MECHANISMS OF WATER IMBIBITION IN CARBONATE-RICH UNCONVENTIONAL RESERVOIRS

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ABSTRACT

The interaction between water and fine-grained source rock has been a widely-discussed subject since the beginning of the shale revolution. It's well understood in carbonate-rich "shales" that some of the water used during hydraulic stimulation leaks-off or imbibes into the formation never to be recovered during flow-back or production. There is no consensus on the mechanisms for water uptake into shale, especially given the large volumes and rate at which the water is lost into the formation. A mechanism associated with capillary forces that result from the very small pore sizes is countered by arguments that the driving force is set up by osmotic pressures generated by differences in water's chemical. A set of Imbibition experiments that examined the effect of water activity were performed on several clay-rich carbonate (marls) core plugs. Drainage and imbibition experiments were done at room temperature in standard Amott cells as several water compositions were allowed to displace oil in a set of equivalent core plugs. Lithium chloride (LiCl) was chosen to make these different salinity brines because it allowed for the identification of any formation water that might be displaced during imbibition along with other geochemical changes. Cation analysis of the pre- and post-imbibition brines was acquired by ICP. Analysis of the post-imbibition brines found evidence of carbonate and silicate dissolution in the samples with the extent of dissolution decreasing with increased LiCl concentrations. Volumetric results for oil and brine from the imbibition tests found that the impact of initial water activity was statistically insignificant suggesting osmosis played a very limited role in water uptake in these samples. These results suggested that in a carbonate-rich unconventional reservoir rock that large differences in water activity were insufficient to create suitable osmotic pressure gradients that would drive water imbibition. In this case the presence of strong capillary forces associated with small pores provide a reasonable mechanism for water uptake.

INTRODUCTION

The injection of large volumes of water into unconventional reservoirs is a critical step in producing hydrocarbons from low-porosity, very low-permeability rock. The injected water generates a network of fractures in the near-wellbore region that aids in production and helps to overcome the nano-darcy permeability of the matrix. In some of these tight-rock reservoirs much of the injected water does not return to the well upon pressure draw

down, suggesting that it trapped in the low-permeability matrix [1,2]. Imbibition of this water into the matrix is the most common explanation for the loss of flow back water, though the mechanisms associated with this process remain unclear. The list of possible mechanisms includes the standard capillary action, osmotic flow and water sorption by clay minerals (3-5). Many of the laboratory studies focus on water and oil imbibition in gas shale where the liquid displaces gas at very low residual liquid saturations. In these studies, the implication is that the imbibed water lost during hydraulic fracturing can become a means for enhanced oil recovery [6]. Recovery efficiency in these studies can exceed 40% Original Oil in Place (OOIP).

The challenges in designing an experiment that focuses on water imbibition as an oil-displacement mechanism center around the petrophysical properties of these rocks. The low porosity and low permeability result in measurements that require more time and have less sensitivity because of errors in volume measurements. Uncertainty with initial water composition and the inability to remove residual liquids add to the difficulty. This study attempts to resolve some of these issues by relying on NMR methods to monitor fluid volume changes and a tailored water chemistry that allows for a clearer understanding of potential mixing of formation and injected waters.

SAMPLES AND METHODS

A set of core plugs from a carbonate mineral-rich unconventional reservoir were selected for the imbibition tests. The samples were selected from a common lithology defined by a mineralogy dominated by calcite with 10-20 wt percent clay minerals. The samples also included organic material that was 5 to 10% of the total volume.

