1 ***In-situ* CH₄-CO₂ Dispersion Measurements in Rock Cores**

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3 Ming Li, Sarah J. Vogt, Eric F. May and Michael L. Johns*

4 Department of Chemical Engineering, University of Western Australia, Crawley, WA,
5 Australia

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7 * Corresponding author

8 Email: michael.johns@uwa.edu.au

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Abstract

Injection of carbon dioxide (CO₂) into a natural gas reservoir is an emerging technology for enhanced natural gas recovery (EGR) realizing increased natural gas production whilst sequestering the injected CO₂. However given that CO₂ and natural gas are completely miscible, simulation of potential EGR scenarios is required to determine when breakthrough of CO₂ will occur at the natural gas production wells. For such reservoir simulations to be reliable (independent of software used), accurate dispersion data between CO₂ and natural gas at relevant reservoir conditions are required. To this end we apply one dimensional (1D) magnetic resonance imaging (MRI) to quantify this dispersion process *in-situ* in both sandstone and carbonate rock cores. Specifically we apply the SPRITE MRI sequence (Balcom *et al.* 1996) to facilitate quantitative axial profiles of methane (CH₄) content during core flooding processes between CO₂ and CH₄. Simultaneously we measure, using infrared (IR), the effluent CO₂ and CH₄ concentrations enabling *ex-situ* dispersion measurements. Via comparison with the corresponding MRI data, the erroneous contributions to dispersion from entry/exit effects and mixing in piping to and from the rock core holder are quantified. Furthermore, we demonstrate how nuclear magnetic resonance (NMR) T_2 measurements can be uniquely used to probe the pore size occupancy of the CH₄ during the core flooding process.

1 Introduction

Carbon dioxide (CO₂) sequestration in suitable geological formations is a promising strategy to mitigate greenhouse gas emission (e.g. Barrufet *et al.* 2010; Kheshgi *et al.* 2012; Leung *et al.* 2014). Injection of CO₂ into natural gas reservoirs can not only serve to store CO₂ within the formations but also potentially improve natural gas recovery. However, complete miscibility between natural gas and CO₂ at all relevant reservoir conditions (Hughes *et al.* 2012; Honari *et al.* 2015a, b) is a significant barrier for the application of this enhanced gas recovery (EGR) technology as it potentially results in contamination of, and CO₂ breakthrough in, the natural gas product. This has prompted several EGR simulation studies (e.g. Oldenburg *et al.* 2002; Patel *et al.* 2016; Patel *et al.* 2017; Pooladi-Darvish *et al.* 2008) of various reservoir scenarios (probing, for example, the effect of permeability heterogeneity and injection rate) in order to estimate the related risks and uncertainties of CO₂ EGR implementation. However, to ensure these simulation studies have a sufficiently high fidelity, an accurate description of the mixing (dispersion) between the CO₂ and the CH₄ (or natural gas) in a reservoir is required. The dispersion data necessary for these reservoir simulations is accessible via laboratory-scale core flooding measurements using cylindrical rock core samples (e.g. Hughes *et al.* 2012; Honari *et al.* 2015a, b; Honari *et al.* 2016; Zecca *et al.* 2017; Zhang *et al.* 2016; Yu *et al.* 1999).

Whilst core-scale measurements of dispersion are in principle transferable to the reservoir scale, these laboratory measurements are nevertheless notoriously difficult to execute and can suffer from many systematic errors including erroneous contributions to mixing that occur both due to entry and exit effects into the rock core sample as well as in piping to and from the rock core holder. Previously we have applied 1D Magnetic Resonance Imaging (MRI) to quantify such gas-phase CO₂-CH₄ mixing *in-situ* in a model glass bead random packing (Honari *et al.* 2015b); here we extend this to actual rock cores at conditions more relevant to the reservoir (supercritical fluids and 100 bar pore pressure versus 45 bar pore pressure). We also complement these dispersion experiments with Nuclear Magnetic Resonance (NMR) *T*₂ relaxometry measurements of pore size occupation by the methane during the core flooding process.

NMR and MRI have been widely employed to measure a range of transport properties of various fluids in porous media including various hydrocarbons in rock cores (e.g. Mitchell *et al.* 2013; Coates *et al.* 1999; Zhao *et al.* 2016; Ramskill 2018; Li *et al.* 2016; Li *et al.* 2017a, b; Mitchell *et al.* 2018; Shikhov *et al.* 2018). Whilst these have predominately focused on liquid phase measurements, due predominately to signal-to-noise (SNR) considerations, gas phase NMR/MRI has been used; for example by Zecca *et al.* (2018), to determine the restricted diffusion coefficient of ethane in sandstone cores and, hence, their tortuosity. It has also, for example, been used by Cheng *et al.* (2005) to study $^{13}\text{CO}_2$ density profiles in a zeolite bed during adsorption/desorption processes. Shikhov and Arns (2017) employed NMR gas diffusion to determine tortuosity as a function of both position along the rock core and fluid saturation. Away from the laboratory, Akkurt *et al.* (1996) employed NMR technology to log natural gas reservoirs and found that NMR provided hydrocarbon saturation results that were consistent with conventional methods. An elegant review of gas flow measurements by NMR/MRI is provided by Newling (2008).

