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Measurement of Natural Gas Isotherms and Imaging Gas in Shale Using NMR

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Abstract

Objectives/Scope: 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. The goal of this work has been to employ NMR T_2 distributions to derive gas isotherms.

Methods/Procedures/Process: Gas isotherms are derived from NMR data as follows. First, the total gas content is derived from the distributions at a series of pore pressures. Next, the volume of absorbed gas is estimated using the pore volume of the rock and the Van der Waals gas equation. The pore volume of the rock was measured in a separate experiment using the fully water saturated core. The adsorbed gas content is then calculated by subtracting adsorbed gas content from the total gas content.

Results/Observations/Conclusions: The NMR method has been successfully employed to derive gas isotherms. With the success of the isotherm measurement via NMR, experiments have expanded to include imaging natural gas in rock cores as a function of time and position. These experiments are difficult as the density of natural gas is approximately 1400 times lower than water at ambient temperature and pressure leading to a significant decrease in the signal to noise ratio when imaging gas as compared to water. Nonetheless, these experiments are valuable for determining where in the core gas is located and how the gas fills the core over time (i.e. into cracks first followed by occupation of pores).

Applications/Significance/Novelty: 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 by crushing the sample and provide no information on the pore size distribution. The NMR method proves advantageous as the NMR analysis can be completed without destruction of the shale core. In addition, NMR pore distributions are obtained at each pore pressure as part of the experiment. These distributions can be further mined for information on adsorption versus absorption.

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 first, the reference cell is then 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.

Method

Two different shale samples were chosen for the study. The characteristic information on each rock studied is shown in Table 1.

Table 1.

Core Sample	BN 1	LHSV
Origin	Barnett	Lower Hainesville
Core Diameter (cm)	3.81	2.51
Core Length (cm)	4.79	2.57
Bulk Volume (mL)	54.61	12.9
Dry Core Mass (g)	129.16	-
Pore Volume (mL)	2.60	1.137
Porosity (p.u.)	4.76	8.80

Two similar experiments were performed, one on each sample.

Experiment 1:

Sample BN 1 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 sample was 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 sample at 500 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. These T_2 measurements were employed to retrieve the total gas content present in the rock as a function of time. Acquisition parameters for the T_2 measurements are shown in Table 2.

Table 2.

Measurement	T_2 , BN-1	T_2 , LHSV
Recycle delay (ms)	750	7500
Tau (μ s)	50	50
Number of Echoes	5000	5000
Filter Width (kHz)	125	125
90° Pulse Length (μ s)	7.5	9.31
180° Pulse Length (μ s)	15.2	18.88

Data acquisition and analysis of the T_2 data was achieved via Green Imaging Technologies software [4]. Pore volumes were determined using NMR volumes from T_2 measurements for the shale. Data analysis is outlined as follows.

- 1) Record background spectrum with 0 PSI CH_4 .
- 2) Record the T_2 distributions as a function of time. Repeat at different CH_4 pore pressures (500 psi increments).

- 3) Background subtract all T_2 distributions. Retrieve CH_4 signal in units of equivalent water signal.
- 4) Convert CH_4 signal to total gas content using hydrogen index of methane and bulk volume of rock. Hydrogen index was measured by filling a vessel of known volume with methane at different pressures and comparing its NMR signal to that of water in the same vessel. For each CH_4 pressure, plot total gas content as a function of time (Figure 3).
- 5) Use the total gas content after stabilization to create a plot of total gas content as a function of pressure – gas isotherm.
- 6) To retrieve the absorbed gas isotherm, use the pore volume of the rock (measured in step 8 with a 100% brine saturated rock) and the Van der Waals gas equation.
- 7) To determine the adsorbed gas isotherm, subtract the absorbed gas isotherm from the total gas content.
- 8) To determine pore volume of the sample the shale was pressure saturated with 2% KCl brine at 10000 psi in a pressure cell for three days. Pore volume is then determined from NMR T_2 data on the fully saturated sample. Experimental setup is shown in Figure 1.