The samples were standard 2.54 cm diameter core plugs, 3 to 4 cm in length. The liquid saturations of the "as-received" plugs were approximately half of the total volume, the remaining liquids were lost during the coring and transportation operations. A liquid filled saturation was determined by NMR techniques. The gas-filled pore volume was measured with a Helium porosimeter, and this value was combined with the NMR-based liquid-filled volume to create a sum-of-fluids total pore volume. The gas-filled pore volume was then filled with light mineral oil (n-Decane) under 2500 psi for several days. The saturated sample was then re-measured in the NMR spectrometer for a total liquid-filled pore volume that was compared with the sum-of-fluids pore volume. Porosity of these samples ranged from 0.10 to 0.13 with an average pore size of 0.3 microns. Permeability to oil for these samples was in the 50 to 500 nD range, with most samples at the high end.

The imbibition tests were set up in standard glass imbibition cells with the graduated tube oriented either up or down depending on whether imbibing water or oil. Four different salinities based on total dissolved solids were prepared using LiCl as the salt. The idea behind the use of a lithium salt was to monitor the water chemistry after the test and any measured cations would result from either exchange with the residual formation water found in the samples or from dissolution of the matrix. The salinities ranged from 100 to 100,000 ppm of LiCl. Oil production was monitored throughout the test over a period of

10 days, with more observations collected in the first few hours. After the test the samples were re-measured with NMR and mass balance to determine changes in saturation. Aliquots of water from each test cell were collected for chemical analysis (ICP) and pH measurements.

The samples were dried after the water imbibition tests with a NMR measurement to determine any residual fluid. The samples were then re-saturated with one of the different LiCl brines, followed by another NMR T_2 measurement. The water-saturated samples were then reloaded into the imbibition cells that were filled with decane. The cells were inverted, the collection column was located on the bottom, to collect any produced water. A final NMR measurement was acquired to compare with observed water production and weight changes.

RESULTS

The initial water saturations of these samples were established by flushing decane through the plugs in a steady-state flow apparatus for a period of several weeks, sufficient time to move several pore volumes of liquid through the samples. The liquid-filled pore volumes of these samples ranged from 3.0 to 5.0 cm^3. NMR relaxation time measurements at this state defined the initial water saturations between 0.08 and 0.30 for most with a value of 0.39 in an outlier low porosity sample.

The water imbibition tests required 10 days for measurable oil production to stabilize. Many of the samples had an initial production of 0.1 to 0.2 cm^3 of oil before the first sample point at 90 minutes after start (Figure 1). After the initial surge of oil collected in the tube, the rates of oil production were similar for the different imbibing water concentrations. The erratic staircase nature of the imbibition curves resulted from the episodic observations and the resolution of the collection tube, approximately 0.05 cm^3. The produced oil represented 6-12% of original oil in place (OOIP) in these samples, though the uncertainty associated with estimates was high.

NMR T_2 measured post-water imbibition showed distinctive changes in the intensity of the fast and slow relaxation components (Figure 2). The fast component increased in intensity and shifted towards slower times in agreement with the idea of a water-wet pore system accepting water. The slow component generally decreased in intensity following the loss of oil. The difference in the slow component intensity between post- and pre-imbibition measurements corresponded to the amount of oil collected in the imbibition cell (Figure 3).

NMR interpretation was based on assumption that these samples were predominately water-wet such that water filled the smaller pores and oil fills the larger pores. This was manifested in bi-modal relaxation time distributions where the fast component corresponded to the water phase and the slower component to the oil (Figure 2). Numerous displacement tests on samples from this carbonate-rich lithology suggested that this was a

valid interpretation, but exceptions abound. There was a pore volume component in the organic matter as visualized with SEM images. These pores fall in the less than 100 nm diameter range, though gas adsorption measurements indicate that volumetrically these organic matter pores are 10-20% of the total pore volume. Most of the pore volume is associated with the mineral matrix, with pores in the 50 to 1000 nm range.

While the samples were not cleaned in a conventional sense, they were dried after the water imbibition test and then re-saturated with the different salinity brines. The dried samples (150°C for several days) have a small amount of detectable liquids, approximately 10% of the original 3.0 to 5.0 cm^3. The brine-saturated samples also have a bimodal distribution of relaxation times, with most of the incremental volume associated with the slower relaxation times (Figure 4). The intensity of the fast component was less than that from the pre-imbibition stage, which suggested that the model of having only water associated with the fast component was overly simplified. The pore system of these samples likely included two sizes or types of pores.