Dispersion is a physical blending phenomenon due to both molecular diffusion and fluid advection and consequential mixing (Blackwell 1962), the latter effect being a strong function of the rock matrix heterogeneity at multiple length-scales. Dispersion is generally quantified by a dispersion coefficient, K (Taylor *et al.* 1954). In the context of the CO_2 EGR process, the dispersion process between the injected CO_2 fluid phase and the nascent CH_4 phase, is affected by the rock matrix heterogeneity (Blok *et al.* 1997; Honari *et al.* 2015a), the presence of connate water (Zecca *et al.* 2017; Zhang *et al.* 2016), reservoir pressure and temperature (via their resulting impact on fluid viscosity, density and diffusion coefficient) (Hughes *et al.* 2012), and fluid injection flow rate (Hughes *et al.* 2012; Zecca *et al.* 2017; Zhang *et al.* 2016; Honari *et al.* 2015a). As a consequence of both practical limitations on injection volumetric flowrate and an increasing front area as the CO_2 migrates away from the injection well, the vast majority of the dispersion process throughout the whole reservoir occurs at very low flow rates. Consequently here we will consider only comparatively slow displacement velocities.

In the current work, 1D axial MRI measurements were employed to monitor CH_4 and CO_2 core flooding processes in both sandstone and carbonate rock cores. The SPRITE MRI pulse sequence (Balcom *et al.* 1996) was employed as it provides better NMR signal

homogeneity than the spin echo MRI method along the core axis. The MRI measurements determine the CH₄ content along the axis of the rock cores as a function of time and hence injection volume. By suitable evaluation of the evolution of these 1D axial profiles as a function of injection time, it is possible to extract the value of the dispersion coefficient quantifying the mixing process. As the measurement is performed *in-situ*, any erroneous contribution to mixing due to core entry/exit effects and piping to and from the core are effectively eliminated. The scale of these erroneous contributions is quantified by simultaneously monitoring the core flooding apparatus effluent CO₂ and CH₄ concentrations using *ex-situ* infrared (IR) measurements. Dispersion measurements were performed for both CO₂ displacing CH₄ and CH₄ displacing CO₂. Simultaneously, NMR *T*₂ relaxation time measurements were performed to quantify the pore size occupancy by the CH₄ during the core flooding.

2 Theoretical Background

2.1 Dispersion in porous media

Dispersion in a porous medium is a physical mixing process (Delgado *et al.* 2007) in which molecular diffusion and mechanical advection dominate the dispersion at low and high flow velocities, respectively, bookending a transition zone in which both effects make a significant contribution (Honari *et al.* 2015a; Hughes *et al.* 2012). Both transverse and longitudinal dispersion processes in porous media have been studied for many decades in a variety of fields including soil, groundwater, and petroleum engineering. When mechanical advection dominates, longitudinal dispersion is generally approximately an order of magnitude larger than transverse dispersion (Delgado *et al.* 2007); when molecular diffusion is dominant, longitudinal and transverse dispersion are approximately equal (Delgado *et al.* 2007).

The longitudinal dispersion coefficient (*K*_L) is described by a one dimensional (1D) advective-dispersion (AD) equation (Taylor *et al.* 1953; Taylor *et al.* 1954):

$$\frac{\partial C}{\partial t} = K_L \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} \quad , \quad (1)$$

where C is the concentration (mole fraction) of the dispersing species, u is mean flow velocity, t is time and x is axial position along the porous media. The solution to Equation (1) with the boundary conditions $C(t=0, x>0) = 0$, $C(t=0, x=0) = 1$, and $C(t, \infty) = 0$ is (Seo *et al.* 2005; Honari *et al.* 2015a; Hughes *et al.* 2012):

$$C = \frac{1}{2} \left[\operatorname{erfc} \left(\frac{x_D - t_D}{2\sqrt{t_D / Pe_{\exp}}} \right) + \exp(x_D Pe_{\exp}) \operatorname{erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D / Pe_{\exp}}} \right) \right], \quad (2)$$

where $x_D = x/L_{\exp}$, $t_D = ut/L_{\exp}$, $L_{\exp}$ is the length of the rock core plug, and the experimental Péclet number is defined as $Pe_{\exp} = uL_{\exp}/K_L$.

