

● *Contributed Paper*

QUANTITATIVE ESTIMATES OF POROUS MEDIA WETTABILITY FROM PROTON NMR MEASUREMENTS

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Nuclear magnetic resonance (NMR) relaxation time distributions provide information on the abundance and distribution of two immiscible fluids in the pores of fine-grain chalk samples. A model based on relative shifts of the water-relaxation component as a function of saturation results in a wettability index that is strongly correlated with independent dynamic measurements of wettability. Scales of wetting-phase film thickness for NMR and dynamic measurements explain differences in results between the two methods. © 1998 Elsevier Science Inc.

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INTRODUCTION

A key attraction of the use of proton nuclear magnetic resonance (NMR) in the study of porous media is that relaxation rates are sensitive to the interactions between protons in fluids and the surrounding pore walls. In a two-phase fluid system the strength of the protons' interaction with the pore is in part determined by the surface wettability, as influenced by the thickness and distribution of the wetting phase on the solid surface, which affects access of protons to the surface. Recent laboratory NMR results illustrate the promise of this technique to characterize the wettability of pores.¹ The purpose of this study is to extend the NMR-based wettability method and to compare results with those from standard laboratory wettability indices. The chalks used in this study provide an ideal porous media for NMR and wettability studies because of their uniform-sized, well-connected pores.

Wettability is a surface relaxivity issue, a measure of the strength of interactions between fluids and pore walls. The major difference between wettability studies and more standard surface relaxivity studies is the complicating role of films (both water and hydrophobic organic) that restrict access of the bulk fluids to the surface. Wettability in a reservoir is strongly influenced by the stability of thin wetting films, especially in rocks that are

distinguished by mixed or alternating wettability.^{2,3} A key assumption is that mineral surfaces are initially water-wet, or that a water film is preferentially stable. The introduction of surfactants and certain hydrocarbon species that can be adsorbed through the initial water film have the ability to create hydrophobic or oil-wet sites on the pore surfaces. This work is based on the assumption that in reservoirs water is the preferential wetting phase, ranging from weakly oil wet to strongly water wet. Laboratory experiments with oil-based drilling muds are able to alter wetting states to more strongly oil-wet conditions.¹

METHODS

Standard laboratory methods for imbibition and forced displacement by centrifuge capillary pressure were used in this study. Isopar-M (Exxon Corp, Houston TX, USA), a synthetic isoparaffinic mineral oil with viscosity of 2.7 cp and bulk T_1 of 600 ms, was used as the hydrocarbon phase. NMR spin-lattice and spin-spin relaxation measurements at a Larmor frequency of 2 MHz (Maran-2, Resonance Instruments, Witney, UK) were made on sample plugs at each step of the fluid displacement cycle. The NMR data was transformed into a distribution of relaxation times by a non-linear least-squares algorithm that utilizes a regularization compo-

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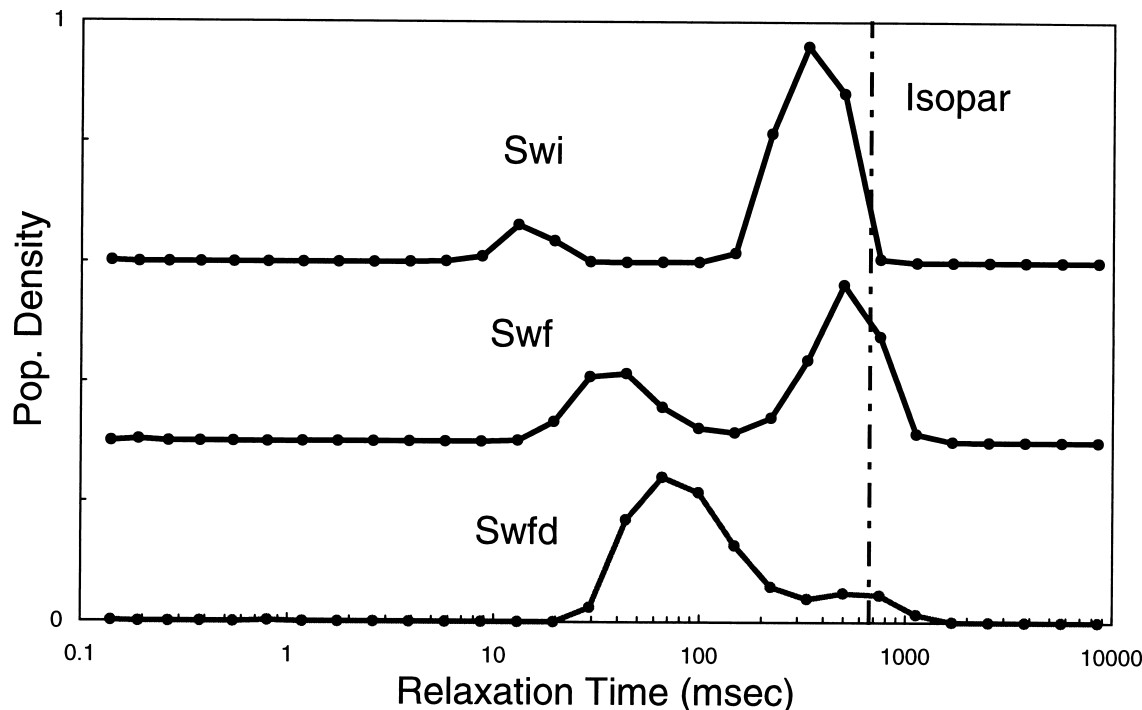