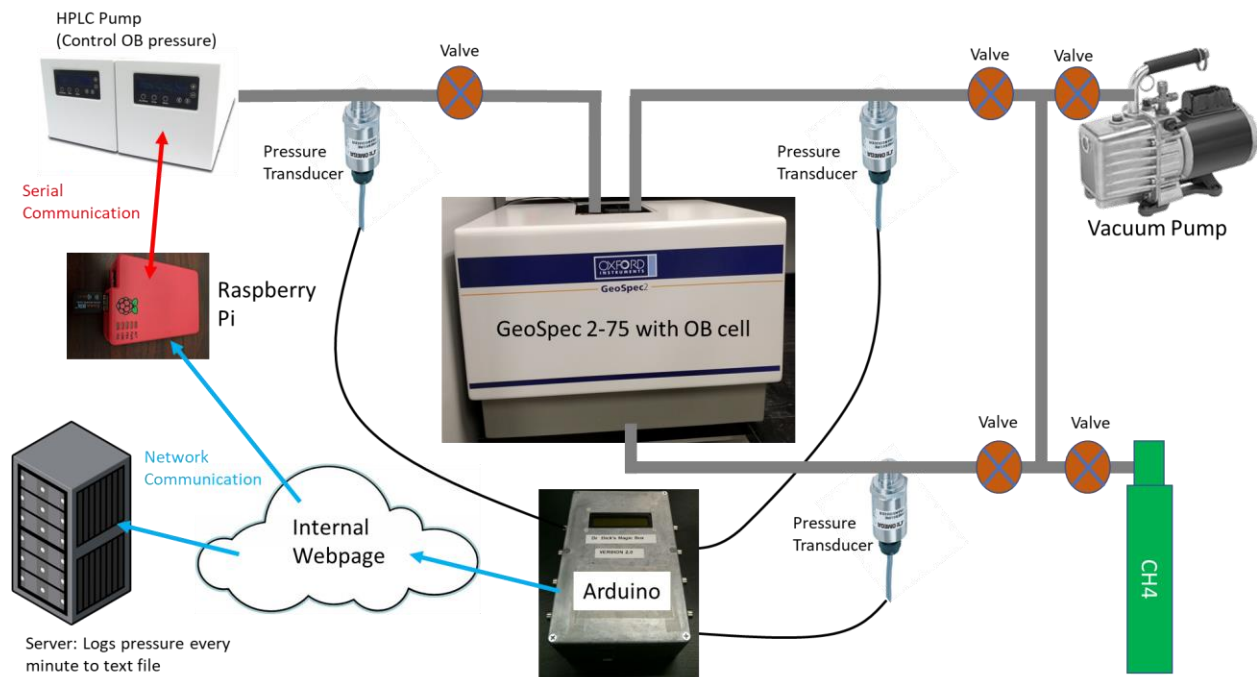


Figure 1. Experimental setup.

Experiment 2:

Ideally the sample should be a cylindrical core plug but due to difficulties in coring the shale sample, the sample was actually three fragments of irregular shape. Coring is an issue with most shale samples but nevertheless this experimental setup was proven to be successful even with irregularly shaped samples. The sample was placed in a Teflon holder (Figure 2). The holder and the sample were then placed into Oxford Instruments P5 overburden NMR probe [2] in an Oxford Instruments GeoSpec 2-75 rock core analyzer [3]. OB probe was then filled with methane at different pressures, no confining fluid was used. The rest of the procedure is the same as in experiment 1.

Both methods were successful in measuring gas isotherms but the second method was easier to implement experimentally. It eliminated the need to use a second pump and an additional fluid as confining fluid. It was also shown that it can be used on irregularly shaped samples as long as a suitable Teflon holder is designed to contain the sample and fill the empty space in the NMR OB probe. It is important that this holder be made out of NMR invisible material. The main difference in the two methods is that the second method had a lot of free gas present in the system due to the “dead space” in the probe which could not be filled. This was easily fixed by applying the T_2 cutoff to eliminate free gas signal from the data.