Generally, C is measured at the exit of a cylindrical rock core following either a step increase in C or a pulse of the dispersing species being injected into the flow at the rock core entry (Honari *et al.* 2015a; Hughes *et al.* 2012; Zecca *et al.* 2017; Yu *et al.* 1999); this process is effectively core flooding. As previously mentioned however mixing of the injected species and the nascent species can occur in piping to and from the rock core as well as a consequence of entry and exit effects into the rock core itself. A number of approaches have been proposed in the literature to deal with this erroneous contribution (e.g. Honari *et al.* 2015b; Hughes *et al.* 2012; Edwards *et al.* 1968; Rajendran *et al.* 2008). A simple correction is to perform the core flooding measurements with and without the porous media being present followed by subtraction of the erroneous mixing contribution (Edwards *et al.* 1968; Guntuka *et al.* 2008); this of course assumes that the contributions are linearly additive (Rajendran *et al.* 2008). Hughes *et al.* (2012) demonstrated a ‘long core and short core’ method, which was improved upon by Zecca *et al.* (2017), to correct for these erroneous effects in which the dispersion of the short core was used as the input to the dispersion occurring in the additional length of the longer core. The erroneous contribution should be identical for both cores and thus is effectively eliminated. The method however assumes that the exit and entry effects are identical and simply additive. Honari *et al.* (2015b) employed MRI to monitor CH_4 displacements by CO_2 in a model glass bead packing, in the process measuring the evolution in the CH_4 concentration along the core length. The *in-situ* effective breakthrough curve measured at an upstream position was used to estimate the *in-situ* effective breakthrough curve further downstream with K_L as the fitting parameter. Erroneous mixing in the inlet was completely captured by the

upstream *in-situ* effective breakthrough curve; erroneous mixing at the outlet was irrelevant to these measurements. The method of Honari *et al.* (2015b) was adopted by Zhang *et al.* (2016), who measured dispersion in a sand packing using X-ray CT images of the gas axial concentration distribution.

2.2 Pore scale fluid characterization using T_2 measurements

T_2 relaxation time distributions are frequently employed to characterize fluids in rock core samples (e.g. Mitchell *et al.* 2013; Li *et al.* 2017a; Coates *et al.* 1999). When T_2 measurements are performed using low magnetic field strengths and short echo times, the following expression can be employed to describe T_2 (Muir and Balcom 2012):

$$\frac{1}{T_2} = \frac{1}{T_{2,\text{Bulk}}} + \frac{1}{T_{2,\text{Surf}}} \quad , \quad (3)$$

where $T_{2,\text{Bulk}}$ is the bulk transverse relaxation time and $T_{2,\text{Surf}}$ is the surface transverse relaxation time. Equation (3) assumes that background magnetic field gradients due to susceptibility differences between the rock matrix and the pore fluid are minimal (Mitchell *et al.* 2010; Connolly *et al.* 2017). The surface relaxation rate ($1/T_{2,\text{Surf}}$) of the fluid in a pore in the fast-diffusion limit is given by (Freedman *et al.* 2003):

$$\frac{1}{T_{2,\text{Surf}}} = \rho_2 \left(\frac{S}{V} \right) \quad , \quad (4)$$

where ρ_2 is the surface relaxivity, S is the contact area of the fluid and pore surface, and V is the volume of the fluid. Assuming that $T_{2,\text{surf}} \ll T_{2,\text{bulk}}$, the pore size can be approximated based on Equation (4) on the assumption of a spherical pore geometry, in which case the representative pore radius, R , is estimated as:

$$R = 3\rho_2 T_2 \quad , \quad (5)$$

where ρ_2 values are approximately 18.2 $\mu\text{m/s}$ and 9.6 $\mu\text{m/s}$ for water saturated Berea sandstone and carbonate samples, respectively, based on the mean of available literature data (e.g. Mesquita *et al.* 2016; Johnson 2015; Carneiro *et al.* 2014).

3 Methodology

3.1 Materials and experimental setup

High purity CH₄ (≥99.995%) and CO₂ (≥99.995%) were supplied by Coregas Pty Ltd (Western Australia, Australia). Fluorinated oil (FC-40) was purchased from 3M company (MN, USA), and was used for the application of confining pressure to the rock cores. A Berea sandstone and a carbonate (Silurian dolomite purchased from Kocurek industries, TX, USA) core plugs were employed in this work. Table 1 lists their physical properties.

