Laboratory Measurement of Total Porosity and Fluid Saturations for Unconventional Tight Rocks: Methodologies, Challenges, and Comparison

Min Cheng[1],*, Rayvan Watson[1], Alberto Latuff[1], Aaron Rodriguez[2], Peter Kaufman[2], Joshua Miller[2], Rafael A. Mendoza[1], Elizabeth Krukowski[1], and *Robert Cole[1]*

[1]Stratum Reservoir, 5200 North Sam Houston Parkway West Suite 500, Houston, Texas 77086, USA
[2]Hess Corporation Exploration & Production, 1501 McKinney St, Houston, TX 77010, USA

Abstract. The core to log calibration is critical in building petrophysical models for formation evaluation. Despite much research and progress in the past decades, the laboratory characterization of unconventional tight rocks is still challenging. The total porosity and fluid saturations obtained by different core analysis methods (Crushed Rock Analysis - CRA or Gas Research Institute - GRI / Retort / Nuclear Magnetic Resonance- NMR) may vary even after the best practices have been applied in the measurement. This is due to the nature of the tests and assumptions / uncertainties associated with these techniques. Operators can better evaluate the core data and select the more efficient testing methods while being cost effective when the differences in applications and limitations of these techniques are understood. This paper will discuss the methodologies and uncertainties of several common laboratory techniques (CRA/Retort/NMR) for measuring total porosity and fluid saturations for unconventional tight rocks. This will be accomplished through the result review of an integrated study conducted on core samples from the Bakken petroleum system, including Upper and Lower Bakken Shale, Middle Bakken, and Three Forks formations. Results will be divided into two groups: Shale and non-Shale. Implications for data variances in fluid types, volumetrics, and mobility among these techniques will be reviewed. Comparisons focused on differences in as received versus extracted state analyses are also addressed. Other geochemical and mineralogical analyses such as Total Organic Carbon (TOC), X-ray Diffraction (XRD), and rock characterization using Mercury Injection Capillary Pressure (MICP) are adopted to aid in data interpretation. In addition to low porosity and low permeability, high TOC and high clay content especially for the shale group, the ultra-high salinity of Bakken formation water also poses challenges to the measurement and data processing. Results highlight the in-situ fluid saturation variations that may or may not be reproducible in the laboratory environment; Applying integrated workflows can help assure data quality and improve data accuracy.

1 Introduction

The complexities and challenges in characterizing unconventional tight rocks have been recognized over time in the past decades, and the associated laboratory methodologies also evolved through time. Besides small pore sizes, low porosity, and extremely low permeability, the organic matter (OM) rich unconventional tight rocks often possess complicated fluid and pore systems. A volumetric model shown in Fig. 1 illustrates various components in organic rich mudstone samples [1]:

1) The matrix includes minerals and immovable organic matter (kerogen/pyrobitumen which are insoluble in organic solvents such as toluene or chloroform; and bitumen which is soluble in organic solvents).

2) The pore space includes air, free water, residual oil post coring as some oil is already lost due to expansion when pulling the core out of the hole, and bound water (capillary bound and clay bound water).

Using traditional Routine Core Analysis (RCA) methodology on intact core plugs could underestimate the total porosity and fluid saturations for unconventional tight rocks due to incomplete penetration into the pore network by organic solvents (for Dean-Stark and core cleaning) and helium (for grain volume measurement). The pioneered Gas Research Institute (GRI) method [2, 3] was developed by crushing the rock samples to increase the surface area to volume ratio. GRI used toluene only since it was developed for shale gas reservoirs. For shale oil reservoirs, especially for systems with high salinity formation brine, additional cleaning cycles involving other organic solvents such as chloroform and methanol were required to remove the

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residual oil and salt, resulting in Crushed Rock Analysis (CRA). For quite a long time CRA became a routine measurement for shale rock properties especially total porosity and fluid saturations. On the other hand, it was reported that CRA could overestimate the total porosity and the oil saturation for organic rich samples [1, 4-6] because bitumen, while immobile during production, was removed by organic solvent extraction.
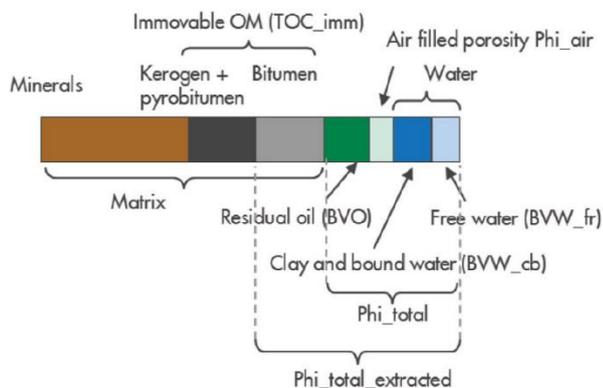

Fig. 1. Volumetric composition of organic-rich mudstone core samples [1].

Retort, a thermal extraction or distillation process, was studied as an alternative method for CRA [1, 6-12]. Crushed core samples were heated to different temperatures, the released water and oil were vaporized, condensed, and then collected for volumetric and gravimetric measurement. In clay rich shales or mudstones, the water components include (1) free pore water – which would flow under normal reservoir producing conditions; (2) capillary bound water – water held by capillary forces in very small matrix pores; (3) clay bound water – water within the clay lattice or near the surface within the electrical double layer; (4) structural water or hydroxyl groups (-OH) in clay minerals, counted as a part of the matrix mineral. Both CRA and retort aim to recover free water and bound water, but CRA can't differentiate these two. An advantage of retort is to separate the free and bound water in core samples by applying temperature cutoffs. Handwerger *et al.* [7] conducted retort and XRD on several clay standards (illite, chlorite, kaolinite and montmorillonite – a subclass of smectite) at three temperature steps (250°F / 121°C, 600°F / 316°C, 1300°F / 704°C). The first temperature cutoff at 250°F was chosen to separate the free pore water and bound water (capillary and clay bound water). At 250°F, very little water was recovered from clay standards except for smectite. The interlayer water molecules in smectite would be released with free water at lower temperatures, so samples with high smectite content are not suitable for free and bound water differentiation using retort. The second temperature cutoff 600°F was used to separate bound water from structural water. These temperature cutoffs are not definitive and may vary slightly in different studies. For example, a thermal decomposition study of illite reported that illite first showed water loss at 110 to 140 °C [13]; 105°C was selected as the first temperature cutoff for free and bound water separation in [6]. It is more important to apply consistent temperature cutoffs on all the samples throughout a study.

No organic solvents are used in retort tests, so bitumen remains intact. By limiting the maximum retort temperature to 300°C [1, 6, 11, 12], the thermal cracking of kerogen or bitumen can be avoided to minimize the chance of generating additional hydrocarbons. Because 300°C retort will mainly recover crude oil components which have a boiling point lower than 300°C, the retort oil may not be a true representative of the oil in-situ nor the produced crude oil at the field. Gas chromatograms of the 300°C retort recovered oil and the produced crude oil showed that the retort oil had a more limited or narrower distributions of n-alkanes, and the API gravity was also higher than the produced crude oil [14]. The non-volatile, high molecular weight petroleum components or distillation residue will still be retained in the core samples post 300°C retort, along with salts.