Fig. 1. Relaxation time distribution for uncleaned chalk at different saturation states. Water and isopar are distributed throughout the pore space in differing proportions at initial water saturation (S_{wi}), after spontaneous imbibition (S_{wf}), and after forced displacement (S_{wfd}). The slow relaxation component corresponding to the isopar is faster than the isopar's bulk relaxation at 600 ms (dashed-dotted line).

ment to reduce noise effects.⁴ Relaxation time distributions from T_1 and T_2 data are quite similar, with the T_2 results shifted to faster times by an average factor of 1.3. T_1 results are reported in this paper.

A simple model for estimating wettability effects was based on an earlier grain consolidation model of partial saturation effects on surface relaxivity where variations in a normalized relaxation time at a given water saturation reflects differences in the strength of fluid/surface interactions.⁵ The non-linear expression:

$$T_n = C * S_w^b, \quad (1)$$

where T_n is the normalized relaxation time of the water-filled component compared to a fully saturated state, C is an empirical correction factor, and the exponent b is correlated with wettability. A decrease in b indicates weaker proton interactions with the pore wall, i.e., less water wet, at a given water saturation. Estimates of b can be made at any saturation. As long as wetting behavior remains constant at different water saturations, then the estimate of b will be constant (i.e., plot on a continuous curve on $T_n - S_w$ crossplot). Because the imbibition end-point is a critical reservoir parameter for predicting

oil recovery under water-flood conditions, the NMR wettability index is estimated from saturation endpoints (S_{wf}) results. Standard water displacement tests produced Amott wettability values of 0.06 to 0.59 for uncleaned samples and 0.65 to 0.95 for cleaned samples.

NMR RESULTS

Relaxation times for fully saturated chalk samples range between 80 and 200 ms. Pore dimensions are approximately 0.5 microns, which results in surface relaxivities of 1.0–2.0 microns/s. Relaxation times for isopar-saturated samples range from 200–400 msec, with a similar narrow distribution as observed with water-saturated samples. The ratio of water-based to hydrocarbon-based surface relaxivities varies from 2.5 to 3.5. Surface relaxivity ratios for strongly water-wet glass bead samples increase as the viscosity difference between water and hydrocarbon increases.⁶ In contrast, these samples show a small relaxivity variation at a constant viscosity that is associated in part with wettability differences.

The displacement tests were first done on a set of uncleaned chalk samples. At initial water saturation, the NMR relaxation time distribution for a sample with an

