Miscible Fluid Displacement in Rock Cores Evaluated with NMR T_2 Relaxation Time Measurements

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Abstract

NMR T_2 relaxation times for fluids in a porous medium are in principle proportional to the relevant occupied pore size. Here we exploit this relationship to monitor the pore size distribution occupied by methane (CH_4) at 100 bar and room temperature in both sandstone and carbonate rock cores whilst it is displaced by a range of miscible fluids: carbon dioxide (CO_2), nitrogen (N_2), nitrous dioxide (N_2O) and helium (He) respectively. The process is then reversed with methane being used to displace these injected fluids. Time resolved T_2 distributions are thus able to probe the preference of the methane for smaller or larger pores during these core flooding processes. In the cases of CO_2 and N_2O , methane was found to preferentially occupy larger pores during both injection and displacement for both rock types. In the case of N_2 , no significant preferential pore size occupation was evident whilst in the case of He, methane preferentially occupied smaller pores. For the fluids used in this work, preferential occupation of comparatively smaller pores during these displacement experiments correlated with a comparatively greater surface adsorption capacity.

1. Introduction

Complete fluid miscibility means that two or more fluids fully dissolve in each other in all proportions forming a homogeneous mixture.¹ Such phenomena are ubiquitous in both nature and industry;² the miscibility of fluids in a host porous medium has been studied in several fields, an example being miscible gas displacement in soil.^{3, 4} Miscible displacements in capillary tubes (effectively a simplified porous medium) between fluids with different viscosities have been extensively studied.^{5, 6} The miscible injection of CO₂ into oil-containing rocks is widely considered to enable enhanced oil recovery (EOR).⁷⁻¹¹ In this case, the miscible CO₂ serves to both decrease the oil viscosity and reduce its interfacial tension with other fluid phases present, both of which serve to improve oil recovery. Enhanced gas recovery (EGR) involves the injection of CO₂ into a natural gas reservoir in order to increase the recovery of the natural gas whilst sequestering the CO₂.¹² There have however only been a few field trials of EGR; this is effectively a consequence of the complete miscibility of the injected CO₂ and the natural gas which could result in highly undesirable early breakthrough of the CO₂ at the natural gas production wells. Understanding the kinetics of these ubiquitous porous media mixing processes (which occur at the pore scale) is one of the motivations of the current study. In particular, we examine pore-scale mixing processes in rock cores during flooding (displacement) processes involving methane and a range of other miscible fluids.

Nuclear magnetic resonance (NMR) T_2 relaxation times are widely employed to evaluate fluid behavior in porous media at the pore scale.¹³⁻¹⁵ Such T_2 distributions can be correlated with pore size distribution in porous media, providing consistent results when compared to, for example, mercury injection pore (throat) size measurements.^{16, 17} NMR T_2 studies have previously been widely used to study miscible displacement processes in rock cores. Muir et al.¹⁸ measured the T_2 of H₂O in multiple rock cores during D₂O flooding and found quite variable T_2 distributions suggesting different pore occupancies were produced by the flooding process in the various rock samples. Wei et al.¹¹ used T_2 measurements to monitor the injection of CO₂ into oil-saturated rocks, which revealed preferential removal of the oil from larger pores. Such NMR T_2 measurements were extended to include an axial imaging dimension by Afrough et al.,¹⁹ who also considered differences in pore-scale displacement between oil and supercritical CO₂. Shikhov et al.²⁰ observed that the T_2 value of air-saturated *n*-decane increased when the fluid was displaced by a miscible

air-free *n*-decane in a carbonate core plug, but that air-saturated water and air-free water had the same T_2 value in the rock sample, which was attributed to the rock water-wettability.