Figure 1 shows a schematic of the experimental apparatus for NMR/MRI and IR monitoring of the gas flooding processes in the core plugs. An NMR compatible core holder (FCH-1.0: S2 Glass and PEEK, Core Laboratories, OK, USA) rated to 345 bar pressure was used for these experiments. Two syringe pumps, pump 2, (260D Teledyne ISCO, NE, USA) and pump 3, (Quizix QX-6000SS Chandler Engineering, OK, USA) were employed for CO₂ and CH₄ injection, respectively. A vacuum pump (949-9315 Agilent Technologies, Torino, Italy) was used to evacuate the rock core samples. Another syringe pump (pump 4, 260D Teledyne ISCO) was connected to the end of the flooding system to provide back pressure control. Pump 1 was a hydraulic pump (87-6-5, High Pressure Equipment Company, PA, USA) filled with the fluorinated oil (FC-40) used for the confining pressure of the rock cores via the core holder. CH₄ spin density and relaxation measurements were exclusively performed using a 0.3 T Maran Ultra permanent magnet spectrometer (Oxford Instruments, U.K.) operating at 12.9 MHz ¹H resonance frequency and equipped with 3D gradient coils. IR measurements of the effluent were conducted with a Varian 640 IR spectrometer located before the pump controlling the back pressure. For the CO₂ displacing CH₄ experiments, flow through the rock core was directed in a vertical direction; this was reversed for CH₄ displacing CO₂. This ensured that the fluid with the greater density was at the bottom and thus prevented erroneous mixing due to buoyancy effects. More details about the effect of gravity on these dispersion measurements are given by Hughes *et al.* (2012).

3.2 Experimental procedure

The core plugs were dried at 120 °C until their weight stopped decreasing over 24 hours and were then mounted into the NMR compatible core holder. The core holder was placed in the magnet chamber and connected to the pumps and the IR spectrometer as indicated in Figure 1. A confining pressure of 50 bar was applied using pump 1; the vacuum pump was then used to remove air from the rock core. For CH₄ displacement by CO₂, CH₄ was first introduced into the core plug by gradually increasing its pressure whilst the confining pressure was also increased. The difference between the confining pressure and the CH₄ pressure was kept at approximately 50 bar. CH₄ injection was stopped when there was approximately 15 ml of CH₄ in the back pressure pump (pump 4) which was operated in constant pressure mode with a set point of 100 bar. The confining pressure was then increased to 160 bar. The NMR/MRI and IR measurements were then commenced followed by CO₂ flooding. The CO₂ flooding process was completed when the IR signal for CH₄ measured at the core exit was zero. These flooding experiments were conducted over a range of displacement velocities. For the experiments where CH₄ was injected into CO₂ saturated rock cores, the process was effectively performed in reverse. All the combined NMR/MRI and IR measurements of the core flooding process, were performed at a temperature of 20 °C and a pressure of 100 bar; at these conditions the CO₂ is a compressed liquid. Core flooding with only IR analysis of the effluent was performed at 40 °C and 100 bar.

3.3 MRI and NMR Experiments

In comparison with the experiments presented in Honari *et al.* (2015b), the current measurements are significantly more challenging in terms of signal-to-noise ratio (SNR) due primarily to the comparatively much lower rock core porosity. Honari *et al.* (2015b) employed a 1D spin-echo MRI pulse sequence to measure the CH₄ axial concentration profile in a model porous medium. Here we employ a more readily quantitative 1D Single Point Ramped Imaging with T_1 Enhancement (SPRITE) MRI pulse sequence (Balcom *et al.* 1996), which is more immune to B_1 imperfections. Figure 2(a) shows 1D MRI axial profiles of a 3 cm diameter bottle of water acquired using both conventional spin-echo and SPRITE MRI pulse sequences. A more homogeneous axial profile reflecting the expected

bottle shape is observed from the SPRITE measurement; therefore it was employed to monitor core flooding processes in this study. The field of view (FOV) of the two profiles was 12 cm and a resolution of 1.9 mm. The signal intensity of the SPRITE pulse sequence is impacted not only by the concentration of the CH₄ but also its T_1 and T_2^* signal relaxation times (Balcom *et al.* 1996). Four mixtures of CO₂ and CH₄ (CH₄ molar concentrations of 2.4%, 33.5%, 65.4%, and 98.0%, respectively) were prepared and pumped into a dry Berea core plug at 100 bar. Figure 2(b) shows the total SPRITE signal intensity against the mole fraction of CH₄ (repeated twice). There is a reasonable linear correlation and no evidence of systematic bias due to NMR relaxation effects. The SPRITE MRI measurement error is estimated at 4% based on the repeat measurements in Figure 2(b).

A standard Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was also employed to determine the T_2 distribution of CH₄ in the rock core plugs. For low flooding rates (≤ 0.1 ml/min), the CPMG and the SPRITE MRI measurements were interleaved. For higher flooding rates (> 0.1 ml/min), only SPRITE MRI measurements were performed due to the rapid change in gas concentrations during the core flooding process. All NMR/MRI measurement parameters are reported in Table 2.

