMR measurements and derived parameters can be used to determine the following properties of rocks and fluids therein:

- Pore size distribution of water and oil saturated pores and their total porosity^{6,7,8},
- Wettability and chemical properties of a pore surface^{9,10},
- Chemical structure and physical-chemical properties of a fluid^{10,11,12},
- Physical-chemical relations and distribution of fluids in the investigated volume^{11,12},
- Change of mobility of hydrogen nuclei during the interaction with a pore surface^{10,11}.

Several publications^{6,12} illustrated the application of NMR spectroscopy for the determination of hydrocarbon viscosity. As indicated in the literature, the composition of oils with various physical-chemical properties can also be investigated. Multiple fractions of a crude oil can be reflected in the NMR spectrum¹². As a result, the NMR characteristics of fluids in porous media properties can be attributed to a variety of causes. This fact in turn necessitates careful planning of experiments for evaluating the reservoir and fluid properties in question and *in-situ*. Under the same logic, usage of any *a-priori* information obtained from other means must be carefully evaluated before it is correlated to NMR properties. Such planning leads to reduced ambiguity in the estimations of required parameters.

If the above precautions are taken, the NMR technology is especially effective in displaying characteristics of displacement processes and rock fluid interactions in porous media.

EXPERIMENTAL

The studies carried out in this work, aimed at demonstrating the potential of combining NMR and Ultracentrifuge methods for detecting the adsorption of heavy fractions of crude oil onto the rock surface, and the simultaneous evaluation of the pore surface wettability at various saturation conditions using different fluids.

For this research, a collection of samples with a wide range of petrophysical characteristics was used. In this collection, core plugs were tested under the following conditions:

- Six core samples from the same carbonate reservoir were aged during a long period of time (more than one year), while immersed in crude oil and at the irreducible water saturation.
- Three additional clean and dry carbonate samples, were cleaned using toluene and acetone-methanol solution prior to saturation with brine.
- Two outcrop samples were used as references (Berea sandstone and Baker Dolomite).

The oil used had a viscosity of approximately 16 mPa.s. The hydrogen index (HI) of this oil was 0.86. The hydrogen index for oil was generated through comparing its NMR signal to that from an equal volume of water. The following measurements were performed:

- Measurements of transverse relaxation times (T_2) for initial bulk fluids and the samples at initial conditions.
- Determination of the irreducible water saturation (S_{wi}) by spinning in the centrifuge (6000 RPM) under air for 5 brine saturated core plugs. The brine used has the following composition: KCl 0.13%; $MgCl_2 \cdot 6H_2O$ 0.24%; $CaCl_2 \cdot 2H_2O$ 1.68%; Na_2SO_4 0.12%; NaCl 3.93%; $NaHCO_3$ 0.06% (all by weight). Measurements T_2 relaxation curves under S_{wi} .
- Saturation of 5 cores (at S_{wi}) by oil under vacuum conditions followed by T_2 measurements.
- Aging of all fresh oil saturated cores at 82 °C for 72 hours, using both NMR and weight measurements for verifying that saturation was complete.
- Displacement of oil by water (forced imbibition) in the centrifuge for all oil saturated samples (aged and fresh saturated). The displacement was performed at 82 °C and it was followed by NMR T_2 measurements of the waterflooded core plugs (described herein as “invasion zone”).
- Aging of samples in brine to demonstrate possible reversal of pore surface conditions.
- Data processing of the measurement results by several programs obtained from a variety of sources (Numar Corp., HBH Consulting and TIPM Laboratory). These programs were used to determine the following parameters (at the signal to noise ratio for the first echo > 200):
 1. Amplitude of NMR signal (A_n), proportional contents of nuclei of hydrogen in the porous media. The error associated with the evaluation of A_n is approximately 1%.
 2. Spectrum of T_2 relaxation times for hydrogen in studied media The errors of restoration of cumulative curves of T_2 spectra are smaller than 5%.

RESULTS

Figure 1 shows the cumulative relaxation curves for a set of conventional oils measured in beakers (bulk volume). In terms of relaxation properties, each oil appears to have its own distinct relaxation curve. The grouping of the relaxation curves is consistent with increasing oil viscosity. Thus, we proceeded in cross-plotting the mean relaxation time (defined as the 50th percentile of the cumulative frequency) as a function of oil viscosity. The results are

are plotted in Figure 2, where a fairly smooth straight line can be obtained in the log-log scale. This line is consistent with results previously published by Numar¹¹, and reasonably close to other published literature^{6,12}. This is an indication that pure hydro-carbon correlations obtained in the literature^{6,11,12} can be extended to crude oils as well.