Recently we showed how NMR T_2 measurements could be employed to monitor the pore size occupation characteristics of methane, which exclusively delivers the NMR signal during CO₂-CH₄ displacements, in both a Berea and a carbonate rock core plug.²¹ In the current work, we extend these core flooding processes to a range of miscible gas combinations: CH₄-CO₂, CH₄-N₂O, CH₄-He, and CH₄-N₂. NMR T_2 measurements were used to explore the pore sizes occupied by the CH₄ as it was displaced from, and then injected into, either a sandstone or a carbonate rock core. The adsorption of these various fluids on the rock cores was also measured independently where possible. The sorption capacities determined for each gas were correlated with the T_2 values observed during the core-flooding tests, and thus were correlated by proxy with the pore sizes occupied by the methane content during the core flooding processes.

2. Background

2.1 Pore-scale fluid characterization using NMR T_2 measurements

NMR T_2 relaxation time has been widely employed to characterize fluids in porous media.²¹⁻²⁵ Three mechanisms contribute to this T_2 relaxation as summarized in Equation (1):²⁵

$$\frac{1}{T_2} = \frac{1}{T_{2,Bulk}} + \frac{1}{T_{2,Surf}} + \frac{1}{T_{2,Diff}}, \quad (1)$$

where $T_{2,Bulk}$ is the bulk fluid transverse relaxation time, $T_{2,Surf}$ is the additional NMR signal transverse relaxation due to interactions with the surface of the porous medium, and $T_{2,Diff}$ is additional transverse relaxation due to diffusion in any magnet field gradient – these occur in rock cores due to magnetic susceptibility differences between the contained fluid and the solid rock material.²⁶

When both sufficiently short echo times in the CPMG pulse sequence used to measure T_2 and a sufficiently weak static magnetic field (magnetic susceptibility induced gradients scale with the static magnetic field) are employed, equation (1) can be truncated as follows:^{21, 27, 28}

$$\frac{1}{T_2} \approx \frac{1}{T_{2,\text{Bulk}}} + \frac{1}{T_{2,\text{Surf}}}, \quad (2)$$

Equation (2) thus assumes that background magnetic field gradients due to susceptibility differences between the rock matrix and the pore fluid are minimal.^{24, 29, 30} Relaxation in the fast-diffusion regime occurs when the Brownian motion of fluid molecules is sufficiently rapid so as to sample all parts of the pore space at least several times during the CPMG train time (as discussed in more detail in section 4.1) and it can be assumed that a moderately homogeneous surface relaxivity is present throughout the pore space.^{31, 32} Based on these assumptions, the surface relaxation rate $1/T_{2,\text{Surf}}$ of the fluid in a pore in the fast-diffusion limit can be expressed as:^{22, 29, 33}

$$\frac{1}{T_{2,\text{Surf}}} = \rho_2 \left(\frac{S}{V} \right), \quad (3)$$

where ρ_2 is the surface relaxivity, S is the contact area of the fluid and pore surface, and V is the pore fluid volume. The pore size can be approximated based on Equation (3) assuming a spherical pore geometry,^{25, 34, 35} in which case the representative pore radius, R , is approximated as:

$$R \approx 3\rho_2 T_2, \quad (4)$$

on the assumption that $T_{2,\text{surf}} \ll T_{2,\text{bulk}}$. The mean values for ρ_2 , as reported in the literature, are 18.2 $\mu\text{m/s}$ and 9.6 $\mu\text{m/s}$ for water saturated Berea sandstone and Silurian dolomite carbonate rock samples, respectively,³⁶⁻³⁸ as are used in the work presented here.

2.2 Gas adsorption capacity in rocks

Adsorption is the adhesion of fluid molecules onto a surface³⁹ at a concentration which exceeds that in the bulk. Adsorption can be physisorption, chemisorption, and/or electrostatic attraction⁴⁰ and in the context of porous media is ubiquitous across a range of processes including water purification and various biochemical and gas separation processes.^{39, 41} In the case of enhanced oil recovery (EOR), the adsorption of injected surfactant solutes on the rock surface can severely compromise the efficacy of the process. In the case of enhanced gas recovery (EGR), adsorption of the injected CO_2 onto the rock surfaces serves to marginally increase the storage capacity of the formation but can also serve to change the process by which the CO_2 displaces the

methane.⁴² In the current work the adsorption capacities of the gases employed (CH₄, CO₂, N₂, He) were measured and compared to the displacement process observed as the core flooding experiments were performed between fluid pairs (which all involved methane). In this manner the influence of competitive adsorption on methane pore size occupation (as revealed by the NMR T_2 measurements) during the core flooding process was explored.