A conventional retort apparatus, referred as open retort, is open to atmosphere at the connection point of the fluid receiver (usually a graduated glass tube) during the whole retort process. It has been reported that the open retort setup caused lower fluid collection efficiency due to fluid loss to air, and a closed retort setup was designed with the fluid receiver connected to the sample chamber hermetically [1]. It was found that the open retort collected 8-10% less water than the closed retort [1]. Similar results were reported in other studies [11, 12].

Besides closed retort, the evolution of unconventional tight core analysis also embraces the transition to better characterize fluid volumetrics, types, and mobility with Nuclear Magnetic Resonance (NMR). NMR has been used extensively over the past decades in the downhole and laboratory environments. NMR analyzes pore networks and fluids by observing the relaxation rate and quantity of the hydrogen nuclei present in the saturating fluids of the porous formation. The interaction of the fluid with the pore surfaces will cause a quickening of the signal decay and consequently a decrease in the T_2 or T_1 relaxation time from its bulk value will occur. In smaller pores, there is a larger surface area to volume ratio so that the fluid interacts frequently with the pore walls, leading to shorter relaxation times. In larger pores, there is a smaller surface area to volume ratio so that the fluid interacts less with the pore walls, leading to longer relaxation times [15]. Numerous new developments and advancements in NMR have been made in the last decade [16, 17]. Applying short echo spacing times (*Te*) enables acquisition of fast decaying $T2$ signals from kerogen, bitumen, structural water, and clay bound water in unconventional source rocks; The two-dimensional (2D) *T1T2* mapping plays a critical role in identifying the physical properties of different components, and quantity water and hydrocarbons in different pore spaces and in different forms [17].

As a non-destructive technique, NMR can also provide useful information when coupling with other laboratory measurements. For example, it has been used to measure the total porosity of intact shale samples when combining with gas- porosimetry [18], or quantify the fluid loss due to sample crushing in CRA / retort, or check residual fluid post CRA / retort [1, 11, 12, 17].

For conventional reservoirs, the NMR $T2$ cutoff for quantification of free fluid (*FFI*) versus bound volume irreducible fluid (*BVI*) is a critical petrophysical parameter for NMR log calibration. When combining NMR with porous

plate or centrifuge desaturation in the lab, the NMR $T2$ cutoff can be determined from the $T2$ measurements at 100% water saturation and at the irreducible water saturation (S_{wir}). However, it is not feasible to reach S_{wir} by porous plate or centrifuge for unconventional tight rocks due to extremely low permeability. Efforts have been made to measure the $T2$ cutoff for tight rocks by acquiring $T2$ before and after 316 °C retort [9] or core drying [16, 19]. The core samples post 316°C retort or post oven drying at specific temperatures (95°C [16] and 80°C vacuum [19]) were assumed to be at the "desaturated" status and the residual fluids were immobile. Based on the introduction above, these methods could either count the bound water as mobile or count a part of mobile oil as immobile. An integrated workflow combining NMR with 105°C / 300°C retort is applied in this study to determine the NMR $T2$ cutoff in liquid rich unconventional tight rocks.

With all the exciting progress made in the unconventional tight core analysis, it could be still challenging when trying to compare and interpret lab data measured by different techniques. In this paper, we strive to review the laboratory methodologies and uncertainties of CRA/Retort/NMR for measuring total porosity and fluid saturations for unconventional tight rocks. A case study on core samples from the Bakken formation will be demonstrated. We hope that understanding in the applications and limitations of these techniques would help operators reconcile lab data or compare with legacy data measured by different techniques, leading to selection of the most representative input for petrophysical models.

2 Experimental Methods and Uncertainties

The general procedures of CRA, Retort, NMR used in this study and the main sources of uncertainties are discussed in this section.

2.1 Crushed Rock Analysis

CRA is similar to Routine Core Analysis (RCA) on core plugs in terms of total porosity and saturation measurement. The main difference is that the core sample is crushed first and then subject to solvent extraction. CRA starts with intact samples which can be chunks or plugs, but it does not work for samples that are already crushed like drill cuttings. For each as received (AR) sample, an initial weight is recorded, and a bulk volume (BV) is measured using the mercury immersion method. The sample is crushed without sieving into a certain size range to minimize fluid loss; a weight averaged particle size ($\sim$ 1.1mm) is determined at the end of the CRA test. The sample post crushing is weighed and loaded into a Dean-Stark apparatus for water extraction. Toluene is the common solvent for Dean Stark, however for high salinity formation brine a higher boiling point solvent such as xylene is used [20]. The water recovery is recorded, and the water weight is measured after the water volume stabilizes. Then the sample is Soxhlet extracted with chloroform or a chloroform-methanol azeotrope, followed by a methanol phase of extraction to remove the residual oil and salt. The sample is dried in a vacuum oven and weighed daily until the weight stabilizes. Finally, the dry grain volume of

the sample is measured by helium injection using the Boyle's law method.

CRA is a weight-based analysis. Because there is always slight weight loss due to sample handling: crushing, transferring, *etc.*, it is critical to keep track of sample weights accurately in each step. Extended periods of sample handling must be avoided to prevent fluid loss. A high initial sample weight (>80 grams; minimum 40grams) is preferred to reduce the error bar.

Some assumptions are applied in CRA data processing:
- Weight loss before sample loading for solvent extraction is considered as grain loss.
- Weight loss after solvent extraction is considered as fluid loss.
- Fluid saturation distribution is homogeneous in the rock; therefore, the bulk volume can be ratioed to account for the weight loss due to sample handling.
- The same brine salinity and oil density are applied for all the samples unless otherwise specified.

Based on these assumptions, the total porosity can be calculated from the bulk volume and dry grain volume after considering the weight loss prior to solvent extraction. The brine volume/saturation is from the deionized (DI) water recovered from Dean-Stark, and a brine volume correction factor, V_b/V_w:

$$\frac{V_b}{V_w} = \frac{\rho_w}{\rho_b} \cdot \frac{1000}{(1000-TDS)} \qquad (1)$$

where ρ_w, V_w are the density (g/ml) and volume (ml) of DI water; ρ_b, V_b are the density and volume of brine; and TDS is the brine salinity in kilo- parts per million (kppm).

This brine volume correction is especially important for systems with high salinity brine, without applying it the water saturation will be underestimated. Sodium chloride solutions' properties are often used when formation water ion analysis is unavailable. The oil volume is not measured directly, instead it is calculated from the mass balance before and after solvent extraction and the Dean-Stark water weight. Brine salinity (or density) and oil API gravity (or density) must be known to convert the measured fluid weights to volumes, so any uncertainties of these inputs will impact the fluid saturation calculation.