3.4 Dispersion Data Analysis

In this work, the K_L correction method of Honari *et al.* (2015b) based on MRI measurements was employed. The effective breakthrough profile measured in the front half section ($x = 1.9$ cm) of the rock core was used as an input to Equation (1) to determine the effective breakthrough curve of the core rear half section ($x = 5.7$ cm), with K_L as the fitting parameter; x is the axial position along the rock core from the core entry ($x = 0$ cm). Equation (1) was solved numerically using a central finite difference method in Matlab (version R2016b).

Based on data in Takahashi and Iwasaki (1970) which span the range (25 to 75) °C and (50 to 150) bar, Hughes *et al.* (2012) fitted the following correlation for the molecular diffusion coefficient of CO₂ in CH₄ ($D_{\text{CO}_2, \text{CH}_4}$ (m²/s)):

$$D_{\text{CO}_2, \text{CH}_4} = \frac{(-4.3844 \times 10^{-13} p + 8.5440 \times 10^{-11}) T^{1.75}}{p}, \quad (6)$$

where p and T are pressure (MPa) and temperature (K), respectively. Equation (6) was shown to be consistent with core flooding data (Hughes *et al.* 2012). We were not able to locate equivalent, relevant data for the diffusion coefficient of CH₄ in CO₂.

4 Results and Discussion

4.1 Sample Core Flooding Data

Figure 3 shows an example set of breakthrough curves for CO₂ flooding to displace CH₄ and CH₄ flooding to displace CO₂ in both a carbonate core plug and the core holder without a core sample present – these were acquired *ex-situ* using IR measurements in the high pressure core flooding apparatus. The core flooding experiments shown in Figure 3 were undertaken at 40 °C and 100 bar at a flow rate of 2 ml/min. The mole fraction of CO₂, y_{CO_2} , increases more rapidly during CO₂ flooding than the increase of the CH₄ mole fraction, y_{CH_4} , during CH₄ flooding, resulting in a sharper breakthrough profile and a slightly shorter overall CO₂ flooding time. This difference may be partially attributed to the gas viscosities of 4.77×10^{-5} Pa·s for CO₂ and 1.39×10^{-5} Pa·s for CH₄ at 40 °C and 100 bar (Lemmon *et al.* 2018; Laesecke *et al.* 2017), which results in a more favorable viscosity ratio for ‘piston-like’ CO₂ flooding to displace CH₄ (Brigham *et al.* 1961; Xia *et al.* 2016). A lag or slow growth region is also evident between 40 and 80 minutes for CH₄ flooding. This we attribute to stagnant region in the core holder when flooding from above.

In Figure 3, the gray dashed line corresponds to an ‘ideal’ situation in which gas displacement occurs instantaneously i.e. it is the input boundary condition leading to the solution shown in Eq. (2). Clearly this is substantially different to the breakthrough profiles obtained with no rock core sample for two main reasons. First, the time delay between them (~10 minutes) is a consequence of the residence time in the system tubing, which has a total volume of around 20 ml. Second, the breakthrough profile shape obtained for the system without a sample is not instantaneous and exhibits a small degree of spreading. This is a consequence of the erroneous contribution to mixing that occurs in the tubing to and

from the rock core holder in addition to entry and exit effects through the distribution plugs of the rock core holder, which is consistent with the observations of Hughes *et al.* (2012). Our MRI measurements, by virtue of their *in-situ* characteristic, directly account for this contribution to the observed mixing via the input breakthrough profile for Equation (1).

4.2 MRI Concentration Profiles

Figure 4 shows only six sample time-resolved 1D CH₄ axial concentration profiles for each series of measurements in the two core plugs (sandstone and carbonate) for the sake of clarity for both CH₄ flooding and CO₂ flooding as acquired using SPRITE MRI; a value of 1 corresponds to the mean CH₄ signal for the whole rock core when it contained only CH₄. In each case, only six profiles are shown, many more profiles were acquired (every 1.7 minutes) during the core flooding processes. The signal intensity of each profile represents the temporally average CH₄ concentration along the rock core over the total MRI profile measurement time of 1.7 minutes. Prior to, and following flooding, a series of five repeat profiles were acquired when the core was saturated with CH₄. This data was used to generate standard deviations and hence error bars which are reported for the equivalent data in Figure 4.

The flooding rate in Figure 4 was consistently 0.5 ml/min (at 100 bar and 20 °C). The profiles have a relatively low SNR as dictated by the limited MRI signal and the need to perform the profile measurements rapidly such that they did not significantly blur due to signal displacement as core flooding progressed during the profile acquisition temporal window. Nevertheless certain trends are distinctly obvious.

