Understanding wettability in unconventional rocks and how it can change over time

Technical Paper

Introduction

In a recent technical paper [1], we described an NMR wettability index (NWI) measurement which we had recently implemented in our software. This measurement was based on the fact that NMR response and hence T_2 distributions [2,3] change as a function of wettability in core plug samples. In order to derive this NWI based on T_2 distributions, the NMR T_2 spectra of 100% brine saturated, 100% oil saturated, bulk oil and bulk brine are needed. These spectra are then mixed to give a predicted T_2 spectrum which is compared (via a least squares fit) to a T_2 spectrum recorded from a sample partially saturated with both water and oil and whose wettability is to be determined. In the previous technical paper, we presented a new method which coupled this T_2 based NWI to spatially resolved T_2 NMR measurements to monitor changes in wettability and saturation along rock core plugs.

This technical paper describes further work we have completed expanding the utility of the NWI measurements on two fronts. Firstly, we have adapted the existing NWI measurement to unconventional samples in order to provide robust wettability measurements for tight rocks. Unconventional samples prove challenging for wettability analysis because of their tight pore structure and their dual pore networks, one associated with organics and the other being the intergranular network. These two networks may have different wetting conditions complicating wettability analysis. Secondly, we have explored the ability of the NWI measurement to track wettability changes in core samples as a function of time. The restoration of wettability in reservoir rock core samples to its original state is highly critical in preliminary core preparation for special core analysis experiments [4,5]. Tracking these changes in wettability can be difficult using Amott or USBM methods. These measurements involve forced imbibition which can be challenging in low permeability unconventional samples. In addition, the Amott or USBM method will alter saturation and wettability conditions in a core sample rendering it useless for further aging studies without cleaning, drying and re-saturation.

For example, to measure the wettability change in a core sample daily using the Amott or USBM methods for 10 days would require 10 identical core plugs, one tested each day. As will be shown in this technical paper, the NWI method allows the wettability to be tracked as a function of time on the same core plug.

Key Findings:

- The NMR wettability index (NWI) is a new method to accurately determine wettability of unconventional rock core samples.
- NWI can be successfully used to non-destructively monitor changes in wettability in real time.

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Experiment:

Two sets of twin unconventional rock core plugs from the same South Texas well, but different units, were used in this wettability study. The physical properties of these samples are summarized in Table 1. For each set of twins (Twins 1: 7-P2/7-P3A and Twins 2: 2-P2/2-P1A), one of the twins was brine saturated (4% NaCl in water) while the other one was decane saturated. See Table 1 to reference which twin was saturated by brine and which was saturated by decane. T_2 NMR spectra were acquired on each sample in these initial states, using a **GeoSpec** 2+/75 NMR instrument [6] and Green Imaging Technologies software [7]. Table 2 summarizes the NMR parameters employed. T_2 spectra for bulk brine and decane were also recorded.

The goal of this experiment was to observe wettability changes in the unconventional samples under study. To achieve changes in wettability, the decane saturated samples were submerged in brine while the brine saturated samples were submerged in decane. Spontaneous imbibition of each fluid/sample combination was monitored over time and T_2 distributions were acquired periodically during the imbibition process. Figure 1 shows water droplets forming on the surface of one of the 100% brine saturated shale samples after imbibition of decane.

Sample	Length (cm)	Diameter (cm)	Rock Type	Original State	Porosity (%) Helium, MICP	LECO TOC (wt%)	XRD Mineralogy (wt%)
2-P2	5.21	2.58	chalk-marl	100% Brine Saturated	4.3, 4.1	0.39	Quartz: 3.8 Feldspar: 2.3 Carbonate: 85 Total clay: 6.6 Pyrite: 1 Marcasite: 0.7
2-P1A	4.59	2.6	chalk-marl	100% Decane Saturated			
7-P2	4.93	2.61	marl	100% Brine Saturated	12.5, 12	4.38	Quartz: 21.1 Feldspar: 3.9 Carbonate: 46.5 Total clay: 23.4 Pyrite: 4.6 Marcasite: 0.6
7-P3A	4.97	2.55	marl	100% Decane Saturated			

