

Enhanced Gas Recovery and Storage: The Role of N₂ during Natural Gas Displacement by CO₂ Flooding in Sandstone Rocks

Mohammed Nuhu

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Enhanced Gas Recovery and Storage: The role of N₂ during Natural Gas Displacement by CO₂ Flooding in Sandstone Rocks

Mohammed NUHU

School of Science, Engineering, and Environment College of Science and Technology, University of Salford, Manchester, UK

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Abstract

Carbon dioxide (CO₂) injection and storage method for enhanced gas recovery holds enormous promise for concurrent natural gas recovery and CO₂ storage from depleted gas resources. However, its potential application as part of climate friendly pilot scale research among industry and researchers is limited by the incessant mixing, while it is possible to reduce the extra length scale of CO₂ mixing with natural gas. Despite the several investigations performed to decrease such a nascent mixing problem, only quite a few achieved significant methane (CH₄) recovery with little mixing issues throughout the Enhanced Gas Recovery (EGR) process. Three (3) distinct sandstone core plugs (Grey Berea, Bandera Grey, and Bentheimer) with diverse petrophysical parameters were employed in this investigation.

A core flooding experiment was carried out to simulate CH₄ displacement by N₂ injection at 1500 psig, 40 0 C, and several injection rates (0.2, 0.4, 0.6, 0.8, and 1.0 ml/min). Maximum CH₄ recovery was achieved at 0.4 ml/min for both core samples. The Berea recovered 18% more than Bandera grey at the same injection. To curtail the effect of incessant mixing an experiment was conducted to investigate the influence of N₂ as a booster during natural gas displacement. This was done in a simulated reservoir situation with varied booster volume percent (6, 13, 19, and 29%). The experimental results indicated that the coefficient of longitudinal dispersion decline with raises in booster gas volume, hence the higher the amount of booster the less the dispersion of CO₂ into CH₄. The higher the booster volume the higher the sequestered CO₂, especially at higher CO₂ injection rates (1.0-1.2 ml/min). The maximum CO₂ storage was obtained in the test at 0.13 PV of N₂. The large differential pressure drops (dp) characterised this value. The maximum recovery, on the other hand, happened when the least amount of booster gas was employed and was marked by the least amount of N₂ product impurity.

The behaviour of CO_2 and N_2 during the natural gas displacement process was also evaluated. This intends to determine why CO_2 has a longer breakthrough time during the EGR process with N_2 gas inclusion. The experiment was constructed with varied injection rates at temperatures of 30 and 40 $^{\circ}$ C. The experiment at 30 °C recorded an extendable breakthrough time over that at 40 °C. The maximum breakthrough of 0.52 PV was recorded at 30 °C at the lowest injection velocity. The displacement efficiency of the current research outperforms traditional CO_2 floods. When compared to traditional CO_2 flooding, there was a 62 & 18% improvement in CH₄ recovery and CO_2 storage, respectively, and a 20% drop in dispersion coefficient when N_2 was used as a booster gas. This study demonstrates that using N_2 as a booster gas can increase CH₄ recovery and CO_2 sequestration, thus can be suitable for pilot application within the oil and gas industry.

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Declaration

I, Nuhu Mohammed, certify that this research is my unique work and that it has not been registered for any other awards. Any piece, paragraph, or wording utilised or taken from other literature or documents lifted has been mentioned at the place of usage and in the thesis work's reference section.

Signature

06/10/2022 Date

Lists of Symbols

yCO₂ CO₂ mole fraction

 yN_2 N₂ mole fraction

- D Diffusion coefficient, m²/s
- Q Flowrate, mil/min
- t_D Dimensionless time
- *x_D* Dimensionless distance
- d Characteristic length scale, m
- K_L Longitudinal dispersion, m²/s
- *L* Core sample length, mm
- Lexp Experimental length, m
- μ Viscosity, cP
- *P* Pressure, psig
- T Temperature, K
- u Interstitial velocity, m/s
- ϕ Core porosity, %
- α Dispersivity, m
- *τ* Tortuosity
- *P*_{exp} Experimental Peclet number
- *P_{em}* Medium Peclet number
- r Radius of core sample, m

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LIST OF PUBLICATION AND CONFERENCES

The list of published and others under review arising from this research are outlined below:

Journal papers

- Nuhu M., Abbas, A. J., Godpower C., Muhammad Kabir Abba, Onukak Imeh Etimb, Bello Saidua, Salihu M. Suleiman, Hassan Kabiru Yar'adua (2022). Investigating the Flow Behaviour of CO₂ and N₂ in Porous Medium Using Core Flooding Experiment. Journal of Petroleum Science and Engineering.
- Nuhu M., Abbas, A. J., Godpower C. Enyi (2021). The Role of N₂ as booster gas during Enhanced Gas Recovery by CO₂ flooding in porous medium, Journal of natural Gas Science and Engineering.
- Nuhu M., Abbas, A. J., Godpower C. Enyi, Donatus E. Edem, Salihu M. Suleiman (2020). Enhanced gas recovery by nitrogen injection: the effects of injection velocity during natural gas displacement in consolidated rocks. Journal of natural Gas Science and Engineering.
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Conference papers