2.2 300 °C Closed Retort

An initial weight and bulk volume are measured at first. Each sample is crushed, weighed, and sieved to remove fines, then the AR grain volume of the crushed sample is measured. Subsequently, the sample is loaded into a sample holder and placed into the retort oven. The sample is heated up to 105 °C to release the free pore water. The retort apparatus is a closed system during the heating process to minimize the fluid loss. Once the fluid production stabilizes for a period, a slight vacuum is applied to the fluid receiver momentarily to complete the fluid drainage from the condenser, and the fluid receiver is disconnected from the system for a quick weight measurement. Then the fluid receiver is reconnected to the retort setup and sealed well to close the loop. The sample is

further heated to 300°C, the bound water and produced oil volume are recorded until readings stabilize. The retort oven is turned off and cooled down to ambient temperature. The sample is unloaded and weighed.

Similar as CRA, retort is a weight-based analysis, so all the best practice in CRA applies to retort: minimizing sample handling time; measuring the sample and fluid weights in each step; and starting with a high initial sample weight.

Those assumptions in CRA also apply in retort data processing. It is also assumed same salinity for both free and bound waters. A total mass balance is conducted to compare the sample weight loss versus the recovered fluid weights. There would always be a small "missing weight" (generally ≤ 0.2 grams) despite a closed retort apparatus is used. This missing weight is assigned to either oil (if oil is detected) or water (if oil is not detected) and introduces uncertainties in fluid volume calculation.

The total porosity reported in retort is a "fluid summation porosity", meaning that the porosity is calculated by adding all the fluid saturations ($\%BV$) together. The gas saturation is obtained from the bulk volume and the AR grain volume. The free and bound water saturations are from the recovered water weights, corrected by the formation brine salinity. The oil saturation is calculated from the recovered oil weight; however, an oil recovery factor is needed to convert the produced oil volume at 300°C to original oil in place. If a crude oil sample is available, then this recovery factor can be determined by running retort on the oil; otherwise, it will be obtained by proprietary correlations based on oil API. The higher the oil API, the higher the recovery factor. Brine salinity (or density) and oil API gravity (or density) are all critical inputs and will affect both the fluid saturation and fluid summation porosity in retort.

An optional step is to place the post retort sample into a Soxhlet extraction unit to clean the residual oil and salt out with organic solvents. Then the sample is dried, and the dry grain density is measured to get another independent measurement of total porosity.

2.3 Nuclear Magnetic Resonance

The NMR signals are acquired at ambient conditions on an Oxford Instruments GeoSpec™ 12 MHz spectrometer using the software from Green Imaging Technologies. Two different echo spacings (Te = 0.1 and 0.2 ms) are selected to acquire the $T2$ spectra. Te of 0.2 ms coincides with complementing open-hole wireline acquired NMR data. Te of 0.1 ms is chosen to capture the signals from fast decaying components like bitumen or fluids in very small pores. $T1T2$ maps with Te = 0.1 ms are generated for characterizing fluid volumes and typing. Choosing the right measurement and data processing parameters are vital for NMR data quality [21, 22]. The test configurations such as resonance frequency, echo spacing, echo train, acquisition time, *etc.*, and the data processing parameters such as the inversion algorithm, the regularization parameter, and the subjective $T1T2$ map interpretation, *etc.*, may all affect the NMR results and are beyond the intended scope of this paper.

Besides NMR testing and processing parameters, rock samples can pose challenges. It will be difficult to measure samples with ultra-low fluid volume, which will result in low signal to noise ratio even with longer acquisition time. The

NMR relaxation rates are affected by the concentration and the mineralogic form of Fe^{2+} and/or Fe^{3+} bearing minerals [23], the presence of paramagnetic materials like pyrite or siderite may enhance the relaxation rate of the compounds, cause the signals to decay faster and not be fully captured by NMR, leading to inaccuracy of NMR volume readings. Finally, just like CRA and retort, the NMR measured water volume also needs to be calibrated or corrected to brine volume, especially for high salinity brines. Hydrogen index (*HI*), the number of hydrogen atoms per unit of volume in samples divided by the number of hydrogen atoms per unit volume of pure water at standard temperature and pressure (68 °F / 20 °C, 14.5 psi), is routinely used in NMR measurement to account for this conversion [24]. A sodium chloride equivalent solution is often prepared for this *HI* correction, or it can be estimated from the density model. Based on the definition of *HI*, it should be equal to Vw/Vb, and can be calculated by inverting equation (1). For oil it is generally assumed that HI = 1.0.

3 A Case Study on Bakken Core Samples

An integrated study was conducted on core samples from the Bakken petroleum system for total porosity and fluid saturation data comparison.

3.1 Core Materials

Fifteen core samples were selected from multi-well whole cores at different depth intervals, covering a wide range of formations: Upper Bakken Shale (UBS), Lower Bakken Shale (LBS), Middle Bakken (MB), and Three Forks (TF). The X-Ray Diffraction (XRD) mineralogy data are listed in Table 1. Samples are divided into a shale group (1-9) and a non-shale group (10-15). The shale group is clay rich (mainly illite/mica), while the non-shale group is relatively carbonate rich. The shale group also contains more additional minerals, with pyrite being the dominant species (2.5-14.1%).

Other rock characterization analyses such as total organic carbon (TOC) and programmed pyrolysis were conducted on the shale group. The result ranges are shown in Table 2. All the shale samples have high TOC content and high hydrocarbon (HC) generative potential.

These samples were from legacy cores with either CRA (on shales) or RCA (on non-shales) performed on their twins at the fresh state about 5-6 years ago. Most of the samples were from the exact same depths, except for samples 6-10 (off by up to 0.3 ft). Samples were taken from the center of the whole cores, with the rind removed to minimize potential mud filtration. Eight out of the fifteen samples (samples 1-7, 10) were wax preserved, while the others were only wrapped with Saran / aluminum foil and stored in cold storage. NMR and closed retort were conducted on these fifteen samples, following a workflow described in Fig. 2.

Mercury Injection Capillary Pressure (MICP) test was performed on the non-shale group. Core plugs with 1″ in diameter and ~ 0.8″ in length were taken and subject to solvent extraction, drying, and ambient porosity measurement. Samples were then weighed, loaded into penetrometers, and installed into an Automatic Mercury

Porosimeter (Micromeretics Autopore IV 9520) for MICP tests with injection pressure up to 60,000 psia.

Table 1. Core sample XRD data (Weight %)

No.	Formation	Silicates	Carbonate	Clay	Other
1	UBS	39.9	10.9	45.7	3.5
2	UBS	70.0	8.7	16.9	4.4
3	LBS	50.8	9.6	34.3	5.3
4	LBS	61.5	5.5	28.0	5.0
5	LBS	49.8	8.0	26.1	16.1
6	UBS	32.7	8.8	50.6	7.9
7	UBS	62.9	4.6	27.6	4.9
8	LBS	58.3	11.1	26.5	4.1
9	LBS	66.6	5.1	24.6	3.7
10	MB	52.9	27.4	18.5	1.2
11	MB	58.8	38.2	3.0	Tr
12	MB	55.9	28.5	14.6	1.0
13	MB	54.9	26.6	17.8	0.7
14	TF	26.3	64.6	6.9	2.2
15	TF	26.6	70.6	2.8	Tr

Table 2. TOC, programmed pyrolysis data ranges (shale)

	Ranges	Mean	
TOC, wt%	7.9 -14.2	9.6	Leco TOC
$S1$, mg HC/g rock	3.36 - 9.08	5.82	Volatile HC
$S2$, mg HC/g rock	19.89 - 40.73	25.52	Non-volatile HCs and remaining HC generative potential
$S3$, mg CO_2/g rock	0.18 - 0.39	0.28	Carbon dioxide content

3.2 Fluid Properties

The stock tank oil API gravity used in this study was 40.4 °API, and an oil recovery factor of 0.663 was applied in the calculation of oil saturations.

