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Original contribution

NMR characterizing mixed wettability under intermediate-wet condition

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ABSTRACT

Applying the concept of effective relaxivity to characterize wettability is based on the configuration of fluid distributions in porous media. However, in mixed-wet porous media with intermediate-wet patches (homogeneous wetting region), effective surface relaxivity cannot fully characterize wettability because fluid distributions are not directly corresponding to wetting patch distributions. Patches with different wettability interact with the same fluid differently, which leads to different surface relaxivity. The distribution of this kind surface relaxivity from porous media saturated with single fluid matches mixed wettability distribution. Here, we apply decay due to diffusion in internal field plus Carr-Purcell-Meiboom-Gill (DDIF-CPMG) method to obtain T_2 and the pore size distribution correlation. The variation of surface relaxivity obtained from the correlation map is used to characterize wettability distributions of mixed-wet porous media. In this paper, we also redefine a parameter based on surface relaxivity distribution to evaluate mixed wettability under intermediate-wet condition. The experiment results with limestones show that, after wettability alteration of the sample, the distribution of the surface relaxivity is changed and closely correlated with pore size distribution, which demonstrates the features of mixed wettability under intermediate-wet conditions.

1. Introduction

Wettability is “the tendency of one fluid to spread on or adhere to a solid surface in the presence of other immiscible fluids” [1]. It is critical for enhanced oil recovery (EOR) in oil industry because it traps wetting fluid in pores and affects fluid transportation in porous media. Wettability is classified as homogeneous wettability and heterogeneous wettability (fractional and mixed wettability) according to surface chemical property distributions [2-4]. The difference between fractional wettability and mixed wettability is whether the distribution of patches with different wettability is closely related with pore size distribution. Wettability distributions in mixed-wet rocks are closely correlated with pore size distributions. Small pores are mainly consisting of water-wet patches and large pores are consisting of oil-wet patches because of the immigration of oil into originally water-wet reservoir. Mixed-wet reservoirs occupy a great portion in oil industry. But they still have not been directly and efficiently measured because it is difficult to directly probe wettability, especially mixed wettability of porous media.

Many methods have been proposed to measure wettability of porous media, such as dielectric method, Amott or USBM method, contact angle method and X-ray CT [2,5]. Those methods will probably ruin the samples or the original state of the sample and time-consuming while measuring. Nuclear magnetic resonance (NMR) has also been applied to evaluate wettability, because it is noninvasive, sensitive to fluid distributions and sensitive to the effects of solid walls. Brown and Fatt showed that T_1 relaxation time is linearly proportional with the ratios of water-wet glass beads in the mixtures of water-wet and oil-wet glass beads saturated with water [6]. The surface relaxivity of water-wet surface to oil-wet surface is around 4:1. Hsu et al. also obtained that relationship with the mixtures of SF 99 coated glass beads (oil-wet) and clean glass beads (water-wet) [7]. Many other scholars also applied this method to qualitatively interpret wettability in porous media [8-11]. Fleury gave the difference of surface relaxivity of water and surface relaxivity of oil and applied it to calculate wettability [12]. However, they did not give a general quantitative method or evaluation standard for NMR method evaluating wettability. Looyestijn made an definition of wettability with NMR method based on effective surface relaxivity [13]. The results of wettability index from NMR and USBM* (modified USBM) showed liner relationship. Other scholars applied this definition and had got good linearly fitting results with Amott or USBM wettability index [14-18]. Zielinski et al. applied Padé interpolation method to obtain effective relaxivity from $D - T_2$ maps [19]. This method was also employed by Minh et al. to obtain effective relaxivity and applied

