Measuring Methane Adsorption in Shales Using NMR

M.J. Dick[1], C. Muir[1], D. Veselinovic[1], and D. Green[1]

[1]*Green Imaging Technologies, Fredericton, NB, Canada*

This paper was prepared for presentation at the International Symposium of the Society of Core Analysts held in Vienna, Austria, 27 August – 1 September 2017

ABSTRACT

Despite the downturn in oil and gas prices, shale reservoir production continues and is expected to grow as prices normalize. The total gas in place is a measure of the total natural gas content in a shale which consists of both free gas in the porous spaces of the shales and adsorbed gas on the surface of the shale matrix. The total gas in place is dependent on the pore pressure and temperature and is vital to the profitable development of a shale reservoir. Traditionally, gas isotherms are measured by exposing the core to helium and methane at ever increasing pressure while tracking the volume of gas absorbed and adsorbed. These experiments involve destruction of the core and provide no information on the pore size distribution.

Free gas can be distinguished from adsorbed gas using NMR T_2 distributions and thus the total gas in place can be determined using NMR. This proves advantageous as the NMR analysis can be completed without destruction of the shale core while providing pore size distributions.

In this work, we present a method for measuring absorbed gas, adsorbed gas and total gas content in shales using NMR. T_2 measurements were taken over time after the introduction of methane to both a sandstone and a shale. Methane absorption was observed in both rocks, while adsorption was only observed in the shale. T_1-T_2 maps acquired in the shale show that methane enters both organic and inorganic pores at similar rates.

INTRODUCTION

Shales are an important source of natural gas. Gas in shales can be absorbed as free gas in the pore network or adsorbed on the surface of the organic material. Gas storage in shales is characterized by plots of the quantity of adsorbed gas, free gas and/or total sorbed gas at different pressures called isotherms [1].

The quantity of free and adsorbed gas is traditionally measured volumetrically using a system of two cells, a reference cell and a sample cell, which are separated by a valve. A crushed rock sample is placed in the sample cell. The reference cell is filled with a gas at a known pressure. The valve is opened and the gas from the reference cell expands into the sample cell and the pressures in the two cells equalize. The procedure is performed first with a non-adsorbing gas, such as helium, to determine the void volume, or free gas content, in the rock sample via the difference in temperature and pressure before and after

opening of the valve between the two cells. The system is then vacuumed to remove the gas, the reference cell is filled with an adsorbing gas and the procedure is repeated. When the valve is opened and the adsorbing gas expands into the sample cell it will fill the void volume and adsorb on the sample. Therefore, the amount of adsorption can be calculated by subtracting the free gas content. The expansion of the gases is repeated at numerous pressures to generate isotherms. The disadvantages of this traditional method are that the sample is destroyed for the measurement, and no information is acquired on the size of the pores occupied by the gas.

NMR can be used to generate gas isotherms. The advantages of NMR measurements are that the samples will remain intact and the measurements will provide information on the samples' pore size distributions. Measuring gas in shales is challenging with NMR due to the low hydrogen index of gas and the small pore volume of shales, both of which result in low NMR signal. However, with recent advances in NMR hardware, gas measurements in shales are possible. In this study we set out to use NMR to generate isotherms by distinguishing the amount of free gas and adsorbed gas in a rock. This paper presents our initial results of the measurement of total gas in place in a shale.

EXPERIMENTAL

A shale core plug and a sandstone core plug were chosen for the study. The characteristic information on each rock studied is shown in Table 1. Each core sample was confined hydrostatically by fluorinert to a pressure of 2500 psi in an Oxford Instruments P5 overburden NMR probe [2] in an Oxford Instruments GeoSpec 2-75 rock core analyzer [3]. The samples were evacuated with a vacuum pump, then as received or dry T_2 measurements were taken before the introduction of methane. Methane was then introduced to the samples at 2000 psi. T_2 measurements were acquired at 2 minute intervals for the first hour, then at 15 minute intervals for the following 3 hours, then at 60 minute intervals for the remainder of the experiment in the sandstone and the shale. These T_2 measurements were employed to retrieve the total gas content present in each rock as a function of time. T_1-T_2 maps were also acquired with and without methane for the shale. Acquisition parameters for the T_2 measurements and T_1-T_2 maps are shown in Table 2. Data acquisition and analysis of the T_2 and T_1-T_2 data was achieved via Green Imaging Technologies software [4]. Pore volumes were determined using NMR volumes from T_2 measurements for both the shale and sandstone. To fully saturate the rocks, the shale was pressure saturated with brine at 10 000 psi in a pressure cell for three days while, the sandstone was brine saturated in a vacuum saturation apparatus.