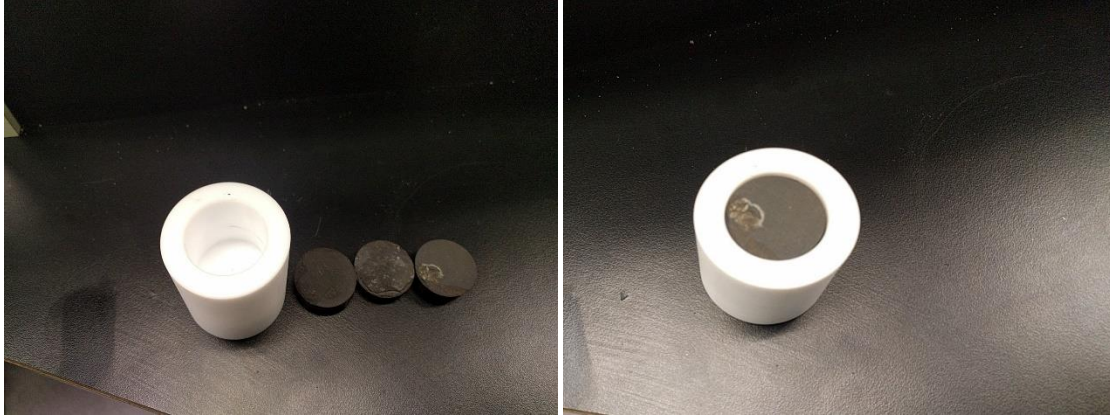


Figure 2. Teflon sample holder and fragmented LHSV shale sample.

Results

As mentioned above, the gas absorption/adsorption characteristics were studied for a shale. The high surface to volume ratio of the pores in the shale coupled with its higher organic content causes the shale to exhibit adsorption of methane. The first set of gas experiments were to record a series of T_2 scans as a function of time. 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) as a function of time.

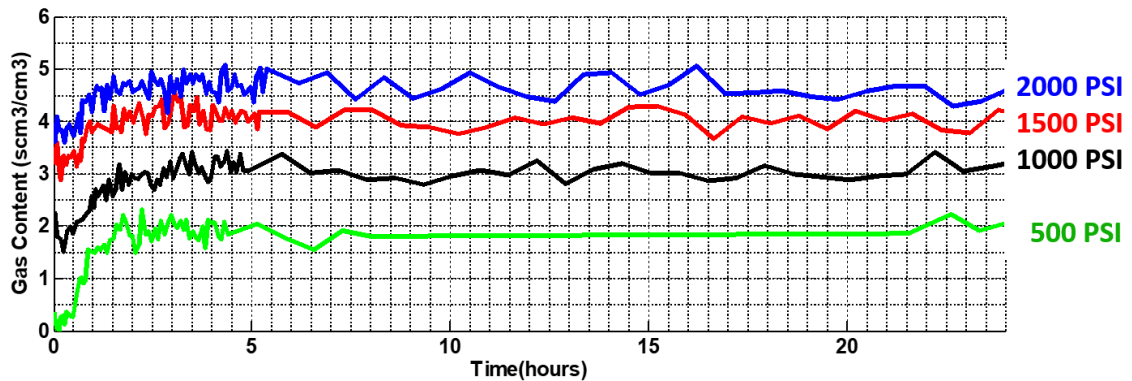


Figure 3. Volume of methane and total gas content as a function of time for shale sample BN 1.

Increase in gas content is evident over a period of several hours. After approximately 5 hours the shale has been filled to its pore volume. In order to retrieve the total gas content, the volume of methane (scm^3) at 2000 PSI (Figure 2) was converted to the volume of methane at standard temperature and pressure (15°C and 1 atm) using the Van der Waals gas equation (1). 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 $5 \text{ scm}^3/\text{cm}^3$ 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.