The oil imbibition tests were allowed to run for 12 days. The amount of collected water ranged from 0.05 to 1.2 cm^3, roughly 1 to 50% of the original water in place (OWIP). There was no obvious connection with the concentration of the water, and since the pore systems of the samples were selected because of their similarity there was no obvious explanation. The NMR T_2 distribution were less illuminating in tracking the changes between pre- and post-oil imbibition samples that with the water imbibition. The changes in sample weight, however, did provide a useful correlation with the amounts of water production (Figure 5). The positive correlation, however, was not sufficient in this case since the volume of produced water is twice what would be expected from the changes in mass, even after correcting for the density of the decane. The non-quantitative nature of the oil imbibition was troubling with no obvious explanation or understanding of the phenomenon. It was suggested by a reviewer that the harsh drying conditions may have damaged the pore system, especially the smaller pores, so that subsequent brine saturation did not restore all of the original pore volume in the allotted time. Whatever the cause for the poor mass balance in this test, this does highlight the need to reconsider many of the sample preparation protocols for fine-grain, organic-rich reservoir rocks.

Analysis of the different salinity brines defined the purity of the LiCl. Since there was 0.2 mg of Na, 0.002 mg of Ca and 0 mg of K per gram of Li in the salt only the 100K ppm brine had measureable amounts of these other cations. The concentration of these cations defined the baseline for the analyses of the brines used in the imbibition tests (Table 1).

The Li content in the post-imbibition brines was the same as the initial brine composition, indicating that Li was neither extracted or added to the rock. The extracted brine compositions were dominated by the presence of excess Ca, Na and Si. The maximum Si concentration in the extracted brines was 7 mg/l, near the solubility of Si at room temperature. Very little Al was detected in the post-imbibition brines, < 0.3 mg/l with no obvious trend associated with the different salinities. The Si:Al ratio suggests that the

soluble Si was associated with the dissolution of quartz phases rather than feldspars or clay minerals, though at these low concentrations it is possible that some of the Al was precipitated in a new alumino-silicate phase [7].

The pH of the initial brines varied from 7.0 to 5.3 with the lower salinity mixtures having the higher pH values. After the imbibition tests the pH of the extracted water was 1 to 2.5 pH units higher (Table 2)

There were two sources of cations in the post-imbibition brines, those produced by the dissolution of minerals and those extracted or exchanged with the initial formation brine that remained in the core plugs. The relationship between Ca and pH indicated a dissolution mechanism with the increased pH in the extracted brine relative to the initial brine composition (Figure 6). The high Na concentrations in the post-imbibition brines represents exchange with the residual formation water found in these samples. There was no correspondence between Na concentration in the post-imbibition water and initial composition. Since there is little evidence of dissolution of Na-bearing phases, (e.g. feldspar) it was likely that the Na came from the residual fluids or precipitated salts. Higher Na concentrations were detected in the lower salinity imbibition brines that suggest chemical potential as a driving force for the movement of Na into the post imbibition brine.

The absence of a correlation between brine chemistry and produced oil volume from water imbibition discounted the osmotic pressure model for imbibition. The lack of correlation between produced oil volume and clay mineral content in these samples discounted the water adsorption model on clay mineral surfaces. The low clay mineral content in these samples may be misleading since the sub-micron particle sizes are all capable of adsorbing some water. The chemical results of the post-imbibition brine indicated some carbonate mineral dissolution, that may have enhanced pore throat sizes and improved capillary-driven processes.