RESULTS

As mentioned above, the gas absorption/adsorption characteristics were studied for a shale (Eagle Ford 1) and a sandstone (Carbon Tan 1). These rocks were chosen due to the

expected difference in their gas absorption/adsorption characteristics. The higher surface to volume ratio of the pores in the shale coupled with its higher organic content should make the shale much more likely to exhibit adsorption of methane. The presence of organic content in the shale (as received) was confirmed prior to the methane absorption/adsorption experiment using T_1-T_2 NMR maps recorded at different temperatures (Figure 1). Organic content is visible in the T_1-T_2 maps as intensity off diagonal at each temperature. The significant increase in intensity observed in the 70ºC data reflects the organic content liquefying with temperature and as a result its T_1 becoming longer bringing more intensity into the scale of the map. This increases the observed NMR porosity of the shale.

The first set of gas experiments were to record a series of T_2 scans as a function of time for both the sandstone and the shale. These scans provided the total gas content in each rock as a function of time. Specifically, the upper panel of Figure 2 shows the volume of methane (@ 2000 PSI) for both rocks as a function of time. From this data, it is clear that there is a difference in behaviour for each rock. At first both rocks are very quickly filled with a volume of methane. For the sandstone, it is filled to approximately its pore volume via absorption. For the shale, it is filled to 75% of its pore volume via absorption. This absorption is most likely occurring in the small fractures and larger pores. After this initial absorption, the sandstone shows no more appreciable increase in volume. Conversely, the shale shows an increase in gas content over a period of several hours. After approximately 1.5 hours the shale has been filled to its pore volume via absorption. The shale continues to take on approximately another 35% of a pore volume due to adsorption over a period of several hours. This yields a final gas content consisting of approximately 65% absorbed gas and 35% adsorbed gas which is consistent for shales with methane pressure around 2000 PSI [5].

The lower panel of Figure 2 shows the total gas content (adsorbed and absorbed) of both the shale and the sandstone. In order to retrieve the total gas content, the volume of methane (scm^3) at 2000 PSI (Figure 2 – upper panel) was converted to the volume of methane at standard temperature and pressure (15ºC and 1 atm) using the ideal gas equation. The converted volume was then divided by the bulk volume of each rock yielding a total gas content in units of scm^3/cm^3. For the shale, a total gas content of approximately 8 scm^3/cm^3 was observed and this is consistent with other shales [5].

One of the main goals of this work was to see if NMR could be used to distinguish adsorbed gas from absorbed gas. Figure 3 shows a comparison of two background subtracted T_2 spectra taken at different times as the shale was being filled with methane. The peaks in the spectra represent the different pore networks in the shale. The red spectrum was taken a few minutes after the introduction of methane into the rock where absorption dominates. The blue spectrum was taken several hours after the introduction of methane where both absorption and adsorption are occurring. The increase in observed methane volume when going from the red trace to the blue trace seems to be occurring in both pore networks equally. There is no distinction between absorption and adsorption. This is not unexpected as the adsorbed methane could have a T_2 very similar to the absorbed methane in the pores of this shale. In addition, the adsorbed and absorbed methane are likely in fast exchange

with one another making distinguishing between them impossible. The ability to distinguish between adsorbed and absorbed methane may be dependent on the shale being studied. Other shales may have pore networks where conditions exist where adsorption could be distinguished from adsorption. Gu et al. have reported seeing differences in T_2 spectra due to adsorption vs. adsorption of methane in a shale [6].

Figure 4 shows a T_1-T_2 map of shale Eagle Ford 1 taken a few hours after the introduction of methane. If the map in Figure 4 is compared to the map in the left-hand panel of Figure 1 (as received), conclusions about where the methane has gone once it entered the shale can be drawn. The long tail in the map at T_2 values greater than 1 ms corresponds to methane filling into the large inorganic pores of the shale. Conversely, the increase in intensity overlapped with the organic content observed ($T_2 < 1$ ms) in the left-hand panel of Figure 1 corresponds to methane entering the smaller organic pores of the shale. The methane seems to be filling all the pores equally within a few hours of methane being introduced into the rock.

CONCLUSION

A method has been presented for using NMR to measure absorption, adsorption and total gas content in shales. T_2 measurements were taken over time after the introduction of methane to both a sandstone and a shale. Methane absorption was observed in both rocks, while adsorption was only observed in the shale. T_1-T_2 maps were also acquired in the shale. They showed that methane filled both the inorganic pores and organic pores equally. This agrees with changes in the T_2 spectra of the shale. T_2 peaks originating from inorganic and organic pores grow at equal rates after the introduction of methane. No distinction was made between adsorbed and absorbed methane in the shale. This is likely due to fast exchange between the absorbed and adsorbed gas. Additionally, the absorbed and adsorbed gas could have very similar T_2 values.