Table 1 *– Sample Information.*

Sample	Recycle delay (ms)	Signal to Noise Ratio	Tau (µs)	Number of Echoes	NMR Porosity (p.u.) or Volume (ml)	Time (min)
2-P2	750	200	50	5000	4.7 p.u.	8.5
2-P1A	750	200	50	5000	4.3 p.u.	11.75
7-P2	3000	200	50	20000	13.7 p.u.	1.0
7-P3A	750	200	50	5000	12.8 p.u.	1.5
Bulk Decane	18750	164	50	125000	4.69 ml	9.0
Bulk Brine	22500	236	50	150000	6.38 ml	12.0

Table 2 *– CPMG Parameters.*

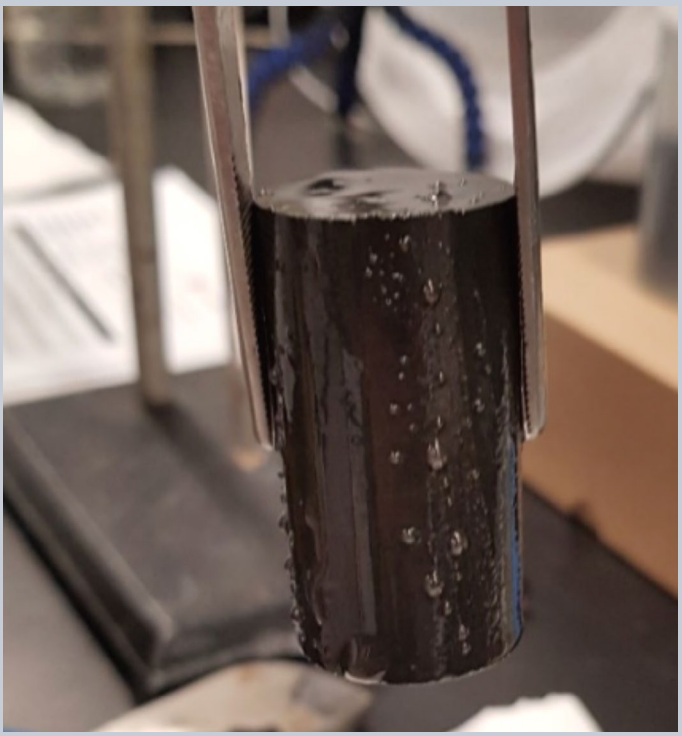

Figure 1: *Water droplets seen on the surface of the sample after it was submerged in decane.*

Results:

1) T_2 Distributions:

Figure 2 shows the T_2 spectra recorded for the first 30-40 days of imbibition for the 2-P1A/2-P2 twin shale samples. The left-hand panel of Figure 3 shows several distributions recorded as twin 2-P1A (originally 100% decane saturated) imbibed brine. The right-hand panel of Figure 3 shows several distributions recorded as twin 2-P2 (originally 100% brine saturated) imbibed decane. At first glance, the T_2 distributions recorded during imbibition seem to be changing more rapidly for sample 2-P1A as compared to sample 2-P2. This was an early indication that these twins are water wet, because the 100% decane saturated sample (2-P1A) is readily imbibing brine while the 100% brine saturated sample (2-P2) is not imbibing decane as quickly.

