A Study of Shale Wettability Using NMR Measurements

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ABSTRACT

Shale gas and oil are significant unconventional energy resources in the United States. Because of their low porosity and permeability, as well as the complex pore systems in organic rich shale formations, their petrophysical properties are not fully understood. Further, it is well known that wettability influences many aspects of reservoir characteristics, especially hydrocarbon storage and recovery; however, wettability of organic rich shale is an enigma.

In this work, rock wettability of various shale formations, including Eagle Ford, Marcellus and Mancos, was studied using Nuclear Magnetic Resonance (NMR) measurements. A special fluid injection device was developed to study the impact of injected fluids on the shale rock properties. The effect of various fluids was studied by monitoring the changes in NMR response caused by fluid injection. After injecting either water or oil into the shale cores, we observed amplitude increases in the T_2 relaxation curve at T_2 values much faster than those associated with the bulk fluids. The results provide a positive indication that the fluids were successfully injected into and incorporated into the rock.

When water is injected, the amplitudes of the NMR signals representing fluids in the water-wet pores are expected to increase, while signals from 100% oil-wet pores should remain unaffected. Similarly, the amplitudes of the oil-wet pore signals increase when oil is injected. Also, NMR signals with relaxation times slower than several milliseconds are considered to be associated with relatively larger pores and micro-fractures. For Eagle Ford and Mancos shale samples, the experiments showed NMR signal amplitudes increase in the T_2 range greater than a few milliseconds when oil and water were injected. This increase can be interpreted as having a mixed-wet condition in the relatively large pores and microfractures. In addition, the injection of oil in the Eagle Ford shale cores did not produce a signal amplitude increase within the relaxation time region below 1 ms; therefore, small pores in these Eagle Ford samples are likely water-wet. On the other hand, our study indicated that the small pores are mixed-wet in the Marcellus shale core samples, since a signal amplitude increase was observed after injecting both oil and water.

INTRODUCTION

Wettability is an important rock property, and it is defined as the preference of a solid to stay in contact with one fluid rather than with another. Rocks can be water-wet, oil-wet or intermediate-wet. The intermediate-wet state means the rock is mixed-wet, in which case part of the rock grains is oil-wet and part of the grains is water-wet, or the rock is neutral-wet, meaning that the rock surface is neither strongly water-wet nor oil-wet. Wettability plays a significant role on fluid flow performance as well as hydrocarbon recovery.

Traditional methods for determining rock wettability, such as the Amott method and the U.S. Bureau of Mines (USBM) test, are not applicable to shale rock samples [1]. Because the permeability of shale rock is usually in the range of nD, these methods could be very time consuming and the results are often questionable. Therefore, alternative methods to determine shale wettability are thus desired. NMR has been used extensively for wettability assessment of sandstone and limestone samples. For example, based on the results from NMR measurements on several kinds of sandstone samples, Chen et al. demonstrated that their proposed NMR wettability indices correlated well with the conventional Amott-Harvey index [2].

Recently, Sondergeld et al. [1, 3] used NMR and imbibition to study shale wettability. Odusina et al. [1] studied shale core samples from four formations: Eagle Ford, Barnett, Flyod and Woodford. They performed pressurized imbibition experiments on these core samples with both brine and oil (dodecane). From these experiments, they concluded that except for Woodford shale, the shale core samples generally display mixed wettability. Further, Sulucarnain et al. [3] demonstrated that their NMR response was consistent with the NMR wettability index developed by Looyestijin et al. [4].

In this paper we demonstrate a novel method for studying shale wettability using NMR. Instead of waiting for two days for the imbibition process, our fluid injection method takes only ten minutes. As a result, the time needed for preparing the samples is greatly reduced. Also, a fluid pressure of 500 psi, much smaller than the pressure used for the imbibition process, is sufficient for our method.

NMR technology

NMR has been used frequently since the 1990s in the oil and gas industry for core analysis and logging applications. NMR is used to obtain porosity and permeability information from reservoirs and to distinguish water, oil and gas via relaxation and diffusion measurements [5]. The T_2 relaxation time for fluids in the pores can be written as

$$\frac{1}{T_2} = \rho_2 \frac{S}{V} + \frac{1}{T_2^{bulk}} + \frac{1}{T_2^{diff}} \tag{1}$$

where ρ_2 is the surface relaxivity, and S and V are the surface area and the pore volume, respectively [5]. T_2^{bulk} is the transerver relaxation time of fluid in the bulk state. T_2^{diff} considers the NMR signal decay from diffusion in the presence of magnetic field gradient.