FUTURE WORK

This paper summarizes the preliminary results of our investigation looking into using NMR to measure gas adsorption and absorption. As the investigation is preliminary, there is still a significant amount of work to complete. First, we will repeat the experiment on the shale sample, acquiring T_2 measurements at shorter intervals initially to get more data relating to absorption. We will then run the experiment for a week to determine whether more methane is adsorbed at later times. We will also acquire T_1-T_2 maps during this longer experiment to see if any changes in the maps over time could be used to distinguish absorption from adsorption. The ultimate goal of the work is to generate a gas isotherm using NMR, so we will repeat the experiment in the shale at several different pressures to generate the isotherm. Finally, we will acquire T_2 measurements on shales of different origins to investigate how the isotherms may vary with shale type.

REFERENCES

1. Alexander, T., Baihly, J., Boyer, C., Clark, B., Waters, G., Jochen, V., Le Calvez, J., Lewis R., Miller, C. K., Thaeler, J. and Toelle, B. E., "Shale Gas Revolution," *Oilfield Review,* (2011), **23**, 3, 40-55.

2. P5 Overburden Probe User Manual, Version 1, Oxford Instruments, Green Imaging Technologies.

3. Geo-Spec 2-75 User Manual, Version 1.8, Oxford Instruments.

4. GIT Systems and LithoMetrix User Manual, Revision 1.9, Green Imaging Technologies

5. Lu, X.-C., Li, F.-C., and Watson, A. T., "Adsorption measurements in Devonian shales," *Fuel*, (1995), **74**, 4, 599-603.

6. Gu, Z., Liu, W., Sun, W., Hu, Z., "NMR Response of Methane in Gas Shale," *Unconventional Resources Technology Conference*, August 1-3 2016, URTeC 2438441.

Tables and Figures

Core Sample	Sandstone (Carbon Tan 1)	Shale (Eagle Ford 1)
Origin	Utah, USA	Eagle Ford, Texas, USA
Core Diameter (cm)	2.51	3.81
Core Length (cm)	5.08	4.79
Bulk Volume (mL)	25.14	54.61
Dry Core Mass (g)	55.54	129.16
Pore Volume (mL)	4.10	2.60
Porosity (p.u.)	16.3	4.76

Table 1. Properties of rock samples.

Measurement	T_2	T_1-T_2
Recycle delay (ms)	750	1000
Tau (µs)	50	50
Number of Echoes	5000	5000
Number of Steps	N/A	30
Filter Width (kHz)	125	125
90º Pulse Length (µs)	7.5	7.4
180º Pulse Length (µs)	15.2	15.0

Table 2. Acquisition parameters for T_2 and T_1-T_2 measurements of sandstone (Carbon Tan 1) and shale (Eagle Ford-1).
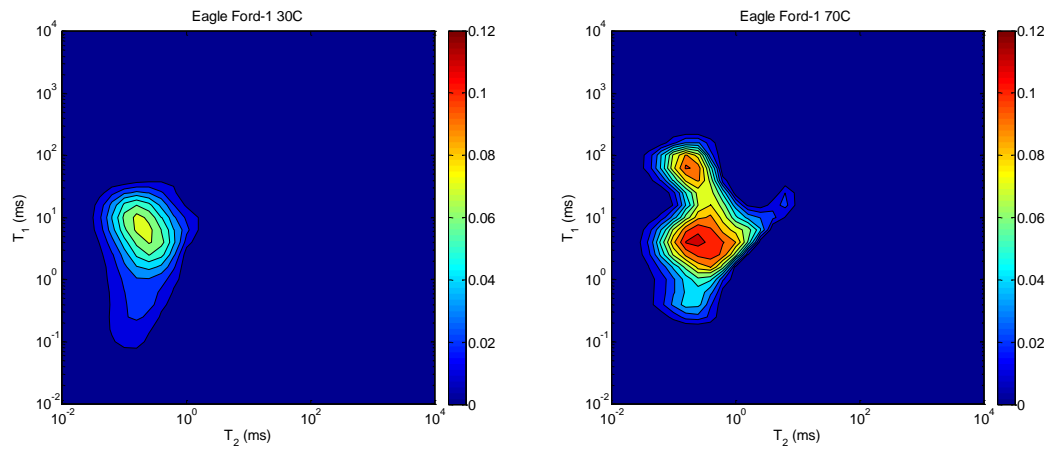
Figure 1. T_1-T_2 NMR maps for the as received shale sample (Eagle Ford 1) tested taken at 30ºC and 70ºC.
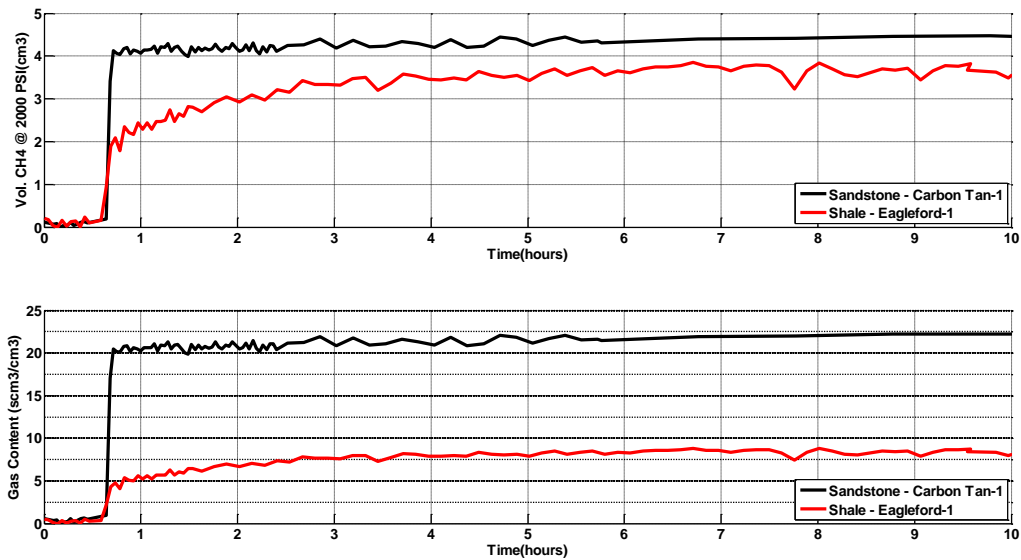