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Table 1. Composition of initial brines

Brine Salinity (mg/L)	Li (mg/L)	Na (mg/L)	Ca (mg/L)	pH
100	15.6	<0.5	<0.01	7.05
2000	357	<0.5	<0.01	6.72
20,000	3649	<0.5	0.19	5.95
100,000	19330	37.5	1.04	5.29

Table 2. Composition of post-imbibition waters

Samples/ Salinity	pH post Imbibition	delta pH	Ca (mg/L)	Na (mg/L)
100	8.6	1.6	4.1	118.6
2000	7.9	1.2	22.5	99.4
20000	7.0	1.1	73.4	82.7
100000	7.8	2.5	37.8	38.7

FIGURES
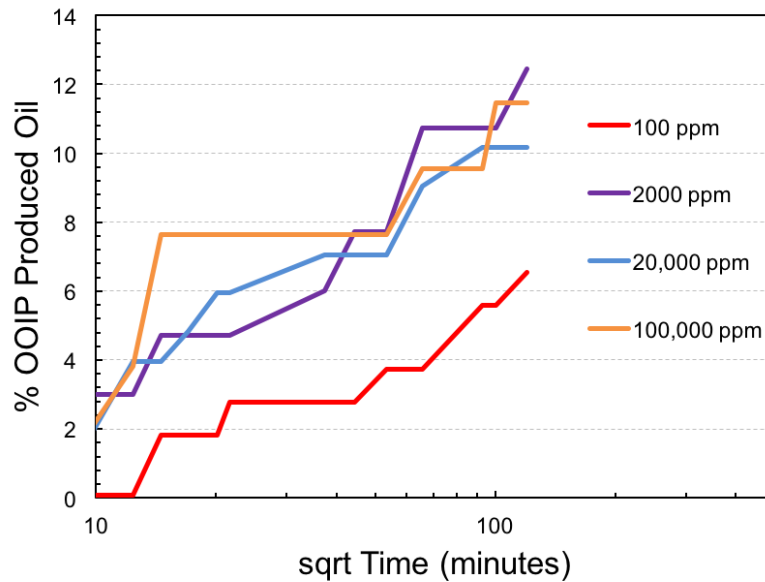
Figure 1. Averaged oil production rate for water imbibition test for the different water concentrations. Produced oil volume was converted to %OOIP using NMR-based estimates of initial water saturation and total pore volume.
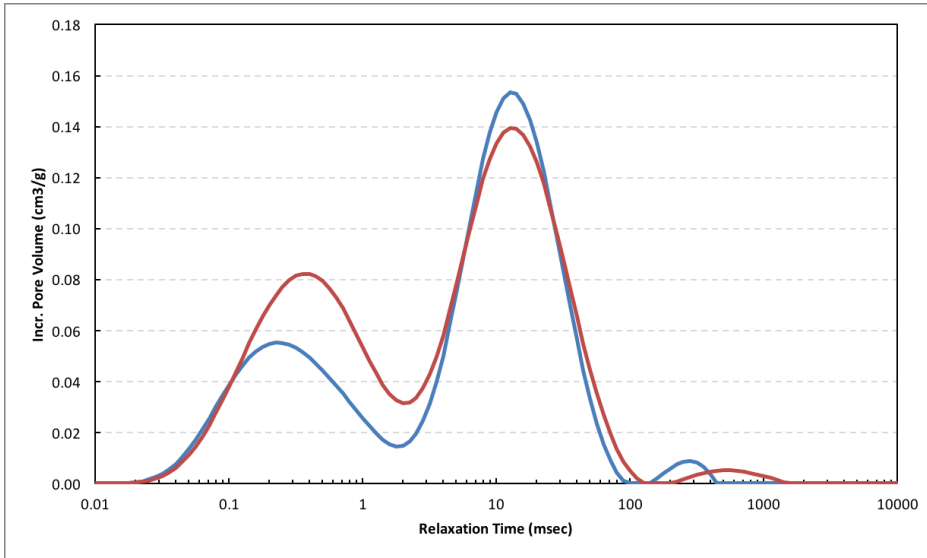