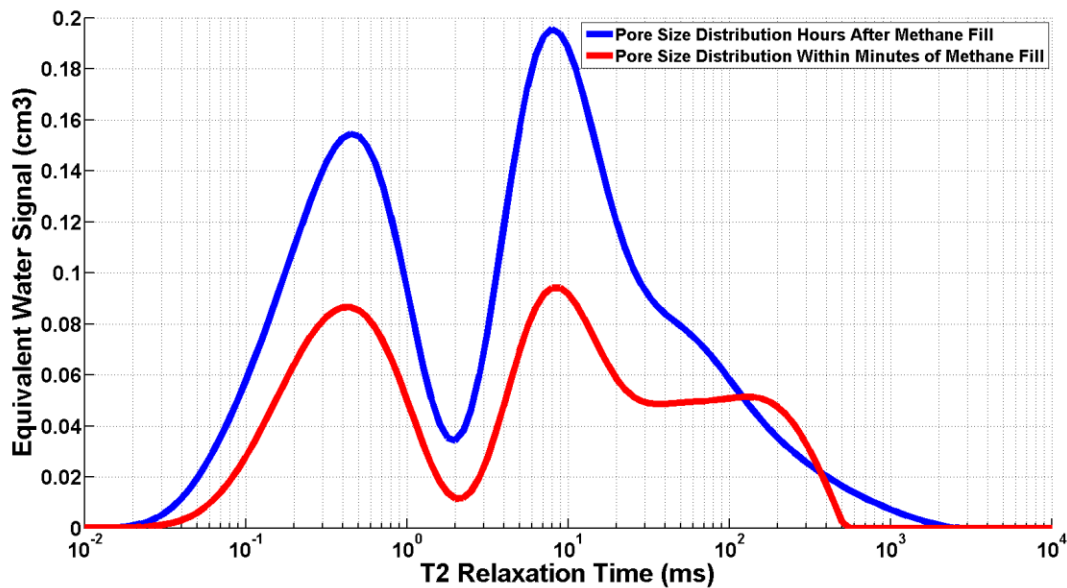


Figure 4. Background subtracted T_2 spectra measured after introduction of methane at 2000 psi to shale sample (BN-1).

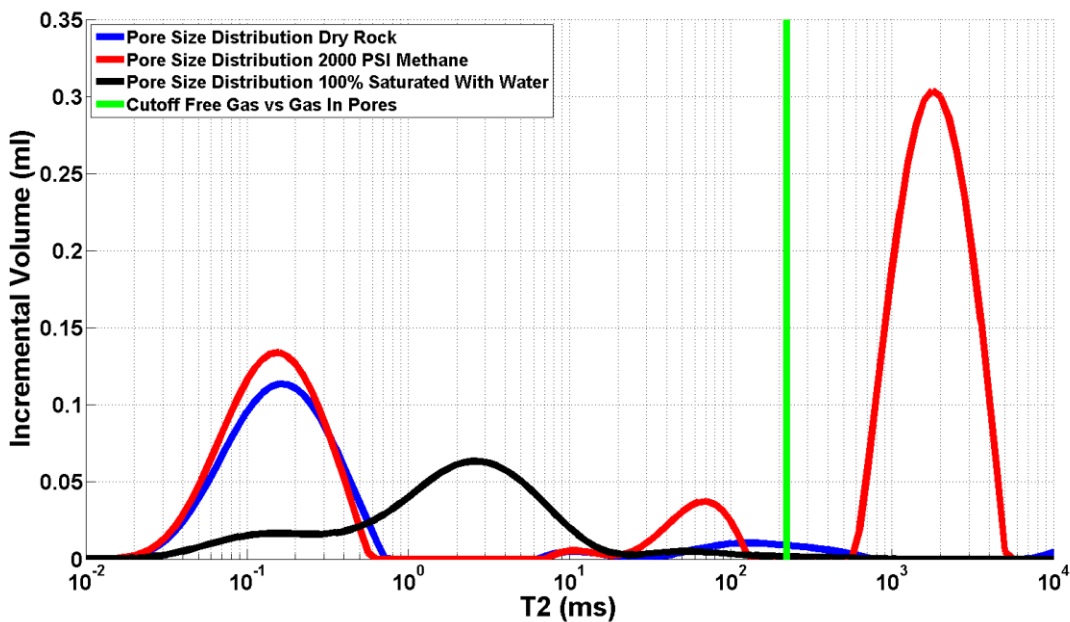


Figure 5. T_2 distributions of LHSV1 sample at different conditions. The green line at ~ 200 ms is the free gas cutoff line.