3. Experimental Section

3.1 Materials

High purity CO₂ ($\geq 99.995\%$), CH₄ ($\geq 99.995\%$), He ($\geq 99.999\%$) and N₂ ($\geq 99.99\%$) were supplied by Coregas Pty Ltd (WA, Australia). N₂O ($\geq 99.8\%$) was purchased from BOC Ltd (NSW, Australia). Table 1 lists the fluid properties at the experimental pressure, 100 bar, and temperature, 20 °C employed in the core flooding experiments. Fluorinated oil (FC-40), which provides no ¹H NMR signal, was purchased from 3M (MN, USA) and used to apply confining pressure to the rock cores. A Berea sandstone and a carbonate (Silurian dolomite, Kocurek industries, TX, USA) core plug were employed in the core flooding tests. The Berea sandstone core plug has a length of 7.6 cm, a diameter of 2.5 cm, a permeability of 100 mD, and porosity of 0.20. For the carbonate core plug, these parameters were 7.7 cm, 2.5 cm, 70 mD and 0.17, respectively.

3.2 Apparatus

Figure 1 shows a schematic of the NMR apparatus assembly employed in this work. An Oxford Instruments Maran Ultra spectrometer (UK) was used with a 0.3 tesla permanent magnet (corresponding to a ¹H NMR frequency of 12.9 MHz). ¹H NMR signal was only detected from CH₄, with all the other fluids being NMR inert. An NMR compatible core holder (FCH-1.0: S2 Glass and PEEK, Core Laboratories, OK, USA) was used to accommodate the rock core plugs. Three syringe pumps (260D Teledyne ISCO, NE, USA, labelled 2, 3 and 4 in Figure 1) were employed for the displacing fluid phase, displaced fluid phase and back-pressure control respectively in the core flooding processes. A vacuum pump (949-9315 Agilent Technologies, Torino, Italy) was used to evacuate the rock core samples and the associated tubing. A hydraulic

pump (Pump 1 in Figure 1; High Pressure Equipment Company, PA, USA) filled with the fluorinated oil (FC-40) was used to apply the confining pressure to the rock cores via the core holder.

A gravimetric sorption analyzer (Rubotherm, Germany) was employed to measure the various gas adsorption behaviours on both the Berea and carbonate rock cores. This type of instrument was designed to measure the adsorption of gases on a porous sample and the density of the gas surrounding the porous sample simultaneously and has been widely used for accurate sorption measurements.^{43, 44} The measurement system operates over the temperature range from 274.15 to 423.15 K with pressures up to 35 MPa. The temperature of the measuring cell was measured with a 100 Ω platinum resistance thermometer and the resistance of the thermometer was measured by a digital multimeter (Millik Precision Thermometer, Isotech, UK). The expanded uncertainty of the temperature-measurement chain was estimated to be 0.3 K over the studied temperature range. The pressure was measured with a vibrating quartz-crystal-type transmitter (range up to 41.3 MPa, Paroscientific, USA, type: 46K-HH) with an uncertainty of 0.01% of full scale, i.e., 4.1 kPa. The weights of the porous samples were determined with an analytical balance (accurate to 1 μ g) via a magnetic-suspension coupling.