Brine salinities of Bakken formation, measured on produced waters at the surface, ranges up to 360 kppm (density of ~ 1.29 g/ml) or greater [25]. It also contains high concentrations of divalent ions such as Ca^{2+}, Mg^{2+}, Sr^{2+} and Fe^{2+}. This ultra-high salinity adds another level of complexity to brine volume quantification because the fluid saturation data are normally obtained on "as received" core samples at ambient conditions; the fluid volumes and properties have

been altered during the coring trip to the surface. It is also challenging to reproduce reservoir conditions in the laboratory environment. A brine salinity of 300 kppm was adopted in this study. A sodium chloride equivalent solution is usually prepared for the HI measurement for NMR brine volume correction. At ambient temperature (20°C) the solubility limit of sodium chloride is 36g in 100g water, *i.e.*, the weight concentration is 36 / (100+36) = 26.5% or 265 kppm. Hence this 300 kppm has exceeded the saturation limit at ambient temperature. A salt suspension or precipitation instead of a true solution will form, hindering the density and the HI measurements. Increasing temperature will not improve the solubility much because no heat releases from the chemical bonds rupture during sodium chloride dissolution, see Fig. 3 [26]. At 100 °C the saturated sodium chloride solution is less than 40g in 100g water, *i.e.,* 286 kppm, still lower than 300 kppm. An assumption was made that a "supersaturated" sodium chloride solution existed at ambient conditions, the brine density and the HI calculated from the density were extrapolated to 1.23 g/ml and 0.86 at 300 kppm, as shown in Fig. 4 and 5. This assumption would impact the water saturation calculation in CRA, retort, and NMR to the same extent.
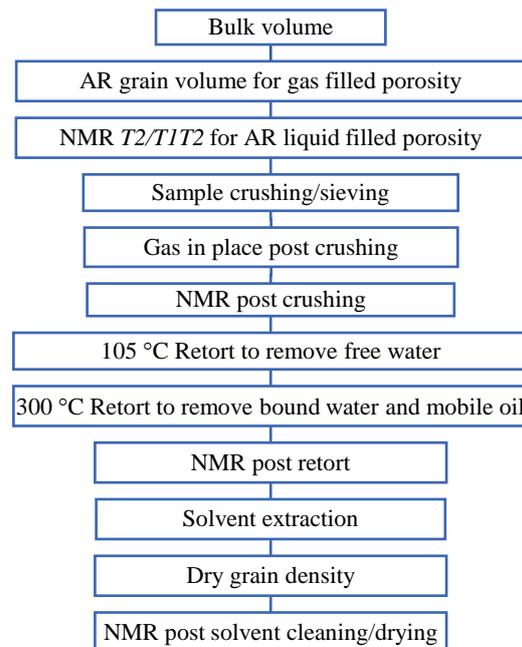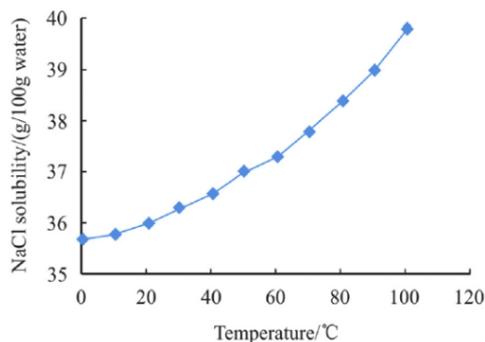
Fig. 2. Experimental workflow.

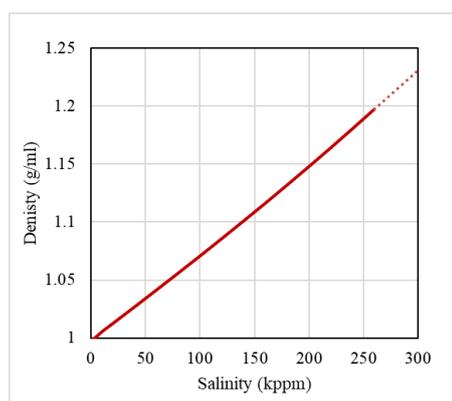**Fig. 3.** Solubility of sodium chloride with temperature [26].

Fig. 4. Plot of the density versus salinity of sodium chloride solutions at 20°C, ambient pressure.
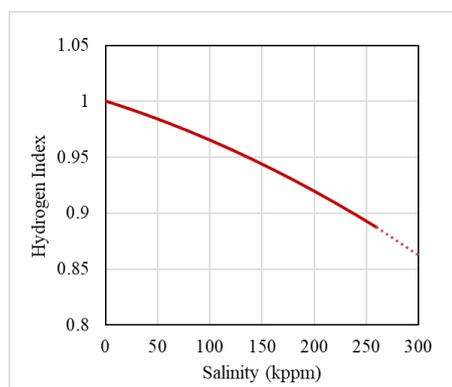

Fig. 5. Plot of the calculated *HI* versus salinity of sodium chloride solutions at 20°C, ambient pressure.

3.3 Results and Discussion

3.3.1 Total porosity comparison

Total porosity data measured by CRA (shale), RCA (non-shale), retort and NMR are divided by a specific porosity value (%*BV*), and then plotted in Fig 6. The asterisk * denotes that the sample depths for retort/NMR are slightly off (up to 0.3 ft) from legacy CRA or RCA sample depths. The NMR total porosity is a summation of the liquid filled porosity from NMR *T2* (*Te* = 0.1 ms) and the gas accessible porosity from Boyle's Law helium porosimeter, measured on intact samples. The data set shown in purple is from an independent dry grain density measurement post retort and post solvent cleaning. The mercury accessible porosity from MICP is also plotted in Fig. 6(b).