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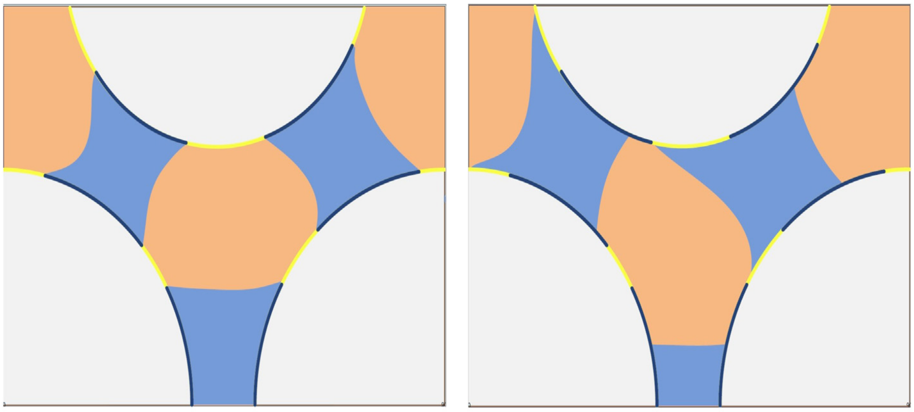
(a)

(b)

Fig. 1. Illustration of oil (yellow bulk) and water (blue bulk) distribution in mixed wet porous media (a) with strongly wetting patches and (b) with intermediate-wet patches. The light yellow lines and deep blue lines are oil-wet surface and water-wet surface. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the definition to characterize wettability in rock samples [20]. However, this definition and the method for obtaining the wettability index, as illustrated by Wang et al. [11], heavily depends on the configuration of fluid distributions which are closely correlated with the interaction intensity between fluids and solid walls. They assumed that porous media is strong-wet and fluid distribution in heterogeneous-wet porous media with strong-wet patches is that wet fluid tends to contact with wet surface. But, with intermediate-wet patches, the distribution of fluids is very complex where non-wet fluid can contact with wet patches as shown in Fig. 1. In Fig. 1, the distribution of effective surface relaxivity is poorly correlated with fluid distribution. The diverse pore structures also make fluid distribution more complex [21]. Thus, the method employing surface relaxivity depending on the configuration of fluid distribution to indicate wettability cannot be used for this mixed-wet porous media with intermediate-wet conditions.

To overcome this dependence and characterize mixed wettability of porous media with intermediate-wet patches, here we employ DDIF-CPMG for porous media saturated with single fluid to obtain $T_2 - \alpha$ (α is pore size) [22]. For patches with different wettability, the interactions between solid patches and the same fluid are different, which results in different surface relaxivity. For wettability altering process, the polar components form a layer of contamination which significantly decrease the surface relaxivity [23]. As this method does not depend on fluid distribution, this method excludes the uncertainty of complex fluid distribution which may caused by intermediate-wet patches. For experiment, to eliminate the influence of minerals distribution, we use limestone rocks whose components are comparatively simple. We use crude oil to alter wettability of the limestone and compare the surface relaxivity changes, before and after the aging processing obtained from the $T_2 - \alpha$ map.

2. Theory

Here, we briefly review how to apply decay due to diffusion in internal gradient field to determine pore size distribution without considering surface relaxivity. Details can be found in references [22,24]. In pore space, the evolution of magnetization density $m(\vec{r}, t)$ is described by Bloch-Torrey equation [25]. The total magnetization M(t) is the integration of $m(\vec{r}, t)$ for the whole pore space V_p. The system is described by diffusion equation with proper boundary condition [26]:

$$\frac{\partial m}{\partial t} = \nabla \bullet (D \nabla m) - \nu m \tag{1}$$

$$0 = \vec{n} \bullet D \nabla m + \rho m \tag{2}$$

$$m(\vec{r}, t = 0) = M(0)/V_p. \tag{3}$$

Eq. (1) is the diffusion equation and D is the self-diffusion of the saturated fluid. ν is the volume sink strength density. Eq. (2) is boundary condition. ρ is the adsorption rate of spin at pore surface and $\vec{n}$ means the direction from inside pore to outside. Eq. (3) is the initial condition for the pore system. The general solution for the equation can be written as [26]:

$$m(\vec{r}, t) = \sum_{0}^{\infty} A_n \phi_n(\vec{r}) e^{-t/T_{1,2}^n} \tag{4}$$