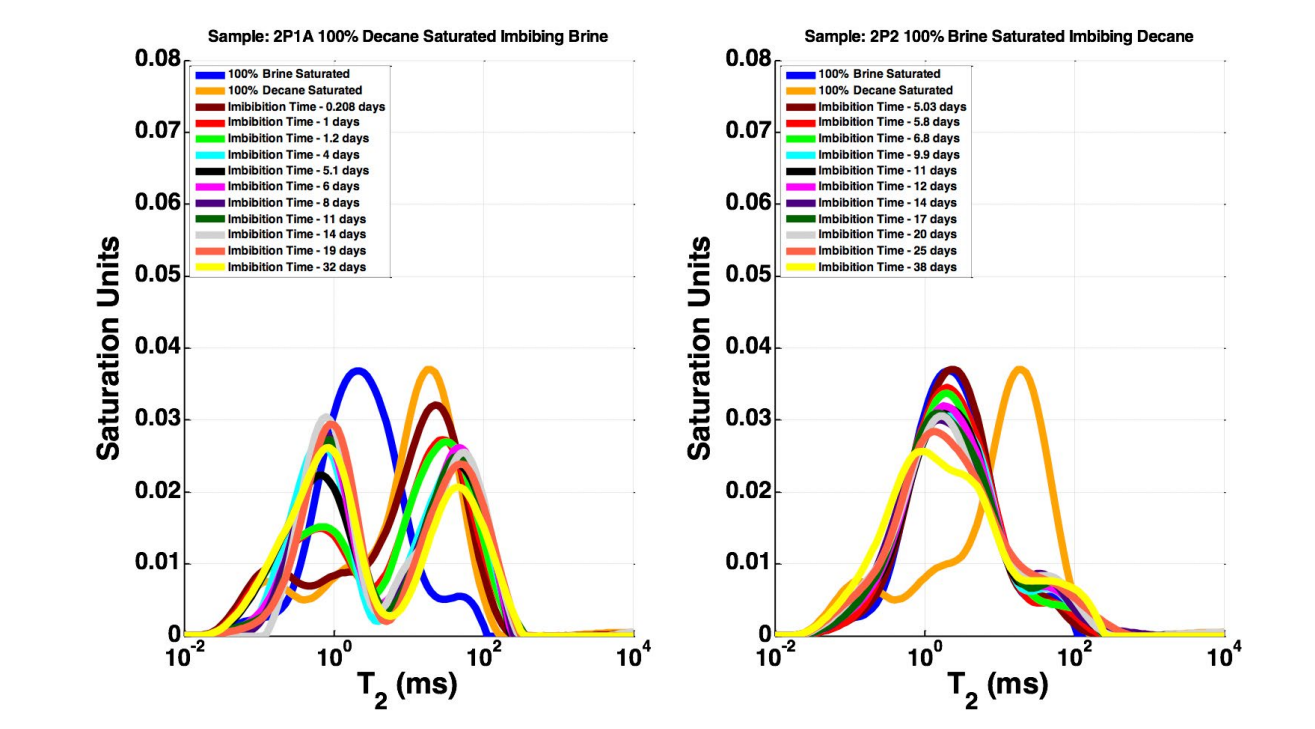

Figure 2: *The T_2 spectra recorded for the 2-P1A/2-P2 twin shale samples. The left-hand panel shows several distributions recorded as twin 2-P1A (originally 100% decane saturated) imbibed brine. The right-hand panel of shows several distributions recorded as twin 2-P2 (originally 100% brine saturated) imbibed decane. Also shown are the 100% brine saturated, 100% decane saturated, bulk brine and bulk decane T_2 distributions. This data was employed to derive the wettability and saturation as a function of imbibition time.*

A similar analysis has also been carried out on twins 7-P3A/7-P2 and Figure 3 shows the T_2 distributions recorded during the first 30-40 days of the imbibition process for each twin. The left-hand panel of Figure 3 shows the distributions recorded as twin 7-P3A (originally 100% decane saturated) imbibed brine. The right-hand panel of Figure 3 shows several distributions recorded as twin 7-P2 (originally 100% brine saturated) imbibed decane. As with the 2P set of twin shale samples, at first glance the T_2 distributions recorded during imbibition gives an indication as to whether these shales are water wet or oil wet. Sample 7-P2 seem to be imbibing decane more rapidly than sample 7-P3A was imbibing brine indicating that the sample is likely oil wet.