Figure 4 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. The blue spectrum was taken several hours after the introduction of methane. 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

by using T_2 data only, 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 5 shows similar information to figure 4. The main differences are, brine saturated data is included (black) and free methane is visible to the far right. Free methane has a long T_2 distribution so a cutoff value of 200 ms can be used to remove it. This is only an issue if the sample is irregularly shaped and if there's a significant amount of "dead space".

At this point, Van der Waals equation (1) was used to calculate the total amount of absorbed methane at each pressure.

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] \left(\frac{V}{n} - b \right) = RT \quad (1)$$

Where P is pressure, a is compressibility factor, n is number of moles, V is volume, b is volume correction, R is ideal gas constant and T is temperature. Total gas content is measured by NMR directly and amount of adsorbed gas is calculated as total gas minus absorbed gas.

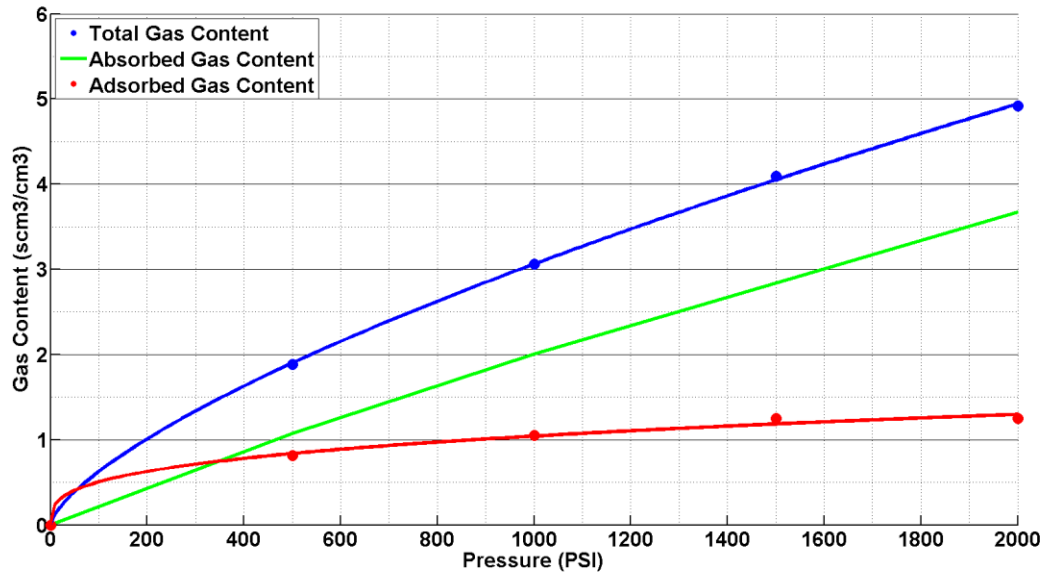


Figure 6. Methane isotherms for sample BN-1.