3.3 Experimental procedure

The rock core plugs were initially dried at 120 °C for one week to remove as much trace water content as possible before being loaded into the rock core holder. This was positioned in the magnet chamber and connected to the pumping system as detailed in Figure 1. An effective confining pressure of 50 bar was applied to the rock core via the confining fluid; this effective pressure was maintained throughout the experimental protocol employed. The vacuum pump was then used to reduce the absolute pressure of the system to 0.1 bar to minimise the air content of the core plug. Following this, methane was flooded into the rock core and the pressure elevated to 100 bar in gradual increments at a constant temperature of 20 °C. Pressure in the system was maintained at 100 bar using the back-pressure control pump (Number 4 in Figure 1). The rock core was orientated in a vertical direction in the magnet system. Consequently, in order to eliminate unstable buoyancy effects, the displacing fluid (CO₂, N₂O, He, or N₂) was injected into the rock core from beneath if it was more dense than methane and from above if it was less dense

than methane. Density and viscosity for the various fluids are summarised in Table 1. Following the displacement of all the recoverable methane from the rock core, methane was then re-injected back into the rock core in the opposite direction, in the process displacing the previously injected fluid (CO_2 , N_2O , He, or N_2).

All core flooding was performed at a volumetric flow rate of 0.1 ml/min. This flow rate corresponds to a superficial velocity of 3.4×10^{-6} m/s in the core, which falls within the range of velocities reported as typical for fluid flow in reservoirs⁴⁵⁻⁴⁷ and is thus essentially comfortably in the creeping flow regime.^{48, 49} For the case of methane being displaced by the other fluids, the viscosity ratio ($M = \mu_{\text{injected}}/\mu_{\text{displaced}}$) is always greater than 1, in which case piston-like displacement is expected.^{47, 50, 51} Conversely when methane is reinjected back into the cores, displacing the other fluids, M is consistently less than 1 and hence viscous fingering is possible. During the core flooding processes, conventional ^1H NMR CPMG measurements⁵² of T_2 distributions were measured for the methane content every 224 s. In the individual CPMG measurements, a total of 1500 echoes were acquired with an echo time (TE) of 400 μs whilst averaging over 32 repetitions (these were required given the comparatively low SNR of the methane content).

After all the rock core flooding experiments were completed, a small rock disk with a diameter of 1.2 cm and a length of 1.5 cm was cut from each of the Berea and carbonate core plugs for gas adsorption measurements. These were performed for all fluids considered in the core flooding experiments with the exception of N_2O which was found to be incompatible with the gravimetric sorption analyser possibly on account of it being a strong oxidizer.⁵³ All adsorption measurements were conducted at a temperature of 20 °C with pressure decreasing in steps from 100 bar to 0.1 bar. An equilibration time of between 30 and 60 minutes was allowed after a change in pressure.

The net adsorbed mass m_{net} on the rock sample was calculated using:^{54, 55}

$$m_{\text{net}} = m_{\text{fluid}}^* - m_{\text{vac}}^* + \rho_{\text{fluid}} \cdot V_{\text{C}} . \quad (5)$$

In equation (5), $m_{\text{fluid}}^* = (W_1 - W_0)_{\text{fluid}}/\alpha$ and $m_{\text{vac}}^* = (W_1 - W_0)_{\text{vac}}/\alpha$, where W_0 and W_1 are the readings of the magnetic-suspension balance at the positions ZP (tare or zero position) and MP (measuring position, where the sample container with the rock sample is lifted up and weighed),

respectively; $\alpha = (1 - \rho_{\text{air}}/\rho_{\text{calib}})^{-1} \approx 1.000150$ is the balance calibration factor with ρ_{air} being the air density in the laboratory and ρ_{calib} being the density of the calibration mass in the balance, and the subscripts ‘vac’ and ‘fluid’ denote that the measurements were conducted with the cell evacuated and filled with the relevant fluid (gas or supercritical fluid, but not liquid), respectively. Additionally, ρ_{fluid} is the density of the fluid and V_C is the volume of the sample container. In other words, m_{vac}^* and m_{fluid}^* are the weights of the sample container with the rock sample at vacuum and filled with the relevant fluid respectively, while $\rho_{\text{fluid}} \cdot V_C$ is the buoyancy force on the sample container. If adsorption occurs on the rock sample, m_{fluid}^* also includes the weight of the adsorbate. For a sample which does not adsorb the relevant fluid (normally this is helium), the volume of the skeleton of the sample V_S can be calculated using:

$$V_S = -m_{\text{net}} / \rho_{\text{fluid}}, \quad (6)$$

In practice, V_S was regressed as the slope of a series of $(\rho_{\text{fluid}}, m_{\text{net}})$ points measured at the same temperature but at different pressure values for helium. The excess adsorbed mass m_{ex} and absolute adsorbed mass m_{abs} can then be calculated by:

$$m_{\text{ex}} = m_{\text{net}} + \rho_{\text{fluid}} \cdot V_S \quad (7)$$

$$m_{\text{abs}} = m_{\text{ex}} + \rho_{\text{fluid}} \cdot V_{\text{sorp}} = m_{\text{ex}} \cdot \rho_{\text{sorp}} / (\rho_{\text{sorp}} - \rho_{\text{fluid}}) \quad (8)$$

where V_{sorb} and ρ_{sorp} are the volume and the density of the adsorbate, respectively, with $m_{\text{abs}} = V_{\text{sorb}} \cdot \rho_{\text{sorp}}$. The value ρ_{sorp} was estimated to be the saturated liquid density at the triple point for carbon dioxide and at the standard boiling point pressure for the other components, these were obtained from the software package REFPROP 10.0.⁵⁶ The sorption capacity q of the rock for the adsorbate gas is then expressed by:

$$q_i = (m_i / M_{\text{fluid}}) / m_S, \quad (i = \text{net, ex, or abs}) \quad (9)$$

where M_{fluid} is the molar mass of the investigated fluid and m_S is the mass of the rock sample.

4 Results and Discussion

4.1 Influence of Transport Processes on T_2 Measurements

Figure 2 shows the T_2 relaxation time distributions for CH_4 as a function of time in the Berea core plug for all eight core flooding scenarios considered. Equivalent data are shown in Figure 3 for the case of the carbonate core plug. Systematic variations are evident in the T_2

distributions observed during the core flooding process. However before discussing these data in detail, the effect of transport (flow and diffusion) on these T_2 measurements is first considered. Specifically, a pertinent consideration in this respect is the extent of mixing of the methane fluid with the other fluid during core flooding over the following time-scales: the echo time of the CPMG sequence (400 μ s), the time for acquisition of a CPMG train (0.6 s), the total time for acquisition of a T_2 measurement (224 s) and the mean residence time in the rock core (64 minutes assuming the extreme case of piston-like displacement during core flooding for the 7.7 cm long core).

In Figure 4 the displacement length-scales of methane due to diffusion ($(6.D.t)^{0.5}$) and velocity ($v.t$) are plotted as a function of time; v corresponds to an interstitial velocity of 2×10^{-5} m/s which was calculated from the imposed volumetric flowrate of 0.1 ml/min together with the porosity and cross sectional area of the carbonate core. The value of D corresponds to the measured value for the self-diffusion coefficient of methane in an equimolar mixture of CH_4 and CO_2 (4×10^{-8} m²/s) at the applied experimental conditions of 100 bar and 20 °C in the carbonate rock core. This value was determined using a standard pulsed field gradient (PFG) NMR measurement.⁵⁷ This does not deviate significantly from the values corresponding to pure methane (4.7×10^{-8} m²/s) or 3 wt% methane in CO_2 (3.8×10^{-8} m²/s) at similar conditions in terms of the following discussion. The diffusion length-scales presented in Figure 4 are indicative of the extent of local mixing occurring over the various timescales summarized above. There are however two forms of relevant mixing: mixing within the methane gas in terms of the distance (and hence volume of pore space) it samples due to self-diffusion and mixing of the injected methane with the nascent CO_2 at their respective interface due to binary diffusion.