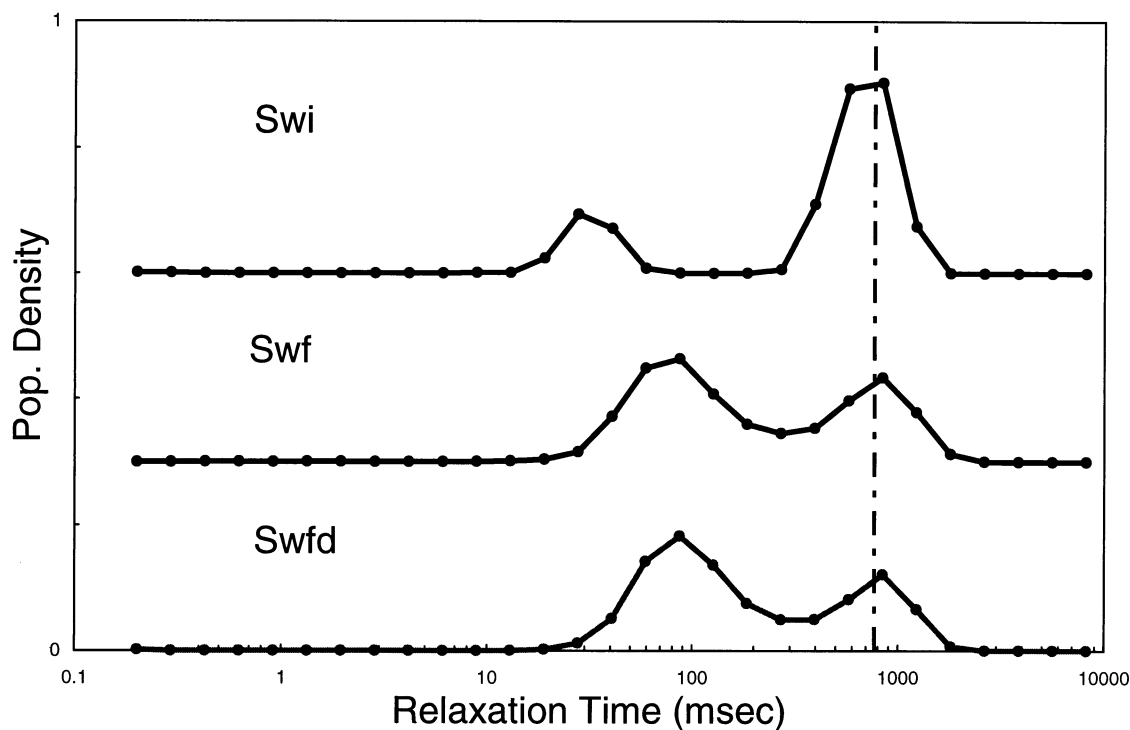


Fig. 2. Relaxation time distribution for cleaned chalk at different saturation states. Water and isopar are distributed throughout the pore space in differing proportions at initial water saturation (Swi), after spontaneous imbibition (Swf), and after forced displacement (Swfd). The slow relaxation component corresponding to the isopar-filled pores is equivalent to the isopar's bulk relaxation (dashed-dotted line).

Amott index of 0.45 is characterized by a distinct bimodal distribution (Fig. 1). The fast relaxation mode is located around 10–20 ms and contains 10–40% of the total intensity, which corresponds to the water saturation. Previous work has shown that the relative intensity of this fast relaxation component is equal to water saturation.¹ The slow relaxation mode is located at 400–500 ms, significantly faster than bulk isopar.

The displacement of hydrocarbon by spontaneous water imbibition was monitored for three weeks on the core plugs in standard imbibition cells. Most of the imbibition occurred within the first several days. Swf from imbibition were determined from the NMR relaxation time distributions. These end points ranged from 0.17 to 0.54 saturation units. NMR relaxation time distributions are characterized by decreases in the slow relaxation time component and a slight shift in the measured relaxation time towards slower times. In contrast, the fast relaxation time component showed both an increase in total intensity and a more significant shift towards slower relaxation times (Fig. 1). Forced displacement of water into the plugs was done by high-speed centrifugation methods with an oil/water capillary pressure of 200 psi. Relaxation time distributions show a significant increase in

the water relaxation component's intensity and a shift towards even slower times, indicating significant uptake of water (Fig. 1).

After substantial cleaning with alternating toluene/methanol cycles, the fluid displacement tests were repeated on the chalk samples. Relaxation time distribution for the cleaned sample, Amott index of 0.81, at initial water saturation again shows the distinct bimodal nature (Fig. 2). Initial water saturations are higher for the cleaned chinks. The relaxation time of the hydrocarbon phase is approximately 600 ms, close to the value for bulk isopar. Water saturations after imbibition are also higher for the cleaned samples than for the uncleaned samples. Unlike the Swi values that show considerable scatter, the Swf values for the cleaned chinks are tightly clustered. The imbibition endpoints are independent of both the total porosity and the median pore throat radius. This suggests that as with the uncleaned samples, pore geometry has little influence on imbibition processes for these samples. Forced displacement of the hydrocarbon with water resulted in very little change in the relaxation time distributions, unlike what was observed with the uncleaned samples (Fig. 2). Results indicate that less oil remains in the uncleaned sample after forced displace-