The cumulative curves of the spectra of relaxation times T_2 for oil and core samples used in this work are presented in Figures 3-6. Figure 3 shows the relaxation curves for the bulk (initial) oil, the oil saturated core at S_{wi} , the produced oil (oil after displacement), the waterflooded plug (invasion zone) and the brine aged core plug (after aging with brine). The observation that is consistent to the curves of Figure 3 is that the spectra change when the fluids are redistributed in the core. Also consistent is the spectra for the bulk oil change when running the samples before or after the displacement test.

The results of Figure 3 indicate that the spectrum of initial bulk oil and the spectrum of the oil saturated core at S_{wi} are quite similar with only a very small shift of the oil saturated core at S_{wi} . The waterflooded core spectrum shows much higher relaxation times indicating that the hydrogen atoms (i.e., water molecules) are more mobile than corresponding hydrogen atoms at 100% water saturation. Some small reduction in the relaxation times is observed after aging under brine. This reduction is currently under investigation. The surprising spectrum is that of the produced (displaced) oil in the waterflood (which was run at a temperature of 82 °C and at 6000 RPM). This specific spectrum has components with significantly higher relaxation times than those of the initial oil. The longest relaxation time is actually longer than the longest relaxation time in the waterflooded core.

Figure 4 shows the experimental results of a plug that was exposed to 100% water saturation, S_{wi} by gas drainage, oil saturation at S_{wi} and waterflood to S_{or} . This plug demonstrates the greatest observed deviation in spectrum between initial oil saturation and residual oil saturation.

Figure 5 is a collection of NMR spectra from a crude oil used in this study taken at different stages in the experimental process. Figure 5a shows the spectrum of the oil before treatment as compared to the spectrum of the oil after treatment. The term “treatment” is the exposure of oil to vacuum saturation procedures and heating to 82 °C for the displacement experiments. Figure 5b shows the spectra of the oils that were produced in the waterflood steps in three samples that underwent the procedure shown in Figure 4.

Figures 6a and 6b are offered as a basis for comparing reservoir rock results to outcrop rock results. Figure 6a shows the sequence of brine saturating, displacing with air, saturating again with brine, spinning to S_{wi} under oil and waterflooding all in a Baker dolomite. Figure 6b shows the same sequence in a Berea sandstone. Trends that were observed in the reservoir rocks are shown here as well but the effects are considerably less dramatic.

DISCUSSION

A review of Figures 1-6 offers the following observations: More than 50% of the NMR signal from all treated (exposed to vacuum and temperatures of 82 °C) oils had a determined $T_2 < 130$ msec. Approximately 35% of the signal can be modeled by applying the single exponent model with a calculated $T_2 = 400$ msec, while the minimum calculated T_2 value is approximately 20 msec, and the maximum calculated T_2 value is approximately 425 msec. With reference to the oil spectra before treatment, less than 10% of the signal has relaxation times $T_2 < 90$ msec. The spectrum of the initial oil has a wide range of calculated relaxation times from T_2 minimum approximately 15 msec to T_2 maximum approximately 1100 msec.

The crude oil used in this project has asphaltenes and resins content less than 2% wt. We suspect that this content although low, has a significant influence on the value of signal amplitude of the NMR spectrum. The significant relaxation times in the T_2 spectra have values of more than 20 msec. The spectra of stabilized and initial oils are distinguished only in the part of spectra with larger relaxation times. This distinction can be explained by the loss of lighter hydrocarbon fractions during the vacuum saturation process and/or the heating process.

Table 1 shows a comparison of porosity and bulk moisture ($= \phi S_{wi}$) evaluations using mass balance and NMR relaxation data. Reviewing the data of this table leads to the following observations:

- The full signal from all hydrogen nuclei contained in the water that saturates the investigated cores is registered by the NMR relaxometer (i.e., there is no loss of signal for the 100% saturated cores).
- The core samples have different pore structures. Previous experience^{7,8,10} indicates that water saturating small pore bodies or clay bound water is expected to yield T_2 values less than 15 msec. Our samples indicated spectra differences in relaxation times exceeding the 15 msec threshold. That implies variability in pores with middle and larger pore sizes. Sample R2 exhibits the largest fraction of large pores (with corresponding $T_2 > 300$ msec) and the minimum value of S_{wi} . It should note, that the S_{wi} value were created using a very high RPM setting during the water displacement by air. Such low S_{wi} is considered to be ideal for the adsorption of asphaltenes.

Review of the S_{wi} spectra in the various experiments reveals the following:

- The evaluations of bulk moisture of rock at S_{wi} from NMR data are statistically identical to the values of moisture obtained by mass balance.
- With respect to the arguments made in the previous paragraph, it follows that these rocks exhibit a significant part of water blocking in larger pores. This is complemented by the fact that only about 10% of the signal at S_{wi} is characterized by the values of $T_2 < 15$ msec.