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- Nuhu M., Abbas, A. J., Godpower C. Enyi (2020). Alternating N₂ and CO₂ injection as prospective technique for delaying CO₂ breakthrough during Enhanced Gas Recovery In consolidated rocks. In SPE Abu Dhabi International Petroleum Exhibition & Conference, Abu Dhabi, UAE.
- Nuhu M., Abbas, A. J., Godpower C. Enyi, & Nasr, G. G. (2019). Flow Characteristics Through Gas Alternating Gas Injection During Enhanced Gas Recovery. In SPE Gas & Oil Technology Showcase and Conference, Dubai.
- Nuhu M., Abbas, A. J., & Godpower C. Enyi, (2019). Enhanced Gas Recovery by Nitrogen Injection: Performance Evaluation of Gas-Gas Displacement. In Salford Postgraduate Annual Research Conference (SPAR 2019), Manchester, UK.

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

The goal of this chapter is to highlight the importance, necessity, and potential of Enhanced Gas Recovery (EGR) as a method of increasing natural gas (CH₄) recovery and artificial carbon dioxide (CO₂) sequestration in the presence of nitrogen (N₂) as a booster. Furthermore, the chapter is separated into sections: Section 1.2 presents the background for greater gas recovery, whereas Section 1.3 presents the problem statement. Section 1.4 describes the research aims and objectives, whereas Section 1.5 examines the thesis structure.

1.2 BACKGROUND

CO₂ emissions from fossil fuels have a significant influence on the environment, and these consequences cannot be overstated. Being a greenhouse gas adds to the environmental challenge of global warming. The worldwide community is becoming more concerned about decreasing the carbon impact of fossil fuel consumption. The use of CO₂ injection as a technology for both Enhanced Gas Recovery (EGR) and Enhanced Oil Recovery (EOR) might be a solution to meet the world's expanding energy demand while reducing CO₂ levels in the environment. These ideas are viable for hydrocarbon recovery and CO₂ sequestration (Khan, Amin, & Madden, 2013). The kind of rock type is also important in the concurrent notion of EGR with CO₂ injection and sequestration. Because of their favourable petrophysical features, which facilitate diverse trapping processes and aid in the recovery of residual hydrocarbons, sandstone formations are the most favoured kind of lithology for natural gas recovery and CO₂ storage (Michael et al., 2010; Riaz & Cinar, 2014).

In the oil and gas business, the practise of injecting CO_2 to recover residual natural gas is gaining traction. A significant amount of CO_2 injected and stored gives an advantage over the traditional Carbon Capture and Storage (CCS) technique. The recovered natural gas can be used to offset other operating expenditures. A tertiary recovery method is used in the Enhanced Gas Recovery (EGR) process. Because CO_2 and CH_4 are both gases, their characteristics were theoretically suitable for reservoir use owing to CO_2 unique behaviour and phase shift at supercritical circumstances (Oldenburg and Benson, 2002). At reservoir states, the density ratio of CO_2 to CH_4 is in the range of 2–6, classifying CO_2 as a very viscous gas (Al-Hasami et al., 2005). As a result, CO_2 may be moved downwards and stored throughout the EGR process (Oldenburg, 2001). Because of its high solubility factor in aqueous solvents, CO_2 is more soluble in formation water than CH_4 . The EGR method is a potential technology for co-current CH_4 gas recovery and CO_2 storage in a porous media during natural gas displacement. However, due to their physical similarities, CO_2 and CH_4 are entirely miscible. This resulted in an early CO_2 breakthrough during the natural gas displacement process, which has been the technology's major disadvantage (Li et al., 2019; Oldenburg and Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This issue has limited its use in the oil and gas sector due to product contamination caused by the large level of CO_2 detected at the outflow stream (Oldenburg and Benson, 2002; Sim et al., 2009).

Abba et al. (2018) evaluated the effect of connate water salinity on the dispersion coefficient in cemented rocks during CO₂ flooding during the EGR process. The experiment was carried out at temperatures of 50 °C and pressures of 1300 psig, respectively. The best CO₂ injection rate was 0.3 ml/min, and the core flooding procedure revealed that the dispersion coefficient decreased with increasing salinity. As a result, the higher the density of the connate water, the slower CO₂ disperses into CH₄. They used different salinity concentrations and reported 20minute extendable CO₂ breakouts at 10% wt. concentration of Sodium Chloride (NaCl). Unfortunately, when the salt