where ϕ_n and $T_{1,2}^n$ are eigenfunctions and eigenvalues respectively. If $n = 0$, it is called ground mode, where surface relaxation dominates in fast diffusion regime. When $n \geq 1$, they are called high modes. The amplitude of each eigen mode is given by A_n:

$$A_n = \frac{1}{V_p} \int_{V_p} m(\vec{r}, 0) \phi_n(\vec{r}) dV. \tag{5}$$

In fast relaxation regime, where $\rho_{1,2}\alpha \ll D$(α is the diameter of the spherical pores), the relaxation in a saturated porous media is directly related to specific surface areas (the ratio of surface to volume) [27]:

$$\frac{1}{T_{1,2}} = \rho_{1,2} \frac{S}{V_p} \tag{6}$$

where S is pore surface area in the saturated pore system. If we assume the pore is spherical, we have:

$$\frac{1}{T_{1,2}} \approx \frac{1}{6\rho_{1,2}} \alpha. \tag{7}$$

This equation is usually applied to obtain pore size distribution in porous media. Obviously, surface relaxivity, ρ is assuming uniform distribution here. However, as described in Fig. 2, solid surface chemical properties e.g. wettability and surface relaxivity, of porous media can be heterogeneous. To obtain real pore size distribution without the assumption of homogeneous surface relaxivity distribution, we need to obtain pore size distribution from high modes. The high modes describes different properties of pore structure. With the above assumption that the pore inside porous media is spherical, the decay times for them follows [28]:

$$T_{1,2}^n \approx \begin{cases} \dfrac{a}{6\rho_{1,2}} & n = 0 \\ \dfrac{\alpha^2}{4D\zeta_n^2} & n \geq 1 \end{cases} \tag{8}$$

In fast diffusion regime, ζ_n is the positive root of equation $1 - \zeta_n \cot\zeta_n = \rho_{1,2}\alpha/2D$. Here, if we just use the first mode ($n = 1$), $\zeta_1 \approx 4.49$ [26]. The distribution of pore size from the first mode is without concerning surface relaxivity. Combined with Eq. (7), we can obtain the distribution of surface relaxivity which would show the different chemical surface distribution, e.g. wettability. Surface relaxivity is

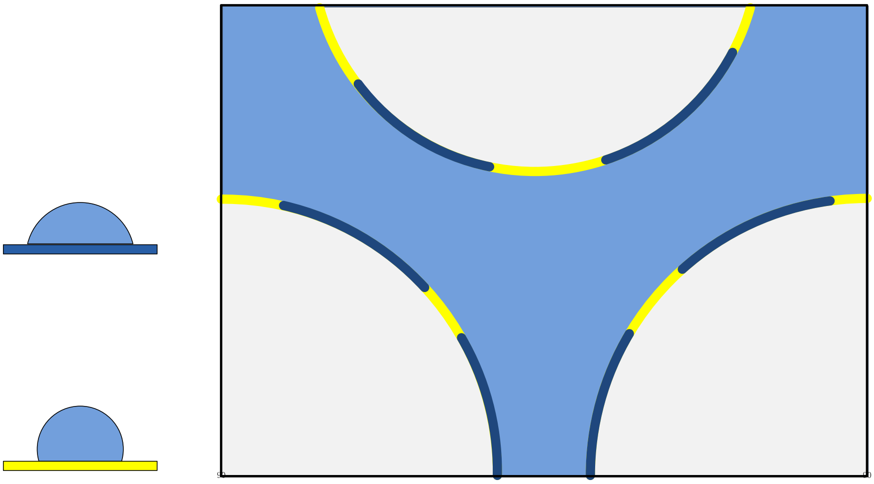

Fig. 2. Wettability distributions of only water saturated rock sample. The deep blue lines and light yellow lines represent water wet surface and oil wet surface. The inlets on left represent the contact angles of water droplet on water wet surface and oil wet surface. Both of the wettability of the surfaces are intermediate-wet. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 3. The limestone sample used for experiment.

obtained by $\frac{d\alpha}{dT_2}$ on the correlation map.