2) Wettability Analysis:

The T_2 distributions recorded during the imbibition process for both twins were processed through the wettability fitting routine described in our previous technical paper [1]. Figure 4 shows the results of the wettability analysis for twins 2-P1A and 2-P2. The left-hand panel displays the wettability as a function of imbibition time for both samples, while the right-hand panel shows the water saturation as a function of imbibition time for both samples. Looking at the wettability change for twin 2-P1A (Figure 4 – left panel - blue trace), it is observed that the rock started oil wet but changed to water wet within the first 24 hours of brine imbibition. The NMR wettability index then continued to increase for the next three days until it stabilized around 0.90 at about day five.

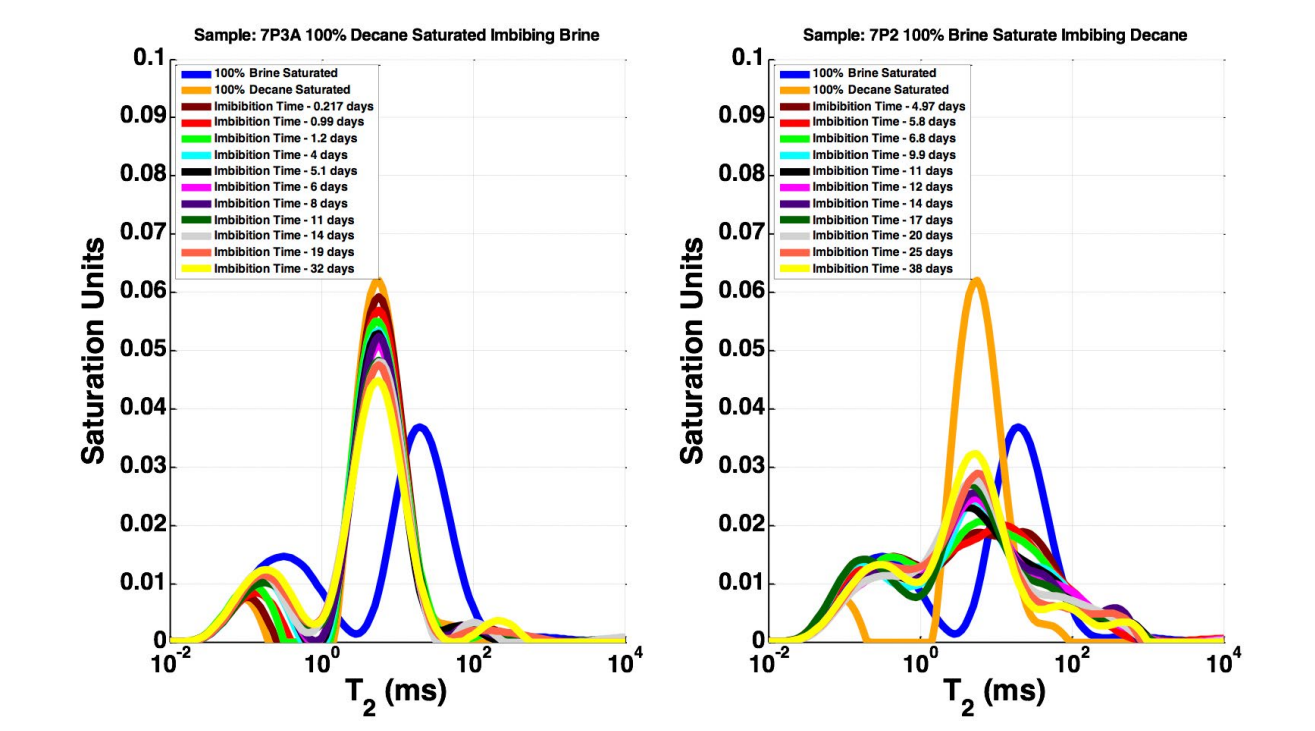

Figure 3: *The T_2 spectra recorded for the 7-P3A/7-P2 twin shale samples. The left-hand panel shows several distributions recorded as twin 7-P3A (originally 100% decane saturated) imbibed brine. The right-hand panel of shows several distributions recorded as twin 7-P2 (originally 100% brine saturated) imbibed decane. Also shown are the 100% brine saturated, 100% decane saturated, bulk brine and bulk decane T_2 distributions. This data was employed to derive the wettability and saturation as a function of imbibition time.*