Pore size in mudrock is in the range of a few nanometers to about 2 µm [6] and thus, the first term in Eq. 1 is always a dorminant contributor to T_2. Water and light oil have bulk relaxation time of more than 500 ms, and thus, T_2^{bulk} can be safely neglected from Eq. 1. Under laboratory conditions without external gradient field and assuming the internal gradient is not large, the diffusion term can also be neglected [7]. In this case, Eq. 1 is then simplified to:

$$\frac{1}{T_2} = \rho_2 \frac{S}{V} \tag{2}$$

Therefore, the T_2 relaxation time from NMR measurements can be used as an indication of pore size. Eq. 2 can be rearranged as a function of pore radius into Eq. 3, assuming the pores have a spherical shape. With additional rearrangement, the pore radius can be calculated as a function of T_2, as shown in Eq. 4.

$$\frac{1}{T_2} = \rho_2 \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = 3\rho_2 \frac{1}{r} \tag{3}$$

$$r = 3\rho_2 T_2 \tag{4}$$

MATERIALS AND MEASUREMENTS

Outcrop shale core samples from the Eagle Ford, Marcellus and Mancos formations were purchased from Kocurek Industries (TX). The plugs were used as-received in the experiments without any further treatment. Shale plugs are 2-in. in diameter and 2-in. in length. For each plug, a hole of 0.25-in. diameter and 0.75-in. length was drilled in the center of one end. A 0.25-in. outer diameter tube was placed and fixed inside the hole at a depth of 0.25 in., leaving an openhole section of 0.5-in. length. The diesel used in the experiments was purchased at a local gasoline station. 3% (wt) KCl solution was prepared by dissolving the calculated amount of KCl (Sigma Aldrich) into filtered water. The KCl solution is referred to as water in the later text for simplicity.

The experimental setup is described in detail by Gomaa et al. [8]. It was originally designed to frack the shale core plugs and includes the following components (Fig. 1): injection pump; fluid accumulator holds up to 250 ml; holding cell; pressure transducer.

NMR measurements were performed with a GeoSpec II rock core analyzer from Oxford Instruments. The resonance frequency was 2 MHz and interecho spacing (TE) was 0.1 ms. The waiting time before each scan is 500 ms. The NMR data were collected at ambient conditions and processed with software from Green Imaging Technology, with an assumed hydrogen index of 1. The number of scans for T_2 experiments was automatically set so that the signal noise ratio of the experiments reached 100.

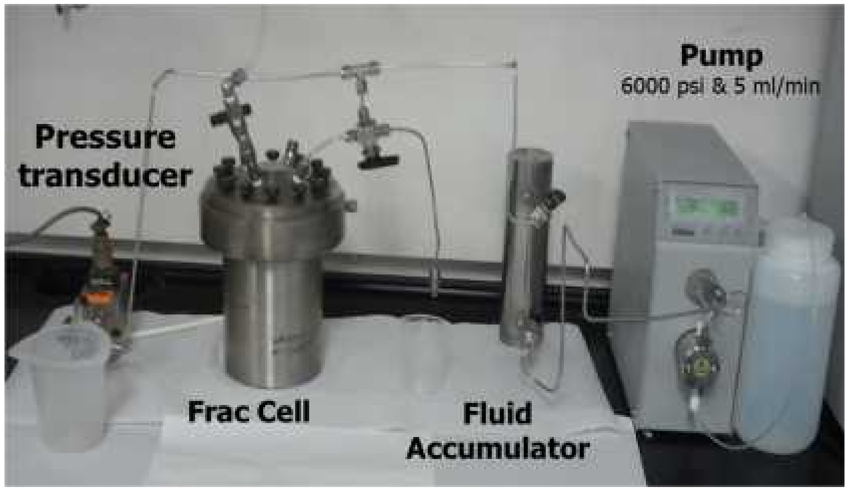

Fig. 1: Experimental setup used to fracture the shale cores.

Before starting the experiments, we confirmed that all lines and accumulators were filled with the testing fluid so that all the air was removed, and there was no leak in the system.

Before injecting fluid into the core plug, an NMR T_2 scan was acquired on the 'as received' shale sample. Next, the shale core was placed inside a rubber sleeve that isolated the shale core from the surrounding environment except from the inlet tubing. The injection pressure started to increase as a function of time during the fluid injection until pressure reached a certain pressure value less than fracture pressure. In this work, 200 or 500 psi pressure was kept for 10 min. Finally, the sample was taken out of the frac cell and trandfered to NMR spectrometer to acquire a second NMR scan. A comparison between the final and initial NMR spectra was used to evaluate the propagation of injection fluid inside the shale core.