Here, we apply DDIF-CPMG pulse sequence, as shown in Fig. 4 to obtain the first mode and the distribution of surface relaxivity. During the encoding time t_e in 2D signal pulse (top in Fig. 4), the magnetization is modulated, including the contributions from ground mode and higher modes. However, the π pulse in reference pulse sequence of domain a, cancels the accumulation of phase dependent magnetization. The modification makes ground mode dominate the decay of reference pulse sequence. The contribution from first mode can be obtained by removing the ground mode contributions and can be expressed as [24,29]:

$$S(t_{diff},\, NT_E) = \int\int \left(F(\alpha,\, T_2)\exp\left(-\frac{4t_{diff}\zeta_1^2}{\alpha^2} \right) \exp\left(-\frac{NT_E}{T_2} \right) \right). \tag{9}$$

N is the number of echo spacing T_E. $F(\alpha,T_2)$ is the correlation of transverse relaxation and pore diameter.

3. Experiment

In this part, the sample is first cleaned and saturated with water and measured with DDIF-CPMG pulse sequence. After the aging process, the sample is saturated with water and is measured with DDIF-CPMG with the same parameters.

The rock sample we used in the experiment is limestone with porosity 16.2 pu and permeability 27 mD as shown in Fig. 3. The sample is 1.5 in. in diameter.

The limestone sample is first washed with solvents. After cleaning the sample, it is baked in an oven at 90 °C for 48 h. The Amott index shows the wettability index of the sample is 0.3 which is water-wet. Then the sample is saturated with water and measured with DDIF-CPMG pulse sequence in Fig. 4. Then the rock sample is flushed with crude oil and aged for 3 weeks. Clean and saturate the sample with water and measure it with DDIF-CPMG and with the same parameters above.

The aging process follows the paper [30,31]. First, the sample is cleaned with solvents and rinsed with deionized water. After clean the sample, it is baked in an oven at 90 °C for 48 h. The dry sample then is vacuum-saturated with water. And then the rock sample is flushed with crude oil (from Shengli oil field and mixed diesel with the ratio 9:1) to irreducible water saturation and aged for 3 weeks at reservoir temperature 90 °C, in order to reproduce the surface properties occurring in the reservoir under consideration [30]. The sample after the aging process is measured by Amott method, −0.26, showing it as intermediate-wet rock. After these steps, the aged sample is cleaned, saturated with water and measured with 2 MHz Magritek Rock Core Analyzer. Parameters used in the experiment are set the same with the first experiment.

The experiment parameters are set as follows. The radio frequency (RF) pulse length is set to be 25 μs. The encoding time period t_e is 9.0 ms. The diffusion time t_{diff} varies logarithmically from 0.5 ms to 6000 ms in 50 steps.

4. Result and discussion

We process the acquired data with fast Laplace inversion [32]. The results of experiment with cleaned limestone and limestone aged with crude oil are shown in Fig. 5.

The results show that the $T_2 - \alpha$ distributions of the sample are different before and after the aging process which alters wettability of the sample according to Amott index. Before the aging process, the $T_2 - \alpha$ distribution follows a nearly linear relationship which means that surface relaxivity distribution of the sample is almost uniform distributed. However, after the aging process, the surface relaxivity distribution varies with pore size distribution. The correlation deviates from the nearly straight line. The slope (corresponding to surface relaxivity) in (b) of Fig. 5 of large pores is smaller than that of small pores. This is because the aging process only changes the wettability of large pores where the crude oil contacts with the surface of the pores. For small pores, water is residual in them because of capillary pressure and dead pores, where the surface is still water-wet. This explains why surface relaxivity in large pores is smaller than that in small pores [23].