During the first five days of the experiment, the water saturation for twin 2-P1A (Figure 4 – right panel – blue trace) did not appear as stable. It started around 30% during day one and dropped to approximately 20% by day five. Clearly it is not physically possible for a decane saturated rock which is imbibing brine to have its water saturation go down. Instead the instability in the data during the first the first five days reflects active changes ongoing in the rock during this period. These changes lead to instability in the predictions. This was confirmed by independent D_2O measurements on another 2P twin sample. The D_2O measurements allowed the water saturation to be measured directly via NMR and are plotted as black dots in Figure 4. The D_2O data confirmed the assumption that the sample is undergoing active changes during the first five days and as a result the saturations predicted by the wettability model during this time are not accurate. Since the wettability stabilized at day five, the water saturation has shown a slow increase from approximately 0.2 to 0.3 and the saturations measured by D_2O agree well with the predicted results.

The wettability and saturation levels for sample 2-P2, decane imbibition into brine, did not change as rapidly as for sample 2-P1A. While there were no measurements during the first five days of decane imbibition, neither the wettability (Figure 4 – left panel – red trace) nor the water saturation (Figure 4 – right panel – red trace) changed significantly between days five and thirty-five. The wettability only slowly decreased from 0.96 to 0.83 during this time while the water saturation decreased from 97% to 92% during the same time.

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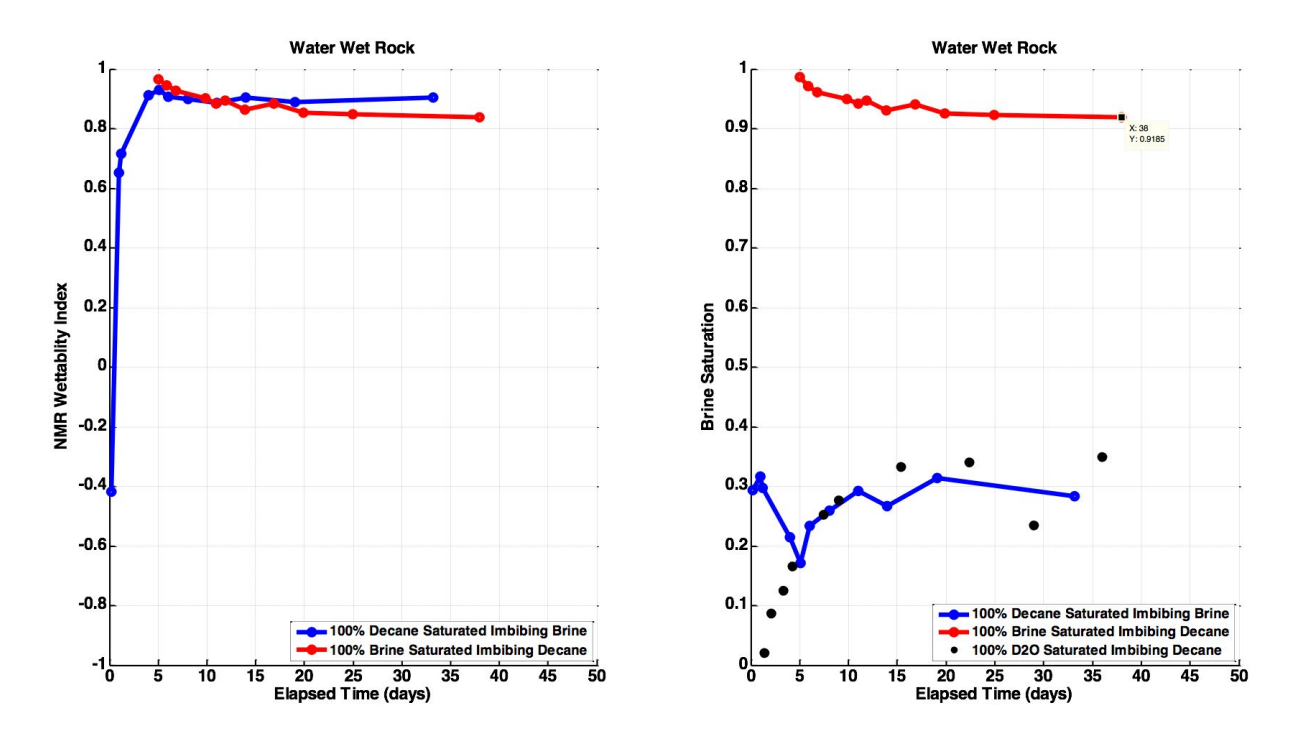