In terms of intra-methane mixing, for the echo time of the CPMG T_2 measurements (400 μ s), the diffusion length-scale is ~ 10 μ m and completely dominates over the length scale associated with flow. The diffusion length scale is comparable with the average size of the pores for the two rock samples considered; as reported previously²¹ these are 6 μ m and 16 μ m for the Berea sandstone and carbonate respectively. With respect to the time-scale of the full CPMG train (0.6 s), Figure 4 shows that diffusion again dominates the transport process and results in an effective mixing length-scale of ~ 400 microns. This comfortably exceeds the mean pore sizes of both rock cores and represents the minimum amount of local averaging with respect to the reported pore size

distributions. However each measurement of a T_2 distribution via the CPMG sequence occurs over 224 s, due to required signal averaging. On this time scale, displacements due to both flow and diffusion are comparable and correspond to ~ 7 mm (which corresponds to 1000s of pores for both rock types). This represents the maximum length-scale over which local averaging will occur with respect to the reported pore size distributions. Thus when interpreting the pore size distributions shown in in Figures 2 and 3 and discussed below it is necessary to consider that they represent the pore size as averaged over local domains up to 7 mm in extent. To explore any effect of flow on the CPMG measurements, Figure 5 shows the T_2 distributions as determined using the CPMG pulse sequence for CH_4 in the Berea core plug at 100 bar and 20 °C both without and with flow at a rate of 0.1 ml/min. The distributions are identical and reproducible (as shown via repetition of the measurements in Figure 5), indicating that flow has no discernable effect on the measured T_2 relaxation times.

In terms of mixing between the methane and the injected fluid due to binary diffusion, an additional length-scale corresponding to the mean residence time in the rock cores should be considered as core flooding occurs. For the mean residence time of 64 minutes, this correspond to a diffusive length-scale of 3 cm, which represents a substantial portion of the 7.7 cm long rock core. This of course assumes equivalence between self-diffusion and Fickian binary diffusion and also assumes that diffusive processes dominate flow-induced dispersion (which is the case for the low velocities employed). Nevertheless it does collectively indicate that the pore size distributions discussed below represent pores in which both full or partial methane occupation occurs (weighted according to methane mole fraction) and where the ratio of partial to full methane pore occupation progressively increases during the core flooding process.

4.2 Estimate of pore size distributions

Returning to Figure 2 and 3, these T_2 data were converted to pore size distributions using Equation 4. As discussed above, these data are weighted by the methane molar density (in all pores where methane is located) and represent local pore size averages over a distance of up to 7 mm.

Figure 2(a) shows that during the displacement of CH_4 by CO_2 flooding, the T_2 distribution signal intensity gradually decreased and the main T_2 peak value increased from about 25 ms to 45

ms. This increase of T_2 relaxation time is consistent with the residual CH_4 preferentially occupying larger pores compared to smaller pores during this CO_2 flooding process. The magnitude of these T_2 values (25 and 45 ms) are significantly smaller than those of the bulk fluids (measured T_2 values of bulk CH_4 ($y_{\text{CH}_4} = 1$) and a mixture of CH_4 and CO_2 ($y_{\text{CH}_4} = 0.52$) are 1.37 s and 1.39 s respectively) meaning that the simplification of equations (3) and (4) is valid: surface relaxation dominates the T_2 of CH_4 in the rock. In contrast in Figure 2(b), the T_2 probability distribution gradually increased as methane was flooded back into the sandstone core, as expected. This occurred primarily via smaller pores as the peak T_2 value was seen to gradually decrease. The process appeared to be relatively symmetrical with CO_2 consistently appearing to preferentially occupy smaller pores. In Figure 2(c) and (d), similar behaviour was observed as N_2O was flooded into a methane-saturated core and the process was then reversed. N_2O showed a greater affinity for smaller pores compared to CH_4 . Contrary to this behaviour, in the case of He being used to displace methane from the sandstone rock core (Figure 2(e)), the T_2 peak value is observed to decrease from 27 to 17 ms. This is consistent with the methane preferentially occupying smaller pores relative to He. The process was reversible as is evident in Figure 2(f). Finally when N_2 was used to displace methane and vice-versa (Figure 2(g) and (h)) virtually no change in the T_2 peak value was observed (~25 ms) in both core flooding directions indicating no clear preferential pore size occupation for these two fluids. We caution against over-interpretation in subtle variations in the minor T_2 peaks between samples and fluids as these are susceptible to the data inversion process applied.