The figures presented can be further reviewed with the emphasis now being shifted to the comparison between oil saturated cores at S_{wi} , and the corresponding cores at the end of the waterflood. All carbonate samples demonstrate that the spectra at initial oil saturation conditions contain T_2 terms that are shorter than the spectra with 100% water saturation. From the absolute amplitude of the signal at these T_2 values, we infer that a considerable amount of oil is either in an immobile state or it occupies the smallest pores. This behavior in turn implies that at least some oil components adsorbed on the pore surface, which in turn implies wettability alteration. This interpretation is made under the assumption that no other thermodynamic or chemical changes occur in the porous medium at the same time. The validity of this assumption will be investigated in another project. If such adsorption is indeed taking place, it must be due to the presence of highly polar oil components such as heavy fractions from oil. If oil is not present in smaller pores, then this adsorption process is to take place wherever the polar materials can penetrate the thinnest water films. That would be more probable in the larger pore bodies. In the current investigation, we have considered as the cut-off point for these changes, the NMR signal with relaxation times $T_2 < 100$ msec.

Following the same logic, if wettability alteration occurs and water films are destroyed, one would expect that following waterflood, the core should behave as more oil-wet system. The invading water is expected to be more mobile (from an NMR point of view) than the water in the 100% water saturation step. Therefore, longer relaxation times are expected to be observed in the waterflooded core. This is shown in the results of Figure 4. Moreover, by comparing the relative magnitudes of the spectra, we observe that the shift to higher relaxation times is inversely proportional to the value of S_{wi} . This indicator could be used for the quantification of wettability changes. This is beyond the scope of this paper and it will be addressed in a separate project.

One of the most intriguing observations in this work was the variability in the spectra of the produced oils after waterflood. Figure 5 clearly demonstrates that the oil used to saturate the core, when compared to the same oil after it was produced from each plug have distinctly different relaxation peaks. This implies both compositional and component changes during the oilflood-waterflood cycles. There are two major facts that are evident. First, there is a consistent shift of the lower relaxation times to higher values. Following the logic of adsorption, heavy component deposition and wettability alteration suggested above, we expect that this shift implies heavier elements were left behind as adsorbed material. The second fact is that lighter components with long relaxation times are now appearing in the produced oil spectra. Such components were not present in the spectrum of the injected oil. This unexpected result implies that there was some chemical change of the oil while in the pore space. Since the longer relaxation components are related to lighter petroleum products, appearance of such peaks implies *in-situ* upgrading of the oil. This possibility is currently under further investigation.

The changes described above have also been observed in the Baker dolomite, but to a much lesser extent. One possible reason is the fact that the experiments with Baker dolomite were done at room temperature to be consistent with other work in the literature. The small changes in the oil spectra are more consistent with changes in the proportions of light and heavy components in initial vs. displaced oil and do not suggest any (significant) chemical changes. The Berea tests show even less changes in the spectra obtained spectra. If we believe that from all the cores tested, Berea sandstone was the most water-wet, then these observations are consistent with the wettability alteration hypothesis. This topic is also under further investigation.

In summary, our experiments have demonstrated that the preparation and production history affect the water/oil/rock interactions and can lead to a variety of adsorption scenarios. If such scenarios can be reproduced intentionally or unintentionally in the reservoir, they can profoundly affect well productivity. Of particular importance will be the association of such phenomena with formation damage.

The NMR method can be useful for the characterization of different reservoirs and for the determination of the thermodynamic conditions, at which additional adsorption of heavy hydrocarbons will not take place. The NMR method can also be used for the evaluation of the efficiency of various methods for the treatment of near well bore zones.

CONCLUSIONS

Assuming no other physical or chemical change of a crude oil inside the pore space, our results indicate that NMR data show adsorption of heavy crude oil components on a pore surface.

This adsorption of heavy fractions on the pore surface can take place in conventional oil bearing rocks. A higher adsorption effect can be expected in heavy oil reservoirs.

The adsorption of heavy components is suspected to take place predominately in largest pores, containing thin films of bound water.

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Table 1: Summary of core properties

##	Mass Balance					NMR		
	K_{air} , mD	K_{brine} , mD	POR,%	S_{wi} , frac	W_w , %	Phi,%	S_{wi} frac	W_w
R2	0.12	0.01	7.07	0.087	0.62	7.29	0.083	0.61
R5	0.06	0.01	6.89	0.162	1.12	7.19	0.173	1.24
R6	45.6	10.4	17.05	0.03	0.52	17.42	0.035	0.61
3m	-		20.26	0.106	2.15	20.07	0.094	1.89