Figure 4(a) shows the result for CO₂ flooding to displace CH₄ in the Berea sandstone core plug. The CH₄ concentration (MRI Signal) gradually decreased from the core plug inlet to the outlet as it was progressively displaced. The opposite is observed in Figure 4(b) as CO₂ was displaced by CH₄ from the rock core. The breakthrough of the displacing fluid was deemed to occur when the CH₄ MRI signal intensity at $x = 7.6$ cm commenced to decrease (CO₂ flooding) or increase (CH₄ flooding) consistently over three successive measurements. In the Berea sandstone core plug, CO₂ breakthrough at the rock core exit occurred at ~31 minutes during CO₂ flooding whilst CH₄ breakthrough occurred

at ~26 minutes during CH₄ flooding. The earlier CH₄ breakthrough than CO₂ may be attributed to the comparatively lower CH₄ viscosity, and is consistent with the results of Brigham *et al.* (1961) for example which showed earlier breakthrough when a lower viscosity fluid was injected into a porous medium. Figures 4(c) shows the corresponding 1D CH₄ concentration profiles in the carbonate core plug during CO₂ flooding. The initial distribution is much less uniform than the sandstone core, reflecting the greater heterogeneity of carbonates as widely reported in the literature (e.g. Lucia *et al.* 2003; Ehrenberg 2005). The CH₄ is gradually removed from the carbonate rock core with no obvious displacement front as was the case for the Berea sandstone. However a comparatively more rapid CO₂ breakthrough is observed at ~27 minutes - indicating that this is predominately controlled by the lower porosity of the carbonate (17% versus 20% for the Berea sandstone – Table 1). This is also broadly the case for CH₄ flooding of the carbonate core in Figure 4(d) which presented a breakthrough time of ~20 minutes.

4.3 Dispersion Coefficient Data

Figure 5 shows a sample set of CO₂ and CH₄ breakthrough curves in the Berea core plug as independently determined by SPRITE MRI (both at $x = 1.9$ cm and $x = 5.7$ cm) and *ex-situ* via IR measurements. The core flooding processes were conducted with a flooding rate of 0.5 ml/min ($u = 0.0829$ mm/s) at 20 °C and 100 bar. The IR data were fit using the analytical solution provided by Equation (2) using the apparent dispersion coefficient, K_L , as a fitting parameter. The MRI data at $x = 5.7$ cm is fit using Equation (1) (as solved numerically using Matlab) using the experimental data at $x = 1.9$ cm as an input, as outlined above.

In Figure 5, the relative delay in gas breakthrough times for the IR measurements reflects that they are acquired significantly after the fluid has exited the core. Whilst there is greater scatter in the MRI data the fits are reasonably good. In Figure 5(a), for the IR data, a systematic deviation between the fit and the experimental data becomes evident at around 100 minutes. This we attribute to stagnant regions in the core holder which are accentuated when the core is flooded with CH₄ from above relative to CO₂ flooding from below. This discrepancy is not evident in the corresponding MRI data indicating that

performing the measurements *in-situ* has facilitated elimination of this erroneous effect. A similar observation was evident with respect to the corresponding carbonate data.

The gas dispersion coefficients (K_L) as determined by fitting Equation (1) numerically to the MRI data ($x = 5.7$ cm) and fitting Equation (2) to the IR data are shown in Figure 6 for all measurements performed on both the sandstone and the carbonate rock core as a function of superficial displacement velocity. It is immediately obvious that the MRI data result in lower values of K_L relative to the corresponding IR data. This is most evident for the CH₄ flooding measurements and is consistent with the observations with respect to Figure 5 where the IR breakthrough curves were obviously adversely affected by contributions to mixing from tube mixing and input/output effects. Nonetheless the MRI data still clearly shows elevated values of K_L for the CH₄ flooding relative to the CO₂ flooding in both rock cores. At 100 bar and 20 °C, the viscosities of CO₂ and CH₄ are 8.25×10^{-5} Pa·s and 1.37×10^{-5} Pa·s, respectively, (Lemmon *et al.* 2018; Laesecke *et al.* 2017) and as discussed previously the more favorable viscosity ratio for ‘piston like’ displacement for CO₂ flooding results in reduced mixing and a lower value of K_L . The K_L values of CO₂ in carbonate ($5 \sim 50 \times 10^{-8}$ m²/s) were also generally higher than K_L in Berea ($5 \sim 25 \times 10^{-8}$ m²/s), which is consistent with data presented in Honari *et al.* (2015a).