In Figure 3, similar variations of T_2 relaxation time distribution of CH_4 in the carbonate core were observed as in the Berea Sandstone core. The T_2 peak values shifted to longer relaxation time when the CH_4 concentration y_{CH_4} decreased during CO_2 or N_2O flooding (Figure 3(a-d)) in carbonate. During the processes of He flooding (Figure 3(e-f)) in carbonate, this T_2 peak shifted to shorter values (Figure 3(e-f)) which is consistent with the results for Berea sandstone and there was no observed variation in mean T_2 for the case of N_2 (Figure 3(g) and (h)).

Figure 6 shows the T_2 logarithmic mean ($T_{2\text{LM}}$) of CH_4 in Berea plotted as a function of CH_4 fraction (y_{CH_4}) during the core flooding processes. The mean pore radii estimated based on Equation (4) are also shown. The equivalent data for the carbonate core are shown in Figure 7.

This quantitative data is consistent with the discussion above regarding Figures 2 and 3: In the two rocks, T_{2LM} decreased significantly when y_{CH_4} increased in the CH_4 - CO_2 and CH_4 - N_2O core flooding processes, but increased slightly when y_{CH_4} increased in the CH_4 -He experiments. T_{2LM} of CH_4 did not change significantly during the CH_4 - N_2 flooding processes. In most cases the core flooding process was reversible (in terms of the measurements presented in Figures 6 and 7). Some evidence of hysteresis was evident for CH_4 and CO_2 in the case of the Berea sandstone and a limited amount for CH_4 and N_2 in the case of the carbonate core. This was reproducible; whilst we do not have an adequate explanation at present, this will be explored as part of intended future work.

4.3 Gas adsorption measurements

The observed differences in preferential pore size occupation by the methane during the core flooding process is consistent for fluid pairs across the two rock types. In Figures 2, 3, 6 and 7, the observed changes of T_2 relaxation times as core flooding proceeded were assigned to the different affinities of the gases to pore size. Although the reasons for these different affinities has not been determined, it is possible that they are related to the adsorption capabilities of the various fluids used in this work. Figure 8 shows the absolute adsorption capacity, q_{abs} , of the Berea core plug for CO_2 , CH_4 , and N_2 measured using the gravimetric sorption analyser. These data are consistent with literature, in which the relative fluid adsorption capacities can be ranked as follows: $CO_2 \approx N_2O > CH_4 > N_2 > He$.^{42, 58-63} The adsorption capacities of CO_2 and N_2O are normally much higher than that of CH_4 , which usually has a slightly higher adsorption capacity than that of N_2 .^{58, 59, 61} The adsorption capacity of He is very low and is commonly assumed to be negligible.^{58, 60, 64} The same order of adsorption capacities for the respective fluids was observed for the carbonate rock cores, this data can however only be treated as qualitative as the measured q_{abs} was of the order of 0.001 mmol/g which is comparable to the measurement uncertainty.

In the case of CH_4 - CO_2 as well as CH_4 - N_2O , the greater affinity of these fluids for the rock surface is at least consistent with their preferential occupation of smaller pores and the preferential invasion of the porous medium by the methane via larger pores. Similarly the greater affinity of the methane for the pore surface relative to helium is at least consistent with its invasion of the rock cores preferentially via the smaller pores. Similar affinity for nitrogen and methane is then also consistent with the observation of little pore size preference during the relevant core

flooding processes. This intriguing correlation will be explored further via a wider suite of fluids, process conditions and porous media types. Future work will also focus on further assessment of the correlation of the values of T_2 to an approximate quantitative pore size – specifically we will further define the relaxation regime occupied by these high pressure liquid and supercritical fluids; ^{28, 61, 62} preliminary analysis suggests they are consistently just within the short-time regime where equations 2 and 3 are broadly valid.