Figure 2. NMR T2 distributions of Pre (blue) and Post (red) water imbibition. The addition of water to the sample is shown by an increase in intensity of the fast component and concomitant decrease in the slower component.
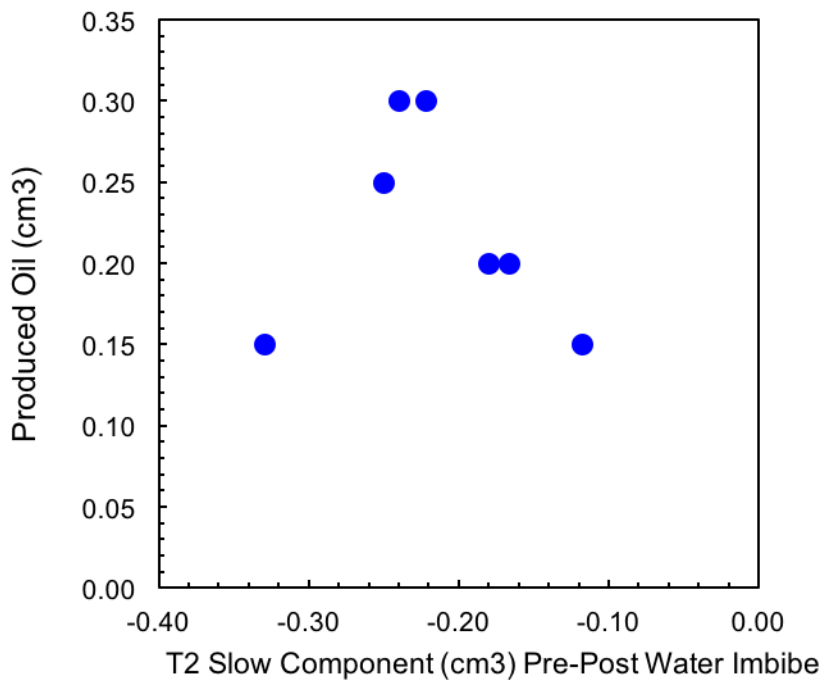
Figure 3. Produced oil volume from water imbibition test compared to the loss of intensity of the T2 distribution slow component after imbibition. There was one outlier from a -1:1 relationship that had a greater change in the NMR intensity than measured in the imbibition cell.
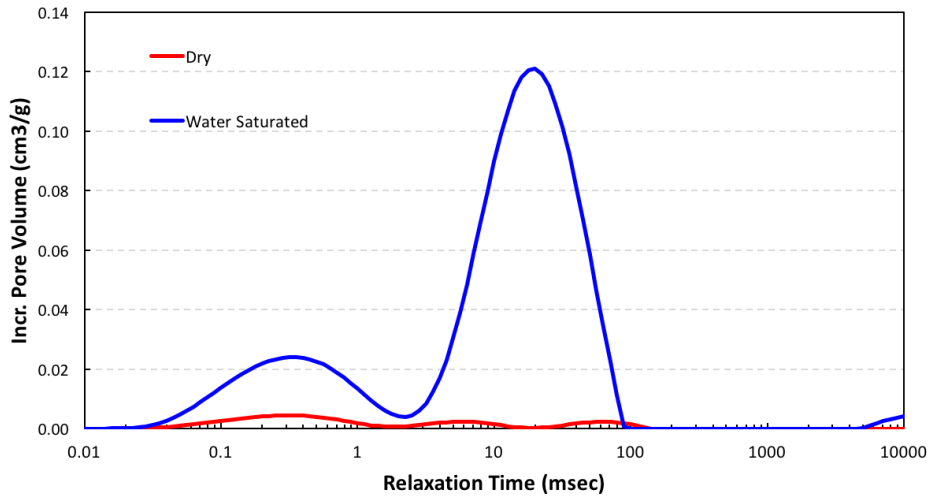