For shale samples, it is obvious that the CRA porosity values are generally higher than those from retort and NMR (~31% higher than retort; 25% higher than NMR, on average). A similar trend is observed in the post retort / post cleaning dataset. It is highly possible that the solvent extraction removed some of the bitumen from these organic rich samples. NMR porosity values are relatively comparable to those from retort. It is not common because for these organic and clay rich shale samples, NMR *T2* at a shorter *Te* should capture a part of fast relaxation signals from the structural water in clays and hydrocarbon signals from kerogen/bitumen, so it is expected that NMR total porosity would be higher than that from retort. It is suspected that the

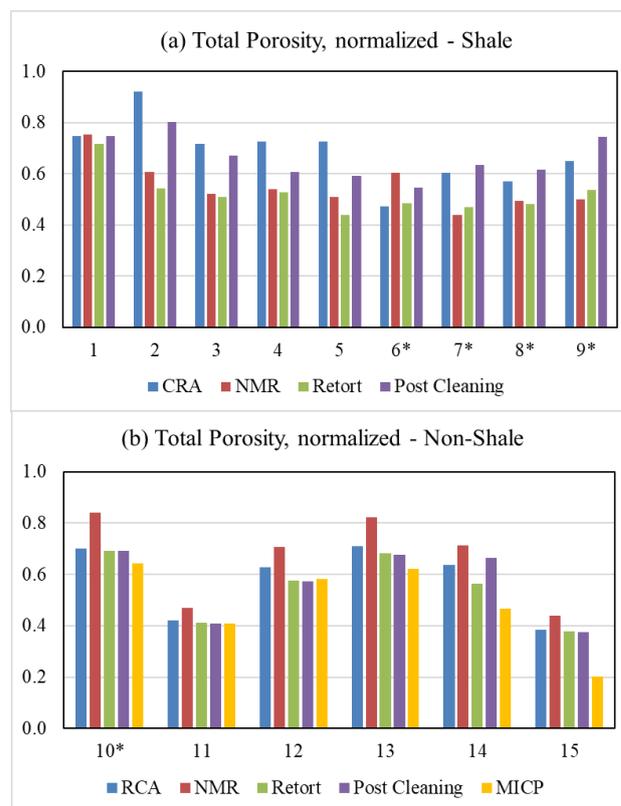high pyrite content in these shale samples may interfere with the NMR measurement and supress the volume readings.

Fig. 6. Total porosity (divided by a specific value) measured by different techniques.

For non-shale samples with trace or low pyrite content, NMR shows the highest porosity among all the techniques as expected (~ 14% higher than RCA, ~ 20% higher than retort). Porosities measured by RCA/ retort are relatively comparable for these organic lean samples, along with values post retort/post cleaning. The mercury accessible porosities measured by MICP match the RCA/retort porosities reasonably well for the Middle Bakken samples (10-13) but are lower for the two carbonate rich samples (14, 15) from Three Forks. MICP porosities are limited by the highest mercury injection pressure (60,000 psia), it is hard to fully access all the micro- or nano-pores especially for carbonate samples which tend to have a higher level of heterogeneity with more complex pore geometry and wider pore size distributions. Another reason could be due to the relatively mild cleaning on MICP samples since only chloroform-methanol azeotrope and methanal cycles were applied, so there might be a chance that these two carbonate rich samples were not cleaned as well as RCA samples, resulting in lower porosities.

3.3.2 Fluid saturation comparison

The fluid saturations are reported in %*BV* so saturation data measured by different methods can be compared on the same basis. Then all the fluid saturations are divided by a specific value (%*BV*). The normalized water saturations *(Sw)* from Dean-Stark and retort are compared in Fig. 7 for wax-preserved and non- wax preserved samples. Again, the

asterisk* denotes that the sample depths for retort are slightly off (up to 0.3 ft) from legacy CRA or RCA sample depths.
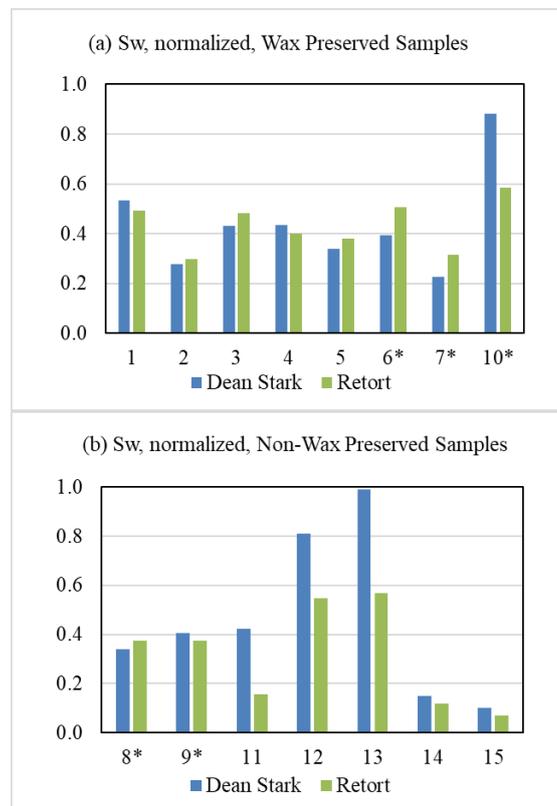

Fig. 7. Water saturations (divided by a specific value) measured by Dean Stark and Retort (Samples 1-9: CRA; Samples 10-15: RCA).

It is shown that the Middle Bakken samples 10-13 are more prone to fluid loss over time, no matter if the samples are wax preserved or not. Compared to shale samples, the higher permeabilities and larger pore sizes of Middle Bakken samples ought to be responsible for this behaviour.

The normalized water and oil saturations *(So)* measured by retort and NMR are illustrated in Fig. 8-9. The NMR fluid typing is interpreted from the *T1T2* maps (*Te* = 0.1 ms) and then normalized to *T2* fluid volumes for AR / intact samples. NMR *T2* at *Te* = 0.1ms generally shows higher liquid volumes / saturations than retort because NMR may capture a part of faster decay signals from structural water in clays and kerogen/bitumen, while these components are all counted as matrix per Fig. 1 and will not be recovered by 300°C retort. Another reason could be due to fluid loss by crushing, since retort was performed on crushed samples while NMR was conducted prior to crushing per the workflow in Fig. 2.

It is noted that the oil saturations from retort are higher than NMR for Middle Bakken samples (10-13). The reasons for this could be: (1) low oil saturations with low recovered oil weights in retort (~0.2 grams), leading to higher uncertainties in lab measurement and NMR oil/water interpretation; (2) only one oil density (API gravity) and one oil recovery factor were used in the retort calculation. However, the recovered oil color ranged from light yellow to dark brown, clearly showing different oil properties at different depths.
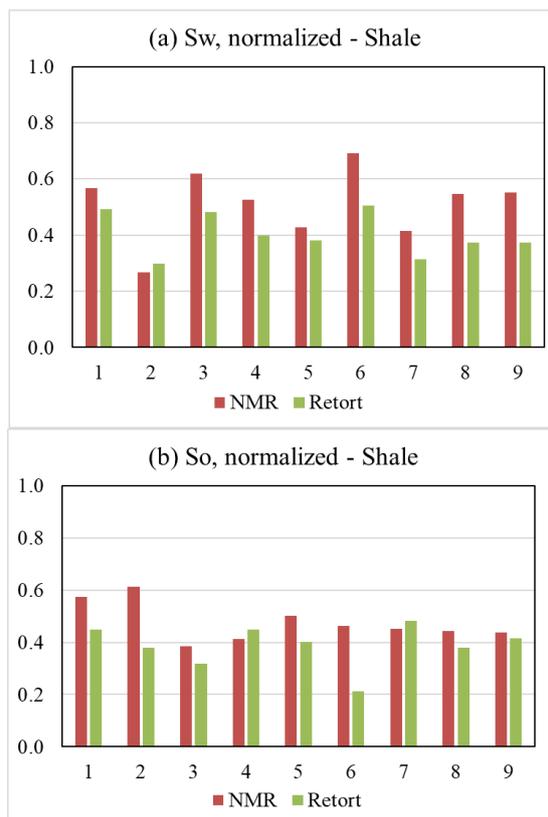