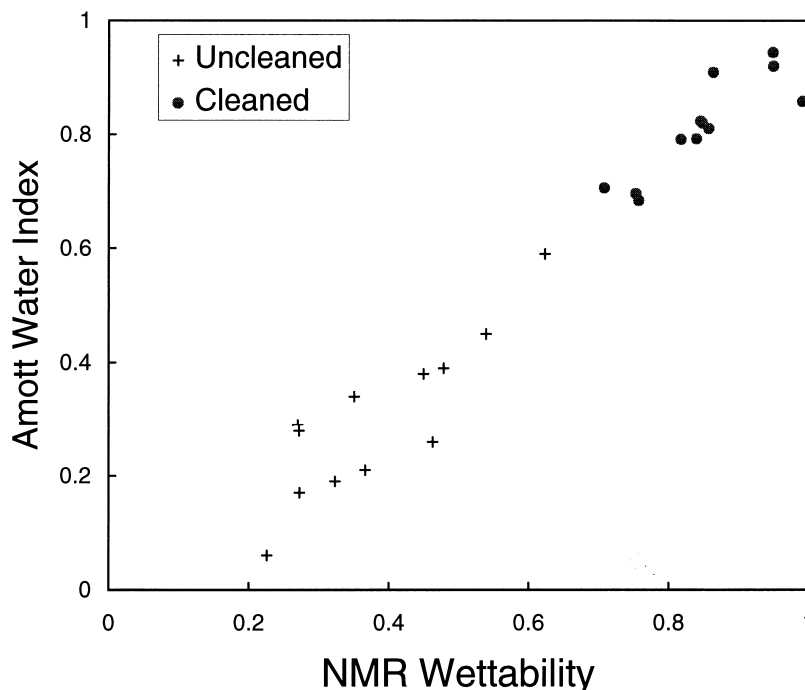


Fig. 3. NMR-based wettability index for uncleaned and cleaned chalk samples compared to Amott water-relative-displacement index.

ment, which suggests more efficient ultimate recovery for the weakly water-wet sample.⁷

There is a strong linear relationship between standard water displacement indices measured on the uncleaned and cleaned chalks and the NMR-based b parameter for the same samples (Fig. 3). This trend is quite pervasive over the entire range of water-wet behavior. This correlation indicates that the surface-sensitive nature of NMR relaxation measurements is responding to significant changes in pore-wall chemistry that affect standard water displacement behavior. These results also suggest that water-displacement indices respond to variations in pore-wall chemistry or wettability and are not solely dependent upon pore volume or pore geometry. In combination these two measurement techniques indicate that changes in imbibition behavior and end-point saturations is strongly affected by the composition of the pore walls.

DISCUSSION

NMR-based estimates of wettability determined from shifts in the water relaxation component as a function of water saturation show a strong correlation with traditional measures of wettability for both uncleaned and cleaned samples. These results suggest that unidentified compositional differences of the pore surfaces are responsible for comparable shifts in NMR relaxation times and for the observed variations in phenomenological water-displacement processes by capillary and viscous components.

Wettability is often defined by the relative affinities two immiscible fluids have between themselves and with a solid surface. This relationship is characterized by a well-defined contact angle on homogeneous surfaces; however, most reservoir rocks do not provide such an easily observable platform.⁷ While clean mineral surfaces are determined to be strongly water-wet, most reservoirs might be characterized as mixed wet, where within a single pore surfaces do not have same affinity for water and oil.⁷

The critical thickness of the wetting-phase film depends on the type of measurement we are interested in. Dynamic displacements of fluids are affected by film thickness on the scale of 10s of nanometers. Thinner films, such as when the disjoining pressure is exceeded, result in patches of surface where non-wetting phase interactions with the surface become more likely, e.g., not isolated from surfaces. In contrast, a much thinner water film can isolate NMR molecular interactions with pore surfaces because bonding forces affect only a few layers.⁸ Thickness of a water film sufficient to alter the electron-nuclear interactions and cause significantly slower hydrocarbon phase relaxation was estimated to be a single adsorbed monolayer.⁹ This difference in scale of effective film thickness indicates that NMR measurements are much more sensitive to the presence of very thin wetting-phase films. The fact that isopar relaxation in the uncleaned samples is generally faster than bulk relaxation times indicates that there must exist surfaces

where not even a monolayer film of water is present. These are related to localized patches of adsorbed or precipitated hydrophobic species, such as waxes and asphaltenes.⁷ The absence of a relaxation component corresponding to bulk water in even the most oil-wet samples suggests that there is not a continuous hydrophobic thin film coating all of the pore surfaces.

CONCLUSIONS

Significant shifts in relaxation time distributions illustrate how water and hydrocarbon are distributed in porous media. For light hydrocarbons characterized by slow T_1 values, the separation between the water and hydrocarbon is very distinct. For two phases in rock, distributions are affected in part by the distribution and thickness of the wetting phase (water) on the pore surfaces.

A wettability model based on surface relaxivity principles takes advantage of the relative relaxation times as a function of water saturation. The NMR-based wettability estimate for uncleaned and cleaned chalk samples compares favorably with traditional Amott–Harvey wettability indices.

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