Figure 6 also presents the diffusion coefficient of CO₂ in CH₄ (as obtained from the literature (Hughes *et al.* (2012), Takahashi and Iwasaki (1970)): 1.7×10^{-7} m²/s at 100 bar and 20 °C. As expected the acquired SPRITE data are consistent with this diffusion value, indicating that the CO₂ dispersion measurements were performed predominately in the diffusion-dominated regime. The diffusion coefficient of CH₄ in CO₂ at the same pressure and temperature condition (100 bar and 20 °) is at least significantly less than 6.8×10^{-8} m²/s (based on data in Takahashi (1972) for a pressure of 49 bar)). Higher displacement velocities are difficult to access whilst still allowing for adequate time for MRI profiling; however as discussed above the diffusion-dominated regime is most relevant to CO₂ dispersion in EGR reservoir simulations.

4.4 Pore scale fluid behavior

In this study, CPMG measurements were performed to monitor the pore size occupation of CH₄ during the core flooding processes when the flooding rates were low (≤ 0.1 ml/min) by determining T_2 relaxation time distributions. After the core flooding experiments, T_2 measurements were also undertaken for the two rock core plugs when fully saturated with brine solution to estimate the pore size distribution according to Equation (5) using literature ρ_2 values as reported above. Figure 7 shows the resultant T_2 relaxation (and pore size) distributions of the Berea and carbonate rocks when fully saturated with brine solution. The T_2 distribution of the core plug fully saturated with CH₄ and the T_2 distribution of the same core plug fully saturated with brine (and hence the pore size distribution) were then compared. Both were converted to pore size distributions using Equation (5) and the difference or error between the two pore size distributions was minimized by adjusting ρ_2 for CH₄. This resulted in ρ_2 for CH₄ in the Berea and carbonate rocks being estimated at 33 $\mu\text{m/s}$ and 26 $\mu\text{m/s}$, respectively.

Figure 8 shows T_2 relaxation time distributions and consequential estimated pore size distributions of CH₄ in the Berea and carbonate core plugs during the gas flooding processes. For the CO₂ displacement by CH₄ in Berea shown in Figure 8(a), the signal intensity gradually increased as the CH₄ concentration increased during the core flooding. The mean T_2 progressively shifted from about 45 ms to about 25 ms. The T_2 of bulk CH₄ ($y_{\text{CH}_4}=1$) and a gaseous mixture of CH₄ and CO₂ ($y_{\text{CH}_4}=0.52$) were measured to be 1.37 and 1.39 seconds, respectively, both of which are much longer than the T_2 of CH₄ in the rock. Therefore, the T_2 of gas in the rock is dominated by surface relaxation $T_{2,\text{surf}}$ (as detailed in Equation (3)), meaning that Equation (5) is valid. According to the correlation between $T_{2,\text{surf}}$ and pore size, shown in Equation (5), the shift of the dominant T_2 peak during CH₄ flooding indicates that CH₄ firstly preferentially entered larger pores to displace CO₂. During the CH₄ displacement by CO₂ in the Berea core plug (Figure 8(b)), the T_2 distribution signal intensity decreases as expected; however the T_2 peak shifts to larger values indicating that the residual CH₄ occupies preferentially larger pores. Similar CH₄ T_2 distribution variations to this Berea sample were observed for the carbonate samples (Figure 8(c) and (d)). A significant difference between the two rocks is that the T_2 values were longer (~ 100 ms) for carbonate than for Berea (~ 30 ms); the validity of Equation (5) nevertheless remains intact. This difference is a consequence of both weaker surface

relaxivity (Chang *et al.* 1994; Timur *et al.* 1972) and larger pore size in carbonates compared to sandstones.

Figure 9 shows the T_2 log mean (T_{2LM}) of the CH_4 signal plotted as a function of CH_4 mole fraction, y_{CH_4} . For both Berea and carbonate, T_{2LM} decreased with the increase of y_{CH_4} indicating preferential occupation of larger pores by the CH_4 . The curves were identical for the carbonate for both CO_2 and CH_4 flooding. This was not the case for the Berea, the reason for this hysteresis is currently unclear and will be explored further in future work. Assumptions with respect to the data in Figures 8 and 9 are that the pores are spherical in shape and that the reduction in T_2 used for pore size occupation is a consequence only of surface relaxation (as per Equation 5) and not diffusion in background gradients (Connolly *et al.* 2019) or as a consequence of local CH_4 - CO_2 composition. Future work will concentrate on further exploration of these assumptions via, for example, spatially resolved T_2 distribution measurements using, for example spin-echo single point imaging (SE-SPI) (Xiao *et al.* 2014).

5 Conclusions

SPRITE axial 1D MRI measurements were employed to monitor the displacement processes in Berea and carbonate rock core plugs. Displacement of CH_4 by CO_2 and the displacement of CO_2 by CH_4 were both axially profiled and used to evaluate the dispersion behaviors of CO_2 and CH_4 in rock cores free from erroneous entry and piping mixing effects. The extent of these erroneous contributions was evident when the resultant dispersion data were compared against conventional analysis of IR data acquired at the core holder exit. This discrepancy was greater for CH_4 displacing CO_2 . NMR T_2 distributions were acquired for the CH_4 during the displacement process and related to pore size occupation. This revealed the preferential occupation of larger pores by the CH_4 during both displacement processes.