Figure 2. Volume of methane and total gas content as a function of time for shale sample (Eagle Ford 1).
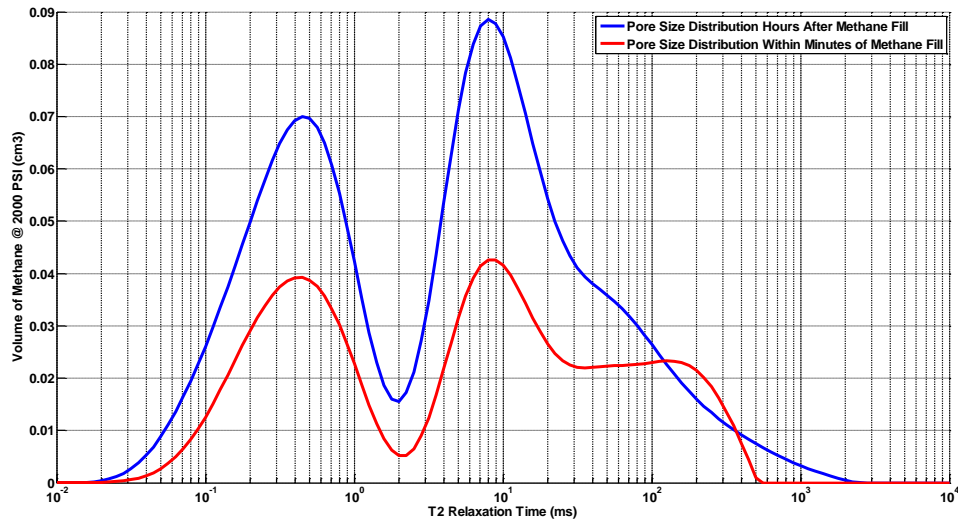
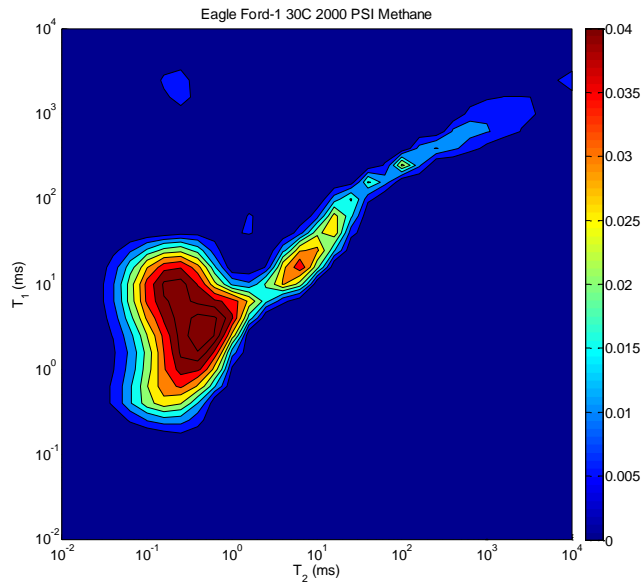Figure 3. Background subtracted T₂ spectra measured after introduction of methane to shale sample (Eagle Ford -1).

Figure 4. T_1-T_2 map recorded several hours after introduction of methane to shale sample (Eagle Ford -1).