RESULTS

Except for Fig. 6, all blue curves in Figs. 2 to 8 represent the T_2 distributions of shale samples from Marcellus, Eagle Ford and Mancos formations as they were received. It can be observed that there is a dominant peak below 1 ms in T_2 spectra, regardless of the sample origin. Although conventional understanding indicates that peaks with T_2 less than 3 ms represents clay-bound water, it is a more complicated issue for unconventional shale samples. As Loucks et al. [6] noted, nano-size pores exist in shales in large proportions. The dominant peak below 1 ms from these outcrop samples can be a combination of clay-bound water and water filling inside the nano-size pores. There are also smaller peaks in the T_2 spectra around 20 to 50 ms. They may originate from water inside larger pores or microfractures in the core samples. The average as-received NMR porosities for these core samples are: 1.20% for Eagle Ford, 2.62% for Marcellus and 3.56% for Mancose.

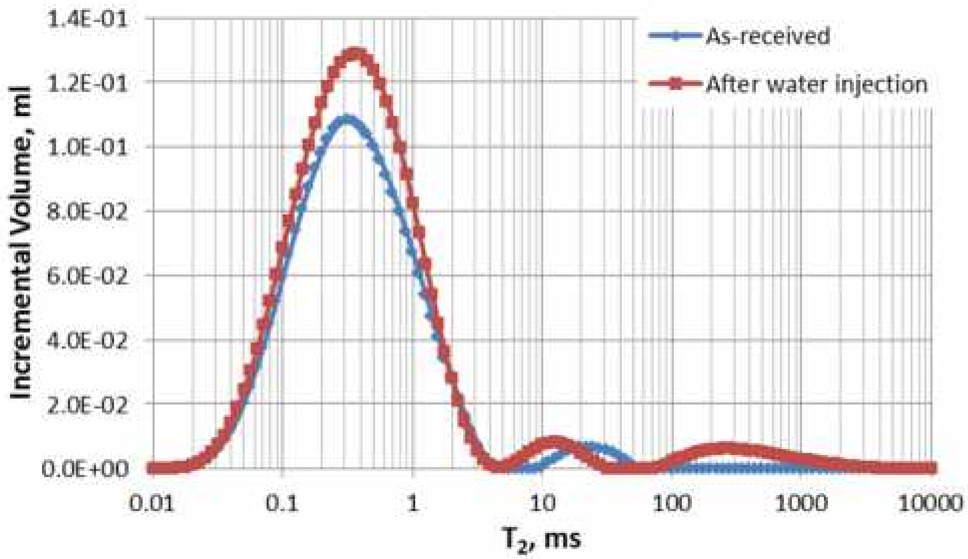

Fig. 2: Incremental NMR fluid volume as a function of T_2 for Marcellus shale core before and after water injection at 500 psi for 10 minutes.

Fig. 2 shows the comparison between the as-received state T_2 distribution and the T_2 curve after water injection for ten minutes for a Marcellus core sample. It can be observed that the amplitude of the prominent peak increases significantly after water injection, although the shape and position of the peak remain unchanged. The accumulative data reveal that the amount of water increase in this region is 0.44 ml, or 18%, compared with the original state. After injection, there is also a slight increase of the small peak centered near 30 ms. However, since the increase (0.01 ml) is within experimental error, the increase should not be over interpreted. A new peak appears around 300 ms, which is considerably faster than the bulk water T_2 of 3 seconds. Therefore, the peak is attributed to water inside the natural or induced microfractures in the core sample.

We injected diesel into another Marcellus core sample with the result shown in Fig. 3. A very similar pattern to that presents in Fig. 2 is observed. A 22% magnitude increase is obtained after the diesel injection for the prominent peak. The new peak around 400 ms records an even larger increase than the new peak shown after water injection. The 400 ms relaxation time here is quite close to that of bulk diesel's 500 ms. Therefore, we consider this new peak as the residue diesel left in the injection tube, rather than inside the core sample. It is also possible that this peak comes from diesel remained in the water-wet fractures, thus having a relaxation time close to the bulk diesel T_2. For comparison, we also superimposed the T_2 measurement of bulk diesel on Figure 3.

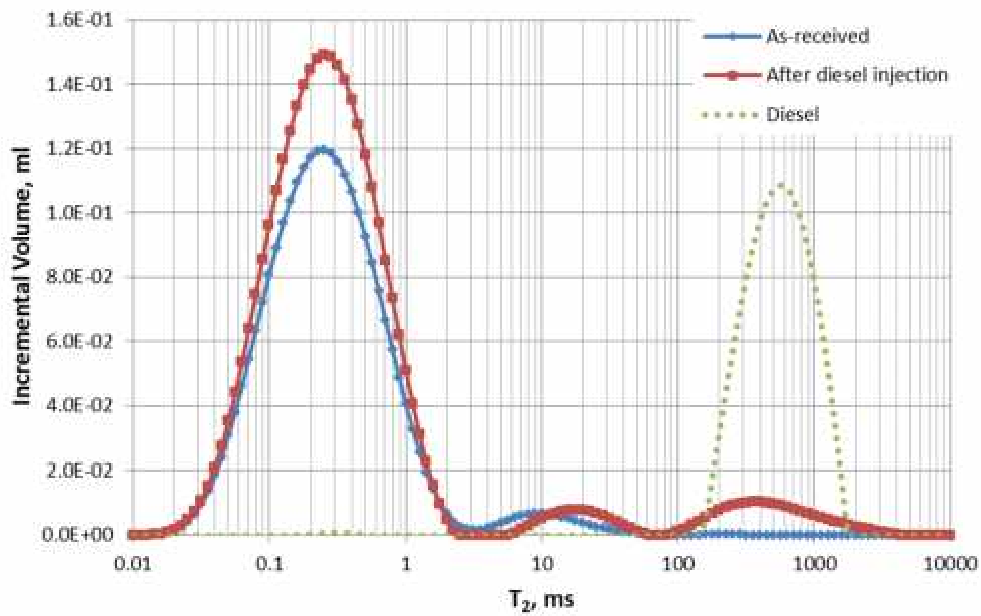

Fig. 3: Incremental NMR fluid volume as a function of T_2 for Marcellus shale core before and after diesel injection at 500 psi for 10 minutes.

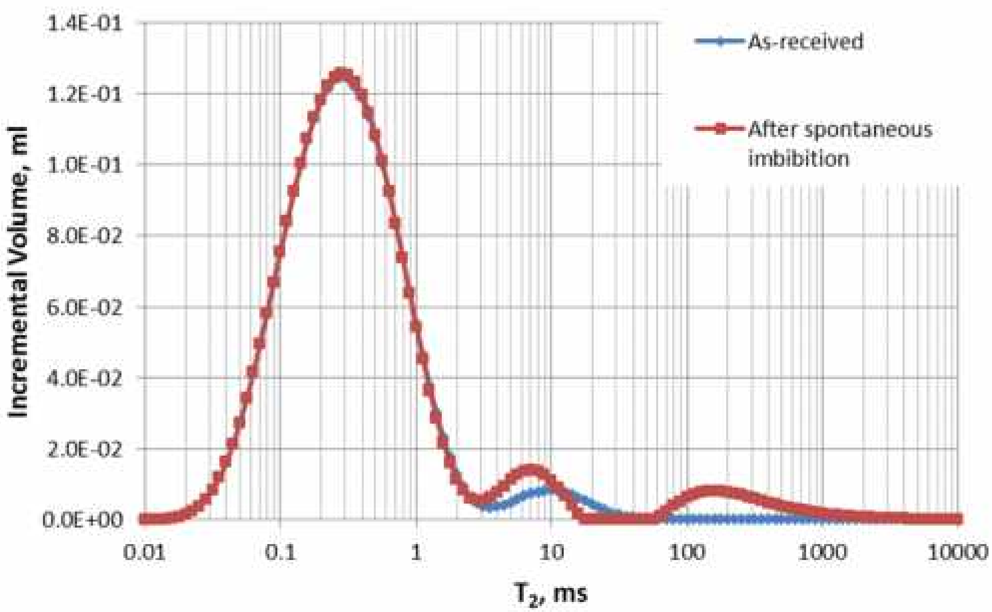

Fig. 4: Comparison of the T_2 spectra for a Marcellus core sample before and after diesel spontaneous imbibition.

The new method with fluid injection takes only ten minutes, and the volume of the fluid inside the core samples increases by about 20% (Figs. 2 and 3). This result can not be achieved in a similar time scale for spontaneous imbibition as demonstrated in Fig. 4. We submerged the Marcellus core sample in diesel for two hours and compared the T_2 spectra before and after the spontaneous imbibition. Although there is a small change in the region around 10 ms, the dominant peak below 1 ms remains unchanged. It is possible that an amplitude increase will be observed in this region if the imbibition time is increased or a higher pressure is applied. However, our method is apparently advantagous in terms of required experimental time.

The method was also applied to Eagle Ford shale samples. As shown in Fig. 5, the as-received core sample has a dominant peak below 1 ms as well. There is also a tail that spans to around 100 ms. After diesel injection, the previous one-peak dominant spectra has been transformed to a bimodal shape. The main peak below 1 ms grows only a small amount. In contrast, a new peak appears between 4 and 500 ms. The volume of fluid increase due to diesel injection is 70% compared to the original state.

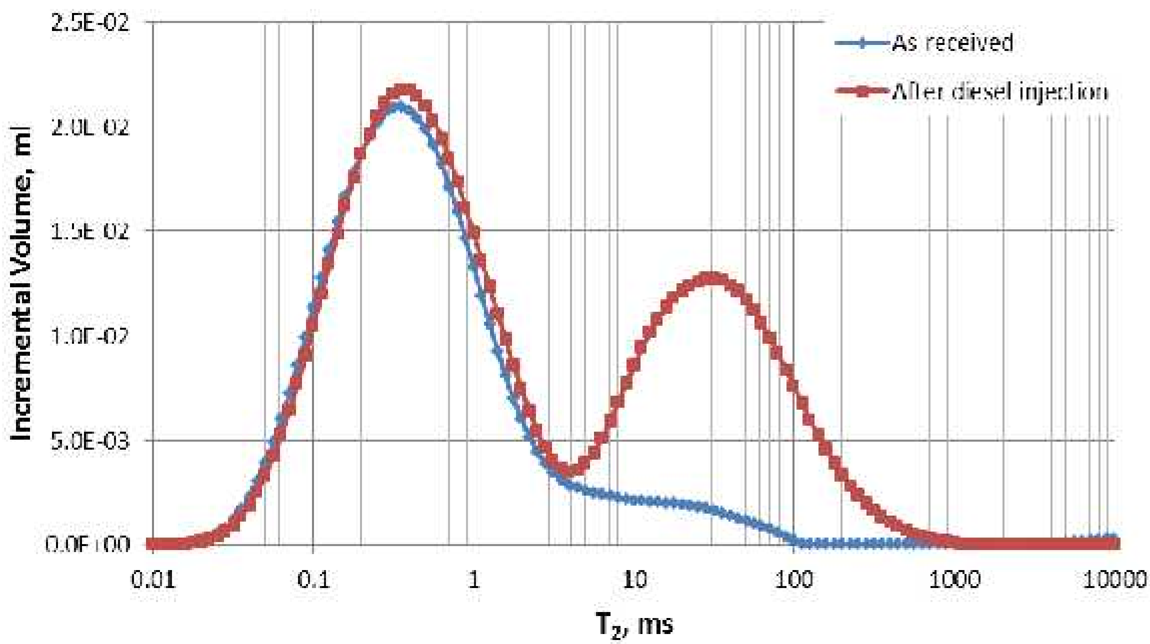

Fig. 5: Incremental NMR fluid volume as a function of T_2 for Eagle Ford shale core before and after 10 minutes' diesel injection at 200 psi.

Another round of fluid injection was conducted with this sample, replacing diesel with water as the injected fluid. The blue curve in Fig. 6 is not exact identical to the red curve in Fig. 5, possibly due to further fluid propergation or diesel evaporation from the microfractures. In Fig. 6, after the water injection, the peak with its center below 1 ms also gains an amplitude increase this time, although the increase is not as much compared with that of the Marcellus sample. The accumulitive value for this peak increases 8% with water injection. Above 5 ms, the spectra becomes complicated. Overall, the fluid volume in this region increases three time more than the increase of the peak below 1 ms. There now seems to be a third peak appearing just around 100 ms, although it is difficult to analyze because it overlaps with another peak. The middle peak also gains amplitude, and it is interesting to see that its center shifts a bit to the left, which is now centered near 10 ms.

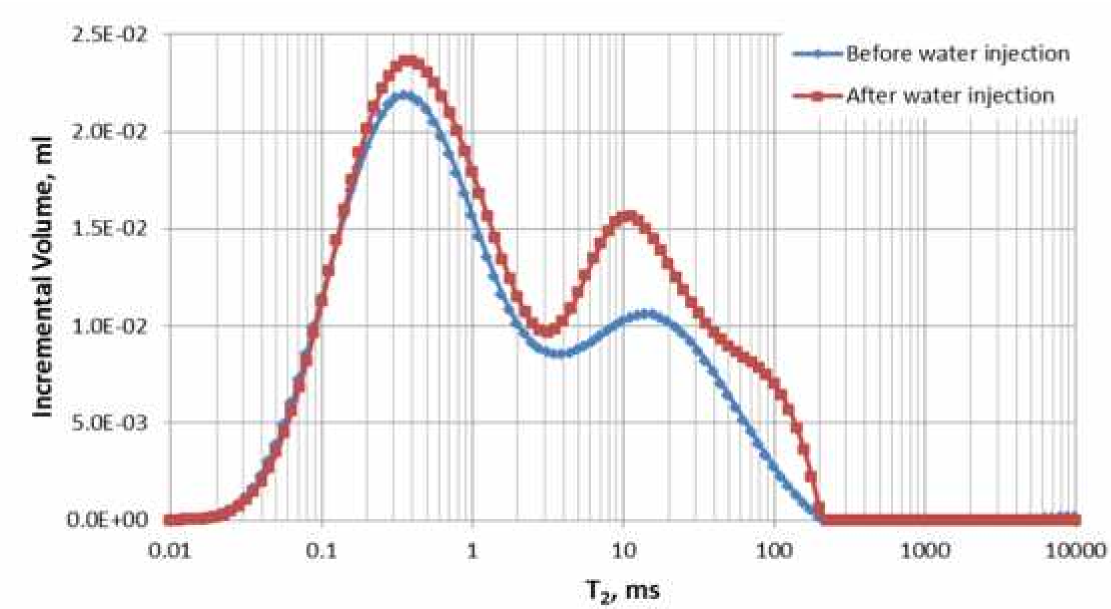

Fig. 6: Incremental NMR fluid volume as a function of T_2 for Eagle Ford shale core before and after 10 minutes' water injection at 200 psi.

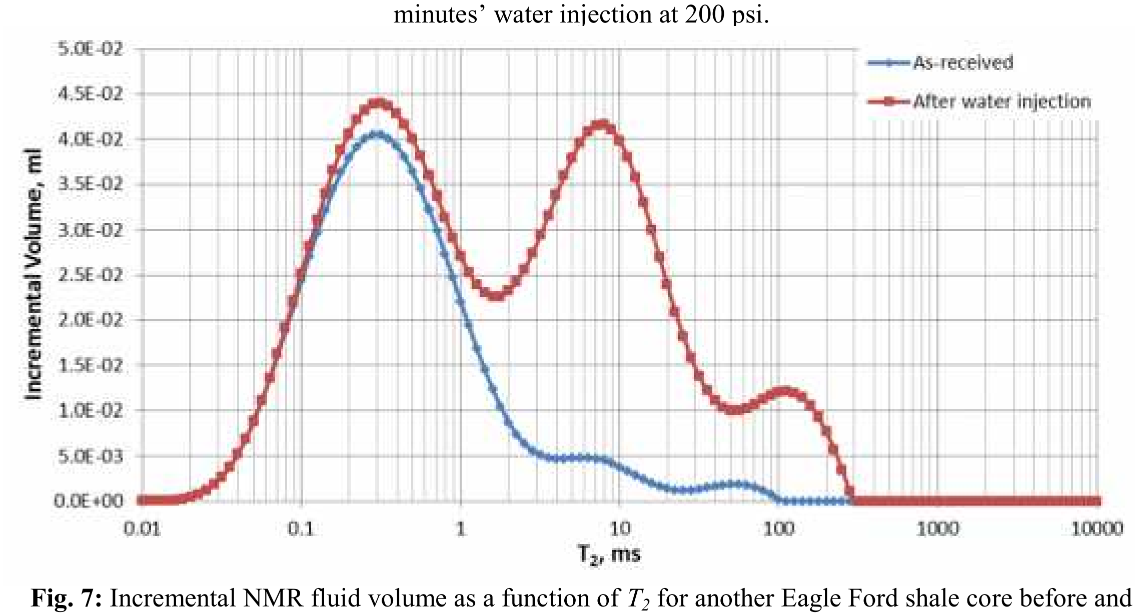

Fig. 7: Incremental NMR fluid volume as a function of T_2 for another Eagle Ford shale core before and after 10 minutes' water injection at 200 psi.

We also conducted the water injection experiment on another fresh Eagle Ford core sample and the result is presented in Fig. 7. For the peak below 1 ms, a similar result is observed to that in Fig. 6 --the peak's amplitude increases only slightly. A peak centered around 100 ms is observed after water injection, and the peak accounts for approximately

16% of the total volume increase across the spectrum. Overall, the water injected into the core sample almost doubled the NMR porosity in this sample, while in Fig. 5 the injection of diesel only increases the NMR porosity by 51%. The peak centered at 10 ms shows an even larger amplitude increase compared to the same peak in Fig. 6. It is evident that the previously injected diesel does have an impact when water is injected into the sample afterwards.

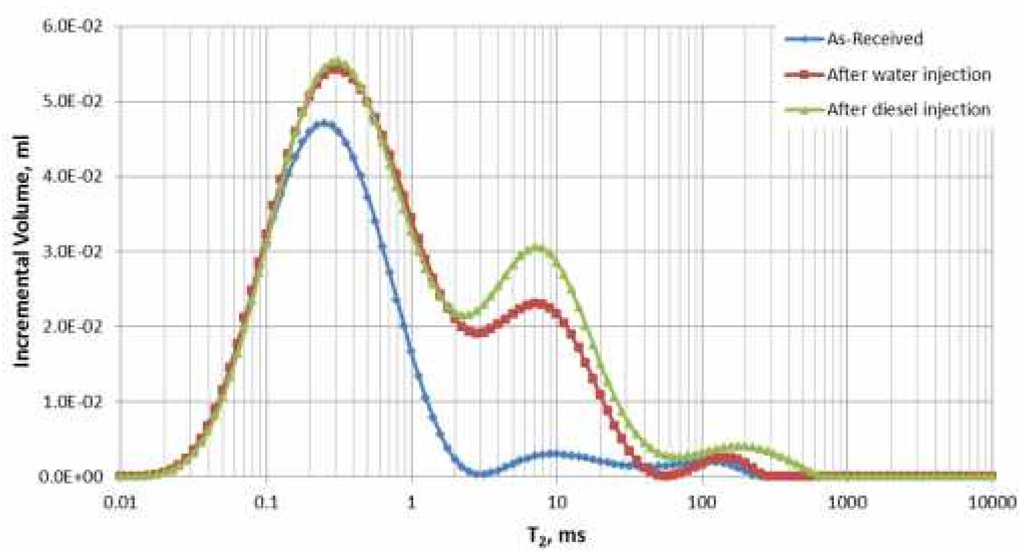

Fig. 8: Incremental NMR fluid volume as a function of T_2 for a Mancos shale core before and after 10 minutes' water and diesel injection at 200 psi.

We also performed the fluid injection experiments with Mancos core samples. The results in Fig. 8 are typical for these experiments. The blue curve is the T_2 distribution for the as-received state. It has a dominant peak below 1 ms and two small peaks centering around 10 ms and 100 ms, respectively. After a water injection for ten minutes, the magnitude of the peaks increase significantly, with the exception of the small peak at 100 ms. The water injection increased the total fluid volume by 71%, and the peak below 1 ms contributed 51% of that increase, while the other peak contributed 49%. The situation is very different for the subsequent diesel injection, after which the dominant peak does not record any change. The small peak above 100 ms seems to become larger, it might be just the contribution of the bulk diesel stayed inside the tube or the remaining diesel inside the water-wet fractures. The major change comes from the peak centered around 10 ms, which increases 30% after diesel injection.

DISCUSSION

After fluid injection, most of the signal increases were observed to be from regions far below the bulk relaxation time of water and diesel. It is logical to conclude that surface relaxation is the dominant relaxation mechanism, indicating the injected fluids have contact with the pore surface inside the shale samples. Following Eq. 4, we can roughly transform the relaxation time to pore size, using the relaxivity value of 4.2 nm/ms estimated by Jiang et al. [9]. With this method, 1ms T_2 represents a 12.6 nm pore radius, while 100 ms means the pore radius is larger than 10 mircometer, which may be considered as a microfracture. It is worth mentioning that the reported relaxivity value is only obtained from a small group of samples and may not be representative, and oil relaxavity value may not be the same as water's. Nonetheless, we used 4.2 nm/ms in our estimation because there is few literature reporting water relaxivity values for shale rocks, and we were unable to find a reported value of oil relaxivity in shales.

The mineralogy data is listed in Table 1, and the volume of fluids injected into the core samples from the three shale formations is summarized in Table 2. Of the three formations, Eagle Ford has the lowest amount of clay, while Marcellus and Moncos shales have about the same amount of clay minerals. However, their response to water injection differs significantly. Particularly, in the fast relaxation region (T_2<5 ms), where clay bound water is located in a T_2 spectrum, the amount of water increase does not correlate with the shale clay content. This is consistent with our argument that for unconventional shale samples, clay-bound water is not the only contributor to the dominant T_2 peak below 1 ms. Rather, water inside small pores will also show up in this region because of their fast relaxation.

Total Organic Content (TOC) may be a good indicator of oil preference for small pores. Among the three shale formations, only Marcellus shale shows a large increase in the fast relaxation regime when diesel is injected. It is reported that Marcellus shale has the largest TOC percentage compared to the Mancos and Eagle Ford [10, 11,12]. It is believed that much of the porosity in shale formations is within the organic matter, nested inside kerogen [6]. With Marcellus' high TOC percentage, it is possible that many of its pores are within the organic content and are oil-wet. Further, the organic pores are usually quite small, mostly in the nanometer range, which translates to a fast relaxation of the NMR signal.

There are several wettability indices available. For example, Sulucamain et al. [3] used the index proposed by Looyestijin [4] to determine shale wettability. Based on our experimental results, we believe that using an index to determine wettability for the whole plug is perhaps not accurate enough. Because the fast relaxation regime (T_2<5 ms) and the region with T_2 between 10 ms and 100 ms respond differently to the injection of water and oil, wettability should be examined separately for pores of different sizes.

For small pores, with radii smaller than 60 nm (T_2<5ms), when water is injected, the NMR signal increases for all the core samples. When oil is injected into the shale samples, only the Marcellus shale samples exhibit an increase in this region, suggesting that the small pores in Marcellus shale are mixed-wet. On the other hand, Mancos and Eagle Ford samples do not exhibit an increase after oil injection, suggesting that the small pores inside these two shales are most likely water-wet. We wish to point out that there may also be some small pores that are not connected with others, rendering them unreachable by the injected fluids.

For larger pores with a radius in the range of several hundred nanometers to micrometers, the Marcellus shale does not exhibit a significant response when water or oil is injected. It is possible that not many pores with such a size exist in these core samples. It is noteworthy that in Fig. 2 we do observe a water peak beyond 100 ms, which means there are possibly some mircrofractures within this sample that is water-wet. For the Eagle Ford and Mancos shale samples, we observe notable magnitude increases when either oil or water is injected. In both cases, the amount of oil or water that stays inside these pores is almost the same, which gives a near zero value if the wettability index is calculated. Therefore, these bigger pores of Mancos and Eagle Ford shale are mixed-wet in terms of wettability.

Table 1: Mineralogy of Outcrop Shale Samples.

	Mancos	Eagle Ford	Marcellus
Quartz %	49	21	38
Illite-smectite %	21	4	21
Kaolinite %	2	5	0
Dolomite %	10	2	5
Calcite %	6	60	29

Table 2: The Amount of Fluids Injected

<table>
<tr><td rowspan="2"></td><td colspan="2">Mancos</td><td colspan="2">Eagle Ford</td><td colspan="2">Marcellus</td></tr>
<tr><td>A</td><td>B</td><td>A</td><td>B</td><td>A</td><td>B</td></tr>
<tr><td>Water injected, ml</td><td>1.29</td><td>1.26</td><td>0.12</td><td>0.91</td><td>0.47</td><td>--</td></tr>
<tr><td>Diesel injected , ml</td><td>--</td><td>1.08</td><td>--</td><td>0.85</td><td>0.58</td><td>--</td></tr>
<tr><td>NMR fluid (as-received) , ml</td><td colspan="2">3.56</td><td colspan="2">1.21</td><td colspan="2">2.64</td></tr>
</table>

A: the T_2 peak centered below 1 ms; B: the T_2 peak around 10 to100 ms.

CONCLUSION

In this paper, we presented results of fluid injection experiments with core samples from three formations: Mancos, Eagle Ford and Marcellus. Water or diesel was injected into the core samples to study their wettability behavior. We conclude that the Marcellus shale samples are mixed-wet in the small pores with a radius smaller than 60 nm. Pores of similar size in Eagle Ford and Mancos shale samples are most likely water-wet. The larger pores in Eagle Ford and Mancos shale samples exhibit mixed-wet wettability.

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