Fig. 8. Fluid saturations (divided by a specific value) measured by NMR and Retort (Shale).
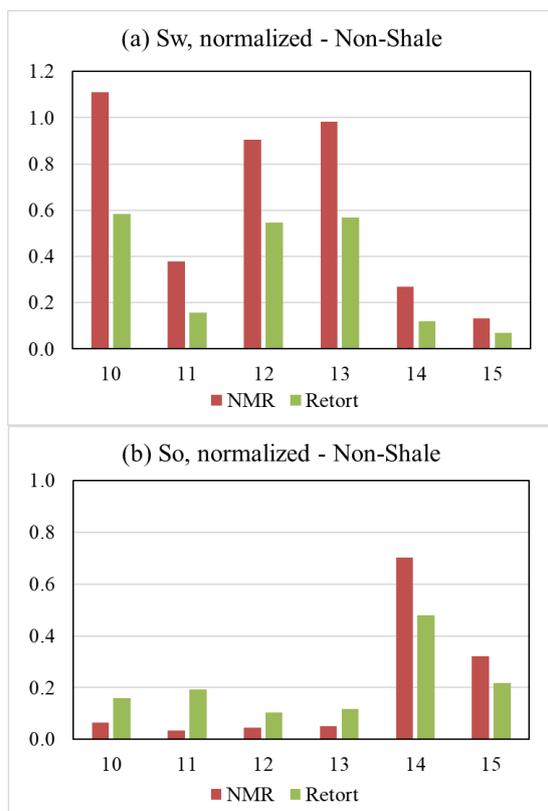

Fig. 9. Fluid saturations (divided by a specific value) measured by NMR and Retort (Non-Shale).

3.3.3 Fluid loss due to crushing

The liquid loss due to crushing was examined by performing NMR $T2$ before and after crushing (Fig. 10). Again, the liquid saturations are reported in %BV and normalized. An average of ~ 3.5 % of the original liquid in place was lost. Retort on intact samples has been reported [27]. In-house studies have also confirmed (not reported here) that the total liquid recovery in retort can be improved by eliminating the crushing step.
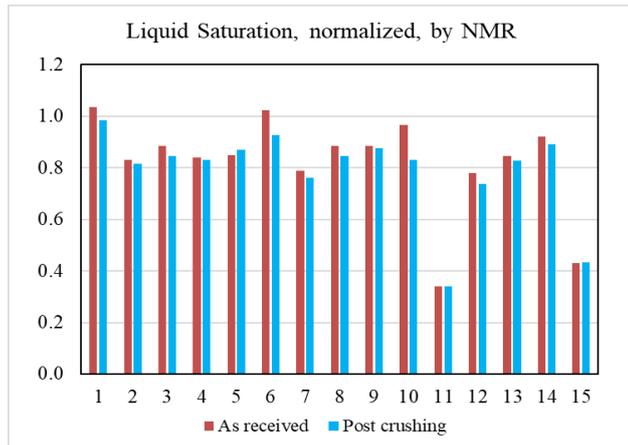

Fig. 10. Liquid saturations (divided by a specific value) measured by NMR $T2$ (Te = 0.1 ms) before and after crushing.

3.3.4 Fluid typing and mobility

NMR is used to help define fluid volume, typing and characterize fluid mobility within the core samples. Fig. 11 presents the NMR $T2$ spectra generated from Te = 0.1 ms and 0.2 ms for two examples: sample 6 (shale) and sample 11 (non-shale). As shown in Fig. 11(a), when dealing with shale samples, the shorter Te needs to be selected as the longer Te will not capture most of the fast-decaying components. There is a large difference, ~1.7 ml, in cumulative liquid volumes between Te = 0.1 and 0.2 ms for sample 6. Its $T2$ spectrum is mainly below 1 ms, and the $T2$ log mean is only 0.16 ms at Te = 0.1 ms, indicating that the sample is very tight and fluids reside in small pores. However, this difference is quite small ~ 0.04 ml for non-shale sample 11 due to low clay and organic content. The NMR signals of sample 11 have a wider distribution, the main peak locates at longer relaxation times with a $T2$ log mean of 1.68 ms at Te = 0.1 ms.

The NMR $T2$ spectra for samples 6 and 11 at different status (AR/intact, post crushing, post retort, and post solvent cleaning) are shown in Fig. 12. Samples at the last three stages have the same BV, slightly lower than the AR BV due to sample loss from crushing. For the shale sample 6, the position of the $T2$ peaks didn't change at each stage. While the peak shifted slightly to the left for non-shale sample 11 post crushing, implying that the lost fluid could be mainly from the larger pores. NMR volumes were reduced significantly post retort, and there were still residual NMR signals post solvent cleaning especially for sample 6. The dry grain densities post retort and post cleaning are plotted against the legacy grain densities measured by CRA (shale) or RCA (non-shale) in Fig. 13. Most of the data fall on the 1:1 line indicating that similar cleaning efficiency is achieved

for post retort samples. The non-shale group shows much higher grain densities than the organic rich shale group as expected. Sample 11 has a clay content of 3.0%, while sample 6 contains 50.6% clay and 9.1% TOC. It is believed that the residual NMR signals mainly come from the structural water in clays, kerogen, and any residual fluids which are not removed by retort nor solvent cleaning.
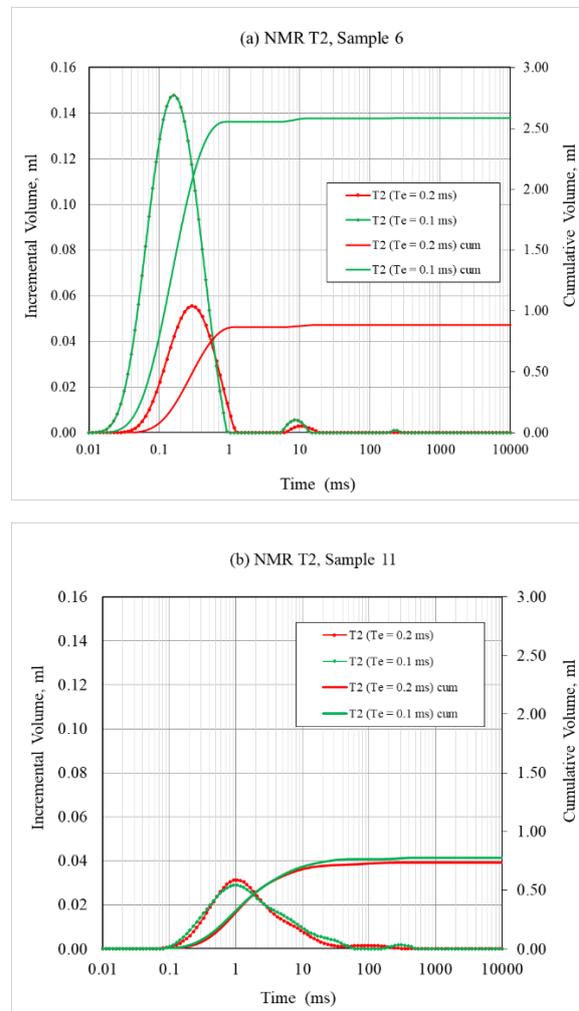

Fig. 11. NMR $T2$ – Samples 6 (Shale) and 11 (Non-Shale) at AR /intact condition.