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Table 1 Physical properties of core plugs

Rock Core	Length (cm)	Diameter (cm)	Permeability (mD)	Porosity
Berea	7.6	2.5	100	0.20
Carbonate	7.7	2.5	70	0.17

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Table 2 NMR and MRI measurement parameters

1D SPRITE MRI	
RF pulse length (μs)	3
RF pulse flip angle (deg)	18
encoding time (μs)	94
field of view (cm)	24
Total number of pixel in profile	64
Resolution (mm)	3.8
repetition delay (s)	0.6
number of averages (high~low flooding rates)	32~192
imaging time (min) (high~low flooding rates)	0.6~3.8
Maximum gradient used (Gauss/cm)	9.7
CPMG	
90° pulse length (μs)	14.6
180° pulse length (μs)	29.2
relaxation delay (s)	5.7
number of averages	16(Berea) 12(Carbonate)
echo time (μs)	400
number of echoes	800(Berea) 1200(Carbonate)

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Figures

Figure 1 Schematic of experimental apparatus employed for CH_4 flooding to displace CO_2 in the rock sample ('top' to 'bottom' direction). For CO_2 flooding to displace CH_4 , a 'bottom' to 'top' direction was employed and the relative positions of core holder inlet and outlet were reversed.

Figure 2 (a) 1D MRI profiles of a bottle of water from spin-echo and SPRITE measurements respectively. SPRITE provides a more homogeneous profile than the spin echo to show the expected geometry of the water bottle. The convex profile shape at about 4 cm is due to the geometry of the bottle neck. (b) SPRITE MRI signal intensity correlates well with the mole fraction of CH₄ (y_{CH_4}) in various mixtures of CH₄ and CO₂ in a Berea rock core plug.

Figure 3 Breakthrough curves during CO₂ flooding to displace CH₄ (y_{CO_2}) and during CH₄ flooding to displace CO₂ (y_{CH_4}) with a carbonate core plug and without a core sample, as determined by IR measurements. These flooding processes were undertaken at 40 °C and 100 bar with a flooding rate of 2 ml/min. The solid lines are added to guide the eye. The gray dashed line represents an ‘ideal’ situation for reference, corresponding to the concentration of the displacing gas phase instantly increased from 0 to 1.

Figure 4 Sample 1D CH₄ distribution profiles along the Berea sandstone (a, b) and carbonate (c, d) core plugs during CO₂ flooding to displace CH₄ (a, c) and CH₄ flooding to displace CO₂ (b, d). A value of 1 corresponds to the mean CH₄ signal for the whole rock core when it contained only CH₄. All the core flooding processes were undertaken at 100 bar and 20 °C with a volume flooding rate of 0.5 ml/min. Red arrows indicate the flooding directions and black arrows the time sequence of the profiles.

541 (a)

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543 (b)

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545 **Figure 5** Gas breakthrough curves determined by SPRITE MRI and IR measurements in
 546 the Berea core plug. (a) CH₄ flooding to displace CO₂ and (b) CO₂ flooding to displace
 547 CH₄. All flooding processes were undertaken at 20 °C and 100 bar with a flooding rate of
 548 0.0829 mm/s. The fits of Equations (1) and (2) to the MRI and IR data, respectively, are
 549 also shown.

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(a)

(b)

Figure 6 Gas dispersion coefficients (K_L) as determined from IR and MRI measurements for (a) Berea and (b) carbonate core plugs. The diffusion coefficient (D) of CO₂ in CH₄ is 1.7×10^{-7} m²/s and is shown by the dashed red line.

Figure 7 T_2 distribution of Berea and carbonate rock core plugs, fully saturated with brine solution (1wt % NaCl). The pore size distribution is also presented as determined using Equation (5) with relaxivity values of 18.2 $\mu\text{m/s}$ and 9.6 $\mu\text{m/s}$ for the Berea and carbonate core plugs, respectively.

Figure 8 Pore size distribution and T_2 relaxation time distribution of CH_4 in Berea (a, b) and carbonate core plugs (c, d) during CH_4 flooding to displace CO_2 (a, c) and during CO_2 flooding to displace CH_4 (b, d).

Figure 9 T_2 log mean (T_{2LM}) of CH_4 in (a) Berea and (b) carbonate core plugs plotted as a function of CH_4 mole fraction (y_{CH_4}). T_{2LM} and y_{CH_4} are determined from the bulk CPMG measurement and the mean of SPRITE signal along the CH_4 profile, respectively. T_{2LM} corresponding to $y_{CH_4} < 0.19$ are not shown due to low SNR.

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