NMR CHARACTERIZATION OF HYDROCARBON GAS IN POROUS MEDIA

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Laboratory investigations of nuclear magnetic resonance (NMR) relaxation properties of methane gas in bulk and in porous media are reported. Measurements were performed for methane alone and together with water in glass bead packs and Bentheimer sandstone. Results indicate that surface relaxation effects can be significant and that diffusion effects dominate observed $T_2$ relaxation. © 1998 Elsevier Science Inc.

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INTRODUCTION

The relatively dense hydrocarbon gasses in underground reservoirs can contribute significantly to the signals detected by nuclear magnetic resonance (NMR) logging tools. Discrimination of the hydrocarbon gas is important for accurate determination of hydrocarbon reserves. Several methods$^{1,2}$ have been proposed to discriminate various fluids in reservoirs based on anticipated differences in relaxation and diffusion properties. However, little is actually known about NMR properties of gas in porous media. Here we report a laboratory investigation of NMR relaxation properties of methane gas, the major component of hydrocarbon gas in underground reservoirs.

EXPERIMENTAL METHODS

The experiments were conducted on a GE 2T OMEGA CSI operating at 85 MHz. Bentheimer sandstone and two different sized glass beads (B. Braun Melsungen AG, Melsungen, Germany) of nominal diameter 0.1 mm (0.10–0.11 mm) and 0.5 mm (0.45–0.50 mm), were used as the porous media. A cylindrical gas cell made of PEEK (Ensinger Special Polymers, Houston, TX, USA) was used, with a sample size 0.8 cm in diameter and 8–10 cm in length. Experiments were conducted at 295 K. Proton spin-lattice relaxation times $T_1$ were measured using the conventional inversion recovery method, and transverse relaxation times $T_2$ were obtained from the Carr–Purcell–Meiboom–Gill (CPMG) sequence. Average relaxation times for fluids in porous media were calculated from the estimated relaxation distributions.$^3$
tion, the spin-lattice relaxation rate for an isolated pore can be written as:

$$\frac{1}{T_1} = \frac{1}{T_{1b}} + \rho \frac{S}{V},$$  \hspace{1cm} (1)

where the subscript $b$ refers to bulk conditions, $\rho$ is the surface relaxivity, and $S/V$ is the surface-to-volume ratio of the pore. The degree to which surface effects contribute to relaxation is important. If surface effects are not significant, the relaxation of methane in porous media is determined simply by the bulk properties. On the other hand, the contribution of surface relaxation will depend on the material with which the gas interfaces.

We investigated the role of surface relaxation by comparing the average $T_1$ of methane at various pressures for the following five cases: 1) bulk methane; 2) methane in 0.1-mm bead pack; 3) methane and water in 0.1-mm bead pack; 4) methane and D$_2$O in 0.1-mm bead pack; and 5) methane in Bentheimer sandstone. Our results are summarized in Fig. 2.

The results indicate that surface relaxation can be important. The average relaxation for methane in bead packs and in Bentheimer sandstone is faster than that for bulk methane. The relaxation of methane in the sandstone is considerably faster than in the glass beads, which is consistent with the sandstone having the greater surface relaxivity. These results indicate that surface effects can be important when the gas is in contact with sedimentary rocks.

When liquids are present with gas in the porous media, the liquids are expected to wet the surface of the media. Consequently, the gas interface will be with the liquid, and not the porous media. The average relaxation for methane when the bead pack also contains water is not significantly different from that of the bulk. This would indicate that surface effects may not be important in reservoirs which contain liquid with the gas. If the spin-lattice relaxation of methane in the presence of water occurs via dipole-dipole exchange between gas molecules and water molecules, we should be able to see the differences in $T_1$ values when D$_2$O is substituted for water. As can be seen from Fig. 2, there is no significant difference in these two $T_1$ values. From these results, we conclude that there is no significant contribution to $T_1$ relaxation of methane from the dipole-dipole exchange between methane and water molecules.

$T_2$ Properties. $T_2$ is of particular interest for well logging because the CPMG sequence is normally used. The response of fluids in porous media can be complicated by the effects of diffusion within local magnetic field gradients. A measure of this effect is provided by the diffusion contribution, $1/T_{2d}$, for unrestricted diffusion in a magnetic field gradient $G$, which is given by:

$$\frac{1}{T_{2d}} = \frac{\gamma^2 G^2 D \tau^2}{3},$$  \hspace{1cm} (2)

where $\gamma$ is the gyromagnetic ratio, $D$ is the diffusion coefficient and $\tau$ is half the echo spacing. Gasses typically have significantly larger diffusion coefficients than liquids, and the values are more sensitive to pressure. At constant temperature, the diffusion coefficient of methane has been found to be inversely proportional to the density up to the critical density. Also, the magnetic field gradients are expected to be different due to differences of magnetic susceptibilities. Consequently, significantly different $T_2$ behavior may be encountered for gas compared to liquid.

We investigated the pressure dependence of $T_2$ of methane in 0.1- and 0.5-mm bead packs as a function of echo spacing. Average values of $T_2$ were determined and are plotted in Fig. 3. $T_2$ relaxation is seen to be quite sensitive to pressure. The initial slopes of $1/T_2$ vs. $(2\tau)^2$ are proportional to the diffusivity, $D$. That slope is in-
versely proportional to pressure, consistent with the dependence of gas bulk diffusion coefficients.\textsuperscript{5}

Another important observation from Fig. 3 is that linearity is observed only up to very small values of echo spacing. The effect of restricted diffusion is apparent in these results, and it becomes more significant as the pressure decreases.

Comparing the average relaxations for the two bead packs at 3000 psia, we see that the contribution of diffusion effects to relaxation is greater for the 0.1-mm bead pack than the 0.5-mm bead pack. This is due to the greater internal gradient effect which arises from the smaller bead size. Its role is represented by $G$ in Eq. (2). The increase in $G$ with the decrease in bead size is consistent with the approximation of the internal field gradient reported by Glasel et al.:\textsuperscript{8}

\begin{equation}
G \propto \frac{\Delta \chi H}{d},
\end{equation}

where $G$ is the internal field gradient, $\Delta \chi$ is the susceptibility contrast, $H$ is the external field and $d$ is the diameter of the beads.

Figure 4 shows $T_2$ distributions\textsuperscript{3} of methane and water in a 0.1-mm bead pack at 3100 psia at various echo spacings. The large peaks corresponding to shorter $T_2$ are due to the methane gas, which has a large signal at high pressure. The water peaks are the small components of the spectra. As the echo spacing is increased due to the difference in diffusivity of the two fluids, the methane peak shifts significantly compared to the water peak and, thus, the two phases can be fully resolved by increasing the echo spacing.

**SUMMARY OF RESULTS**

We measured NMR properties of methane in bulk, in glass bead packs and in Bentheimer sandstone. For $T_1$, surface relaxation can be significant when gas interfaces with the porous media, but appears to be insignificant when water is present. The observed $T_2$ relaxation is very sensitive to echo spacing, which indicates a dominating diffusion effect. The behavior of $1/T_2$ was found to reflect the change in the diffusion coefficient with pressure as well as the change in internal field gradient with grain size. However, the effect of diffusion cannot be adequately represented by the expression for unrestricted diffusion in a constant field gradient.

**REFERENCES**