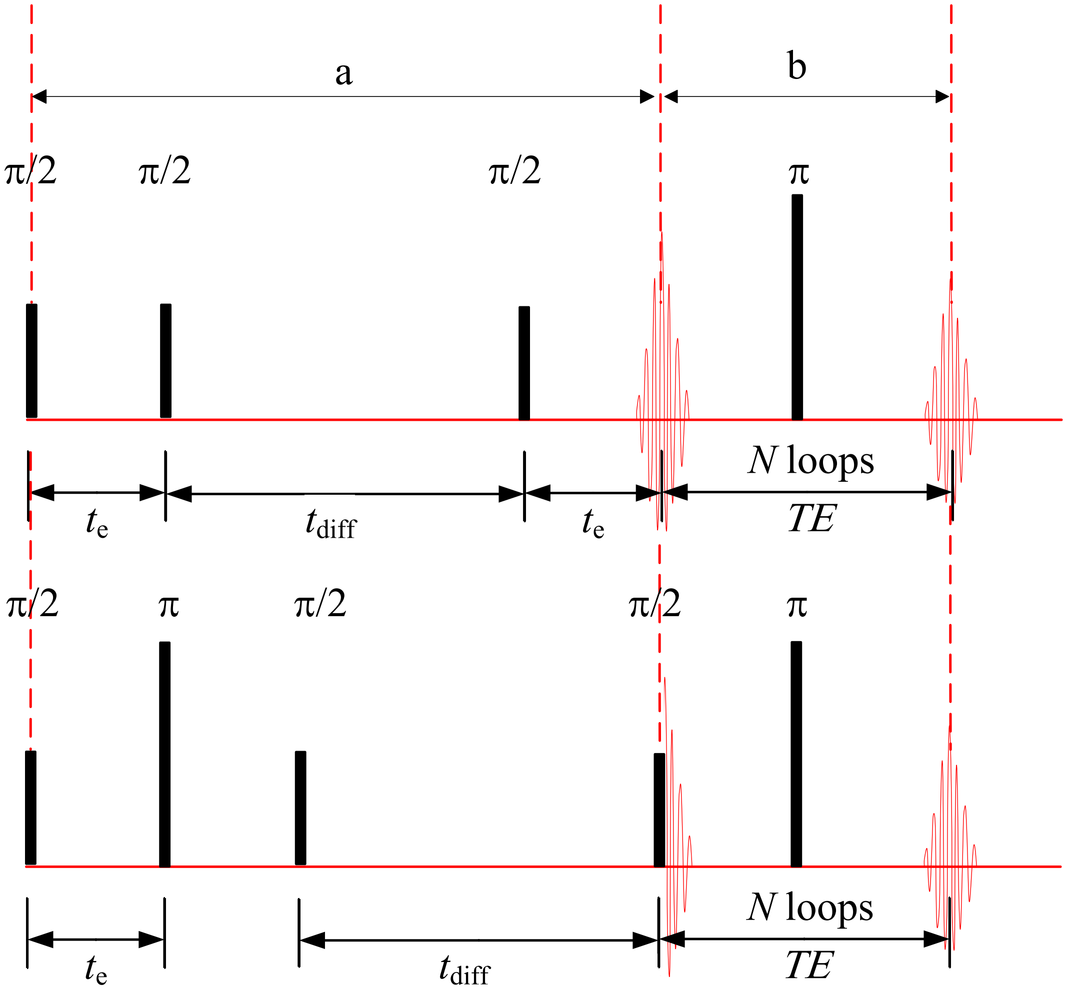

Fig. 4. DDIF-CPMG pulse sequences detailed in Refs. [24,29]. Top is the signal pulse sequence and the bottom one is the reference pulse sequence. In DDIF pulse sequence (a domain), t_e is the encoding period and t_{diff} is the observation time for diffusion. *TE* is echo space for CPMG part (b domain). Compared with the top pulse, the bottom pulse sequence is added a π pulse, which is used to conceal phase accumulation caused by internal gradient.

Thus, we can conclude that the difference of surface relaxivity in different pores is caused by mixed wettability. These results demonstrate that the correlation of $T_2 - \alpha$ can be introduced as an indicator for mixed-wet limestone with intermediate-wet patches. Besides, we can obtain the ratio of water-wet to oil-wet surface area and the critical pore size below which the wettability can be changed from the map. The deviation time is around 70 ms below which the crude oil cannot penetrate into the pores. Surface relaxivity is obtained by $\frac{d\alpha}{dT_2}$on the correlation map.