Figure 4: *The results of the wettability analysis for twins 2-P1A and 2-P2 are shown. The left-hand panel shows the wettability as a function of imbibition time for both samples, while the right-hand panel shows the water saturation as a function of imbibition time for both samples. The black dots the water saturations as determined in a separate NMR measurement on a different 2P sample 100% D2O saturated imbibing decane.*

Figure 5 shows the results of the wettability analysis for twins 7-P3A and 7-P2. These samples were tested for over ninety days, considerably longer than the 2P samples. The left-hand panel displays the wettability as a function of imbibition time for both samples, while the right-hand panel shows the water saturation as a function of imbibition time for both samples. The wettability change for twin 7-P3A (Figure 5 – left panel - blue trace) shows that the NWI started around -0.7 and slowly increased to around -0.4 by day thirty of the 100% decane saturated sample imbibing brine. During this same time period, the water saturation for twin 7-P3A (Figure 5 – right panel – blue trace) slowly increased from approximately 15% to around 30% by day thirty. Since day thirty both the wettability and saturations were relatively constant.

The wettability and saturation levels changed more rapidly for sample 7-P2 as compared to sample 7-P3A. Unfortunately, there were no measurements during the first five days of decane imbibition. However, after the fifth day, the wettability (Figure 5 – left panel – red trace) and the water saturation (Figure 5 – right panel – red trace) changed significantly. During the first forty days, the NWI decreased steadily from ~0.05 to -0.30 while the water saturation remained relatively constant (~35%). After day forty, both the wettability and saturation seemed to have stabilized.