Figure 4. NMR T2 distribution of the dried sample (red) and after saturation with a brine. The dried sample retains a small fraction of liquid. 0.1 to 0.2 cm3). The bimodal distribution of the saturation sample indicates two distinct pore regimes.
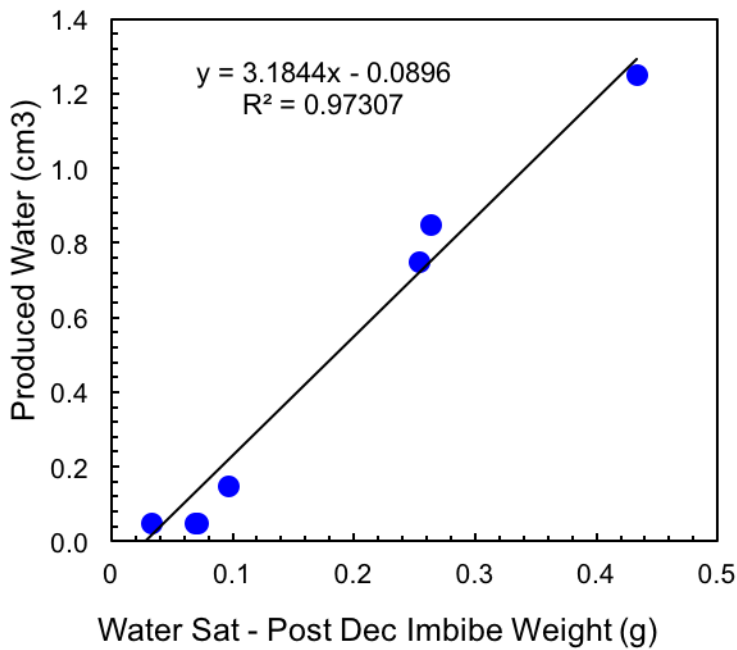
Figure 5. Correlation between the volume of produced water from oil imbibition test and the change in sample weight. While the correlation is positive, the mass balance is off significantly.
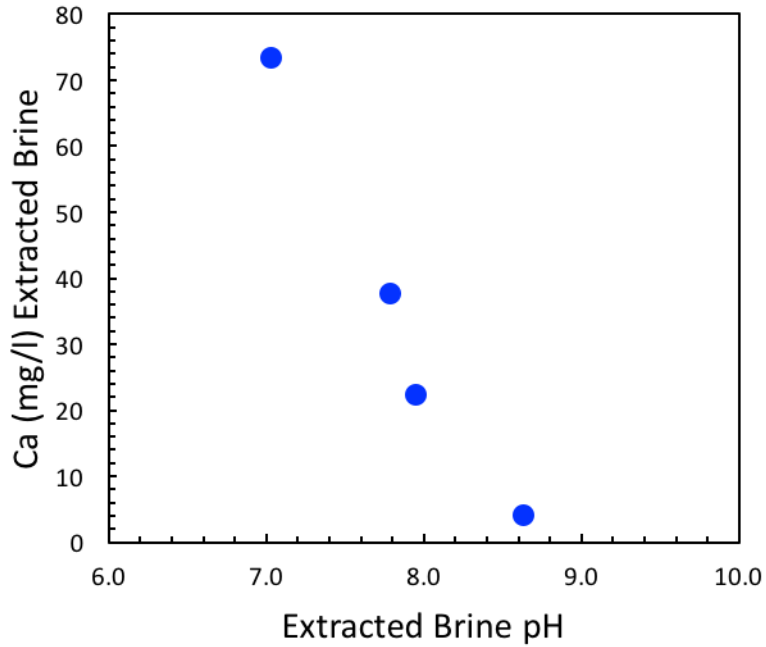

Figure 6. Changes in water chemistry after the water imbibition test. More Ca detected in solution generated by the dissolution of carbonate in the matrix test matches the lower pH.