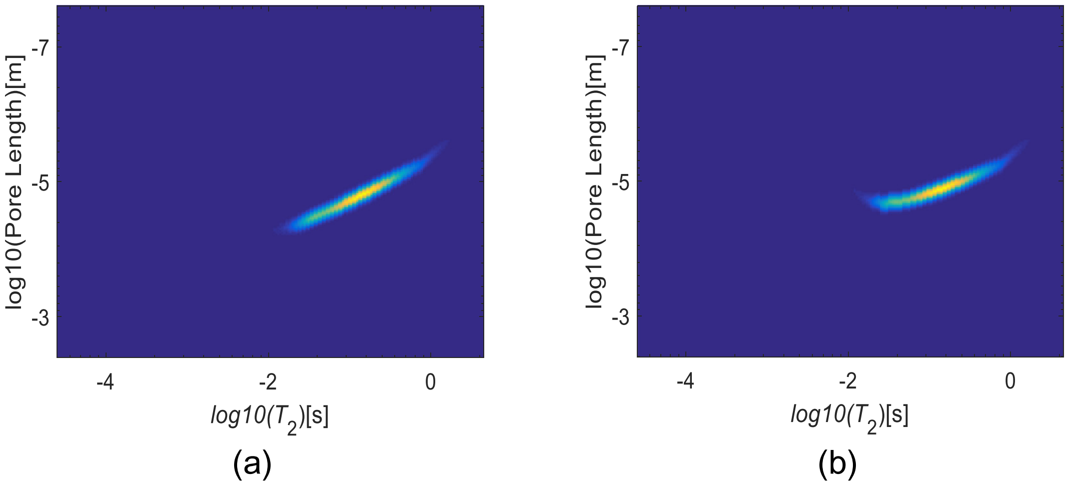

Fig. 5. $T_2 - \alpha$ correlation of limestone. (a) is before aging process and (b) is after the aging process. The slope in (a) is almost linear but in (b) in large pores it deviate from the linear relationship.

To evaluate mixed wettability with intermediate patches, we define a parameter, wettability index(*WI*):

$$WI = \frac{\rho_\alpha - \rho_{\min}}{\rho_{\max} - \rho_{\min}} \tag{10}$$

where ρ_α is the averaged surface relexivity over whole pore surface area. $\rho_{\max}$ and $\rho_{\min}$ are the maximum value and minimum value of surface relaxivity. For this definition, samples with values larger than 0.5 are water-wet and for samples smaller than 0.5 are oil-wet. This is an estimation of the averaged wettability of samples with heterogeneous wettability. We define such wettability index for heterogeneous-wet porous media under intermediate-wet condition, because under intermediate-wet condition, the distributions of water- and oil-wet surface dominate, not fluid distributions [11]. This means surface relaxivity dominates. Wettability indexes of the sample before and after the aging process are 0.79 (water-wet) and 0.32 (oil-wet). Amott indexes of the sample before and after the aging process are 0.30 and −0.26. The values of the defined wettability index for NMR method before and after the aging process match the Amott index, which verifies this definition.

5. Conclusion

The method of DDIF-CPMG enables us to correlate the distribution of surface relaxivity and pore size distribution ($T_2 - \alpha$). The experiment results of limestones before and after the aging process demonstrate that after the aging process, the surface relaxivity is closely related to pore size distribution, where small pores are with large surface relaxivity and large pores with small relaxivity, which is not obvious before the aging process. This distribution of surface relaxivity and pore size illustrates the features of mixed wettability where the pore surface of small pores (relaxation time smaller than 70 ms) are water-wet and large pores (relaxation time larger than 70 ms) are mainly oil-wet. This also shows the relaxation time for the critical pore size is about 70 ms below which oil cannot penetrate because of capillary pressure. This is a feature of altering wettability of porous media. The values of new defined wettability index match the values of USBM index, which supports the new definition of wettability index. This also validates the method of DDIF-CPMG and the new definition of wettability index to represent wettability of heterogeneous-wet porous media under intermediate-wet condition.

However, T_2 measurement is affected by internal magnetic field gradient which would result in larger surface relaxivity. This question will be talked in our near future paper.

Disclosure statement

The authors have no conflicts of interest to declare.

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