NMR $T1T2$ 2D maps can provide a clearer definition for fluid types in the rock matrix. Fig. 14 shows a series of 2D maps for samples 6 and 11 with the same color scale. Fig. 14(a) presents the 2D map for sample 6 at AR/intact condition. There are two regions of interest in the map. The area close to the 1:1 axis is mainly from water signals, and the area on top of it could be from heavier components such as bitumen. The locations of these two regions remain the same post retort with reduced signal intensity. Figure 14(c) shows the 2D map for sample 11 at AR / intact condition. Based on the location in the map and the relatively low $T1$T2 ratio, this region of interest appears to be mainly water. The residual NMR signals post retort are minimal due to low liquid volume and low clay content.
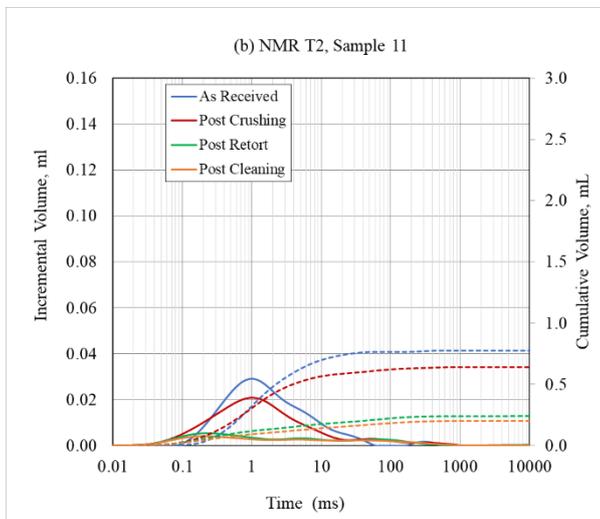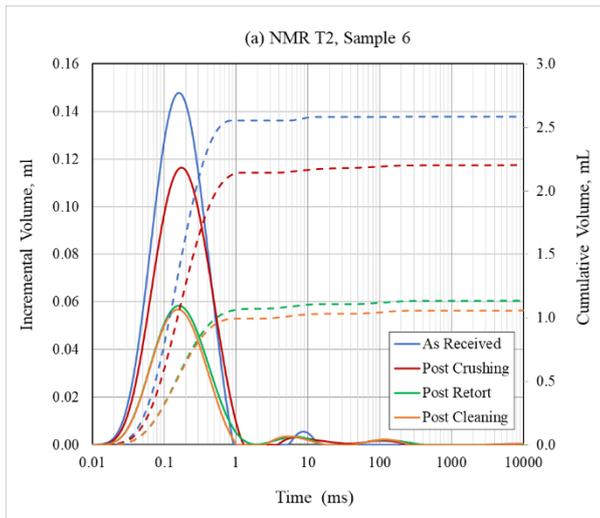
(a) NMR T2, Sample 6

(b) NMR T2, Sample 11

Fig. 12. NMR *T2* - Samples 6 (Shale) and 11 (Non-Shale) at different stages. Solid lines - incremental volumes; dashed lines - cumulative volumes.
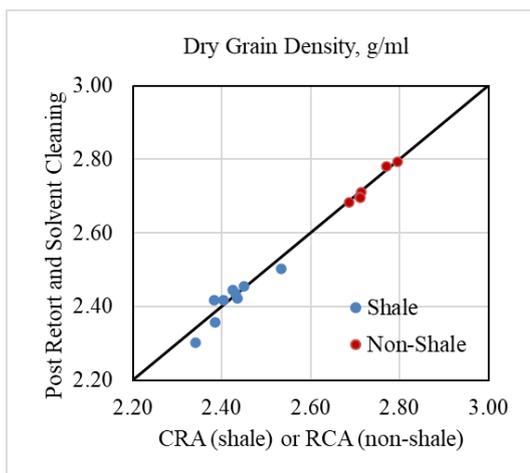

Fig. 13. Grain density measured by legacy CRA /RCA and Post retort- Post solvent cleaning.
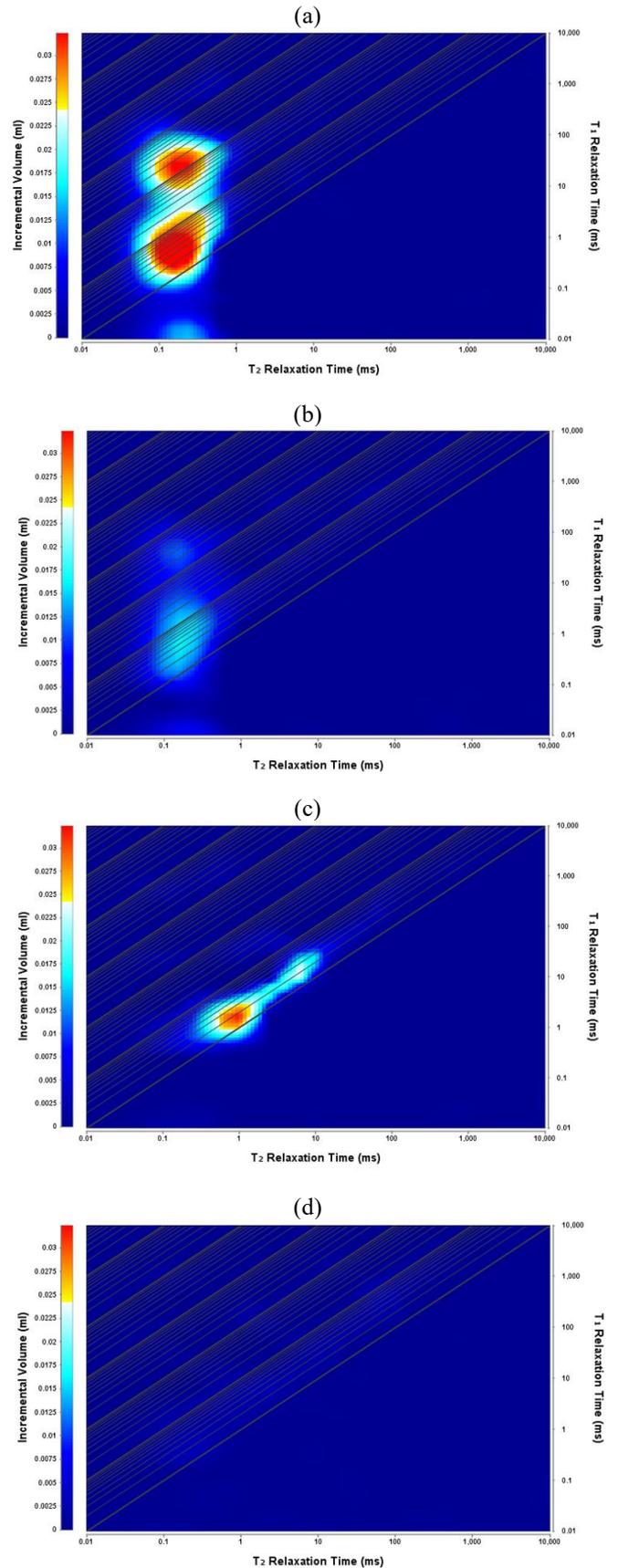