5 Conclusion

In this study, NMR T_2 relaxation times were acquired during CH_4 displacement/flooding with CO_2 , N_2O , N_2 , and He in both Berea sandstone and carbonate core plugs to reveal pore scale fluid behaviors during these core flooding processes. The T_2 increase when the CH_4 fraction decreased suggests the preferential occupation of larger pores by the CH_4 in both $\text{CH}_4\text{-N}_2\text{O}$ and $\text{CH}_4\text{-CO}_2$ mixtures. In the $\text{CH}_4\text{-N}_2$ mixture, significant T_2 lifetime changes were not observed during core flooding processes suggesting that CH_4 may not have much affinity for a specific pore size relative to N_2 . The increase of T_2 values with the increase of CH_4 fraction during displacement of He is consistent with a preference for smaller pores by the CH_4 . The different affinities of these gases for smaller pore sizes are consistent with their measured relative adsorption capacities: $\text{CO}_2 > \text{CH}_4 > \text{N}_2 > \text{He}$. The NMR T_2 results are also consistent with literature data suggesting that CO_2 and N_2O have similar relative adsorption capacities. These data serve as robust validation case studies for the development of pore-scale EGR simulations of miscible fluid displacements.

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Table 1 Properties of the fluids at 100 bar and 20 °C

Item	Viscosity ($\mu\text{P}\cdot\text{s}$)	Density (mol/L)	Density (g/L)	Phase
CH ₄	13.68	4.88	78.31	Supercritical
CO ₂	82.52	19.46	856.30	Liquid
N ₂ O	80.12	19.37	852.40	Liquid
He	19.97	3.92	15.68	Supercritical
N ₂	19.73	4.10	114.84	Supercritical

Sources of data: Default models in REFPROP 10.0⁵⁶

Fig. 1 Schematic of experimental apparatus employed for the NMR T_2 core flooding measurements using the example of CH_4 flooding to displace N_2O in the rock core plug sample ('top' to 'bottom' direction). For N_2O flooding to displace CH_4 , a 'bottom' to 'top' direction was employed and the relative positions of core holder inlet and outlet were reversed. The same apparatus was used for the core flooding experiments between CH_4 and the other fluids (CO_2 , He, and N_2) - the flooding direction was always selected such that the more dense fluid occupied the bottom of the core plug being studied.

Fig. 2 T_2 relaxation time distribution of CH_4 in the Berea sandstone sample during different core flooding processes, together with the estimated pore size distribution (top horizontal axis). The

red arrows indicate the direction of the T_2 probability change with time. Distributions are normalised against the maximum portability value at full methane saturation.

Fig. 3 T_2 relaxation time distribution of CH_4 in the carbonate sample during different core flooding processes, together with the estimated pore size distribution (top horizontal axis). The red

arrows indicate the direction of the T_2 probability change with time. Distributions are normalised against the maximum portability value at full methane saturation.

Fig. 4 CH₄ molecular diffusion length-scale and fluid flow length-scale during core flooding at a volumetric rate of 0.1 ml/min for the carbonate rock sample. The diffusion estimate is based on an equimolar mixture of CH₄ and CO₂. Dashed vertical lines indicate relevant experimental times as discussed in the text.

Fig. 5 Near-identical T_2 distributions measured for CH_4 in the Berea core plug at 100 bar and 20 °C when the CH_4 either did not flow or was flowing at the rate of 0.1 ml/min (repeated twice).

Fig. 6 T_2 logarithmic mean (T_{2LM}) of CH_4 in the Berea sandstone plug during different core flooding processes. The estimated pore radii are also shown. T_{2LM} values corresponding to $y_{CH_4} < 0.19$ are not shown due to low signal-to-noise ratio (SNR).

Fig. 7 T_2 logarithmic mean (T_{2LM}) of CH_4 in the carbonate plug during different rock core flooding processes. The estimated pore radii are also shown. T_{2LM} values corresponding to $y_{CH_4} < 0.19$ are not shown due to low SNR.

Fig. 8 Absolute adsorption capacity q_{abs} of the Berea sandstone sample for N_2 , CH_4 , and CO_2 along isotherm $T \approx 20^\circ\text{C}$.

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