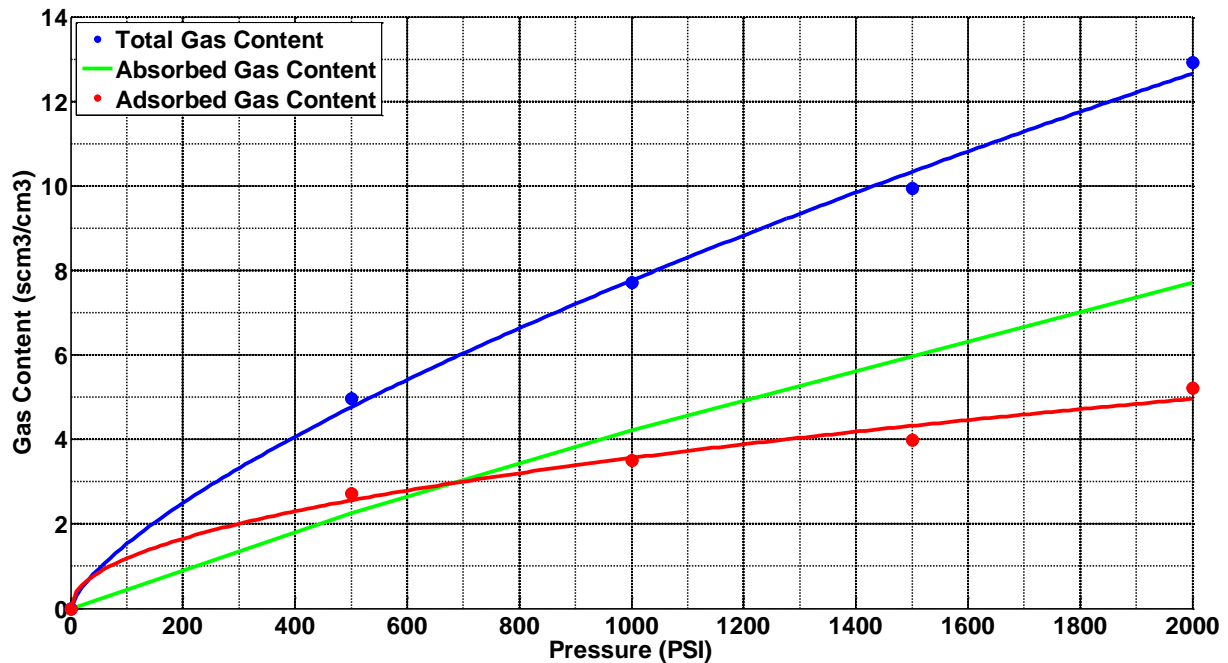


Figure 7. Methane isotherms for sample LHSV.

The gas isotherm derived for the rock samples tested are shown above. The absorbed gas content (green plot) is for the most part linear with pressure because as the pressure increases so does the amount of gas inside the pore volume. This linearity breaks down at higher pressures when the Van der Waals equation diverges from the ideal gas law. The adsorbed gas isotherm is shown in red. The amount of adsorbed gas increases rapidly at low pressures and levels out at higher pressures. This reflects the pore walls becoming saturated with gas as the pressure increases. Once a critical pressure is reached there is no more room for gas to adhere to the pore walls and adsorption will cease to occur. The total gas content gas isotherm (blue plot) is the sum of the adsorption and absorption isotherms. Each rock shows ~ 60% -40% absorption to adsorption ratio at 2000 psi which is consistent with other shales.

Discussion

The following lists the possible sources of error associated with the measurements performed in this study.

- Short NMR relaxation times. The fluids present in shale have very short NMR relaxation times. This is due to the small pore sizes and the solid like nature of some of the hydrogen. Some hydrogen will likely not be accounted for in the measurements due to their short lifetime and equipment limitations. For a T_2 measurement the first measured point is acquired after 0.1 msec. This means signals with T_2 shorter than this become increasingly difficult to quantify.
- Grain Loss. Samples are constantly losing grain mass as a result of handling. Depending on the sample, this can be a significant source of error although it is not expected for these samples.

Conclusions

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 a shale. Methane absorption and adsorption was observed in the shale. Two experiments were used for this study, one with using Flourinert as confining fluid to create overburden pressure and one with using methane both as confining and saturating fluid. Both experiments proved successful but the second experiment proved to be more robust and easier to implement. Second experiment also has the advantage that it can be performed on irregular shaped samples and cuttings.

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