Fig. 14. NMR *T1T2* maps – (a) Sample 6 (Shale) at AR/intact condition; (b) Sample 6 post 300°C retort; (c) Sample 11 (Non-Shale) at AR/intact condition; (d) Sample 11 post 300°C retort.

Good correlations between bound water saturations from retort and the total clay content from XRD are observed in Fig. 15. Because the measured bound water includes contributions from both capillary bound and clay bound waters, so the bound water saturations at x (clay content) = 0 may be considered as the minimum capillary bound water saturations for different groups.

This free and bound water differentiation from retort provides a viable way to reconcile the AR NMR data and determine the $T2$ cutoff for free and bound fluid separation. It is assumed that 300°C retort can recover all the movable oil (after volume correction), free water, and bound water in the pore space. The AR liquid filled porosity from NMR $T2$ (at $Te = 0.1$ ms) is reduced by the free water and oil saturations from retort, along with the fluid loss due to crushing (as a part of free fluids), to calculate the immovable or bound fluid porosity. Then a $T2$ cutoff can be obtained from the cumulative $T2$ relaxation time distribution, an example is shown in Fig. 16. The $T2$ cutoff values of each sample are listed in Table 3. Despite limited data points especially for the non-shale group, distinct T2 cutoff values are observed for different rock types. For the Upper and Lower Bakken Shale, the $T2$ cutoff values range from 0.10 to 0.20 ms, with an average of 0.16 ms; for the Middle Bakken samples, the $T2$ cutoff values range from 0.66 to 1.04 ms, with an average of 0.91 ms; for the two carbonate rich samples from Three Forks formation, the $T2$ cutoff values are 3.40 and 5.79 ms respectively, with an average of 4.59 ms. This effort aims to overcome tight rock challenges associated with conventional fluid desaturation techniques such as centrifuge or porous plate; and provide an independent method (retort) for free and bound fluid differentiation to support NMR $T2$ cutoff determination. Finding free and bound cutoffs for water and oil in NMR 2D maps sometimes can be difficult especially when water and oil signals partially overlap. Future work will explore the feasibility of determining $T1$, $T2$ and/or $T1/T2$ ratio cutoffs for free and bound water and oil by integrating retort results and NMR $T1T2$ maps.
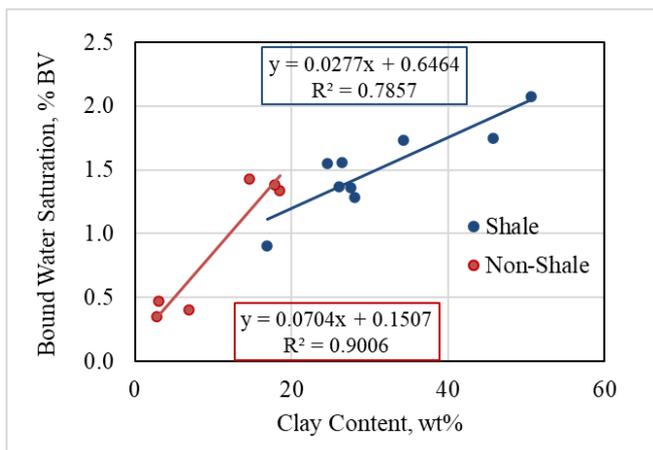

Fig. 15. Bound water saturations measured by retort versus clay content from XRD.
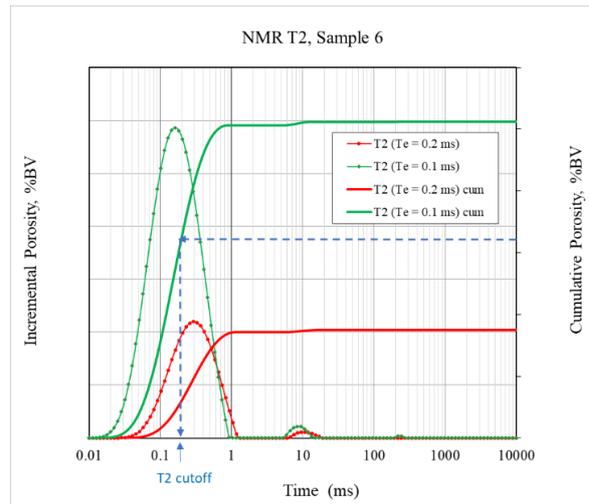

Fig. 16. Sample 6 (Shale) – $T2$ cutoff.

Table 3. NMR $T2$ Cutoff

Sample No.	Formation	NMR $T2$ Cutoff (ms)
1	UBS	0.13
2	UBS	0.17
3	LBS	0.17
4	LBS	0.13
5	LBS	0.18
6	UBS	0.20
7	UBS	0.10
8	LBS	0.20
9	LBS	0.20
10	MB	1.03
11	MB	0.66
12	MB	1.04
13	MB	0.93
14	TF	3.40
15	TF	5.79

4 Conclusions

The laboratory measurement of total porosity and fluid saturation for unconventional tight rocks is challenging. Values obtained by different core analysis methods (CRA / Retort / NMR) may vary even after the best practices have been applied in the measurement. A case study performed on Bakken core samples was presented for data comparison. The methodologies, applications, assumptions, and main sources of uncertainties for each technique were reviewed in this

paper, which could serve as a reference for operators when designing core analysis programs or analyzing laboratory data.

CRA is a well-established routine measurement for total porosity and fluid saturations in unconventional rocks. It may overestimate the total porosity and oil saturations for organic rich source rocks due to dissolution of bitumen in organic solvents. Retort is an alternative method with bitumen being intact; free and bound water can be differentiated for samples with none or low smectite content by applying a temperature cutoff; an oil recovery factor is needed to account for the heavy oil components retained in the core sample post 300°C retort test. NMR as a non- destructive technique finds wide applications in unconventional rock characterization; it has its own uncertainties tied to acquisition, interpretation, rock/fluid composition and properties. Integrated workflows combining strengths of different techniques such as CRA, 300°C retort, and NMR can improve interpretation and quantification of fluid types, volumetrics, and mobility in unconventional tight rocks.

A new laboratory method involving as-received NMR and closed retort was developed to obtain the NMR $T2$ cutoffs for free and bound fluid separation in unconventional tight rocks.

Acknowledgement

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