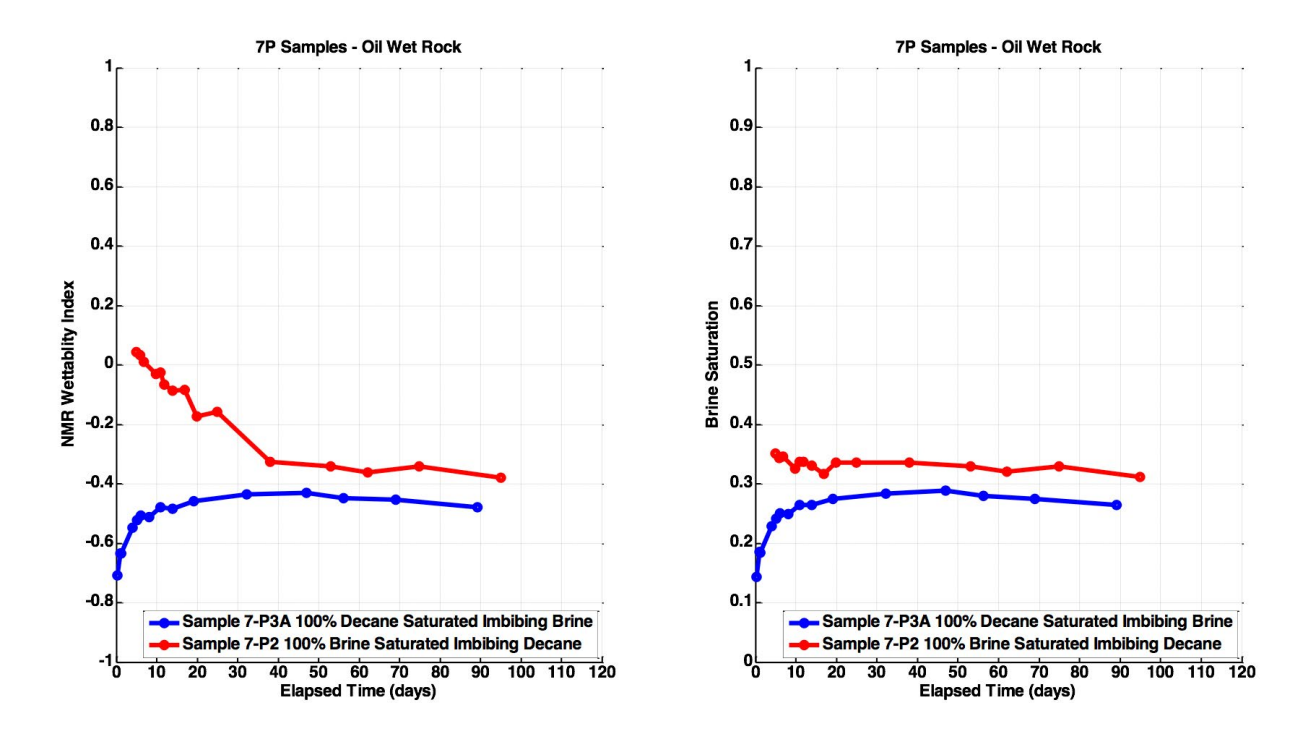

Figure 5: *The results of the wettability analysis for twins 7-P3A and 7-P2 are shown. The left-hand panel shows the wettability as a function of imbibition time for both samples, while the right-hand panel shows the water saturation as a function of imbibition time for both samples.*

Both the 7P and 2P samples display a dynamic wettability index that slowly asymptotes towards equilibrium as imbibition proceeds. Despite significantly lower porosity than sample 7-P3A (see Table 1), sample 2-P1A, a chalk, imbibes water more successfully than sample 7-P3A, an organic-rich marl; correspondingly, the NWI for the chalk sample is very high, > 0.8, indicating strongly water wet. The majority of brine imbibition in the chalk occurred very quickly, within 24 hours, and the chalk did not readily imbibe decane, remaining highly water wet in terms of NWI. Meanwhile, sample 7-P2 imbibed decane only slightly more rapidly than sample 7-P3A imbibed brine, indicating that the sample is slightly oil wet. leaning towards mixed wet; correspondingly, the NWI for these sample is within the bounds of -0.4 to 0.2 for the duration of the experiment.

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Conclusions:

The NWI has been successfully tested on unconventional samples for quantifying changes in sample wettability over time. This is an important result for two reasons. Firstly, it establishes a new method for determining the wettability of unconventional samples. Determining wettability of unconventional samples can be difficult due to their tight pore structure and their dual pore networks, one associated with organics and the other being the intergranular network. Secondly, it has been shown that NWI can be employed to non-destructively monitor changes in wettability in real time (i.e. during a flooding experiment or an aging procedure). This is potentially a powerful new tool in Special Core Analysis (SCAL) because unlike Amott or USBM wettability methods, a single core sample can be employed to monitor wettability change as a function of time. This should lead to greater efficiency in determining how to restore core samples to their original wettabilities in preparation for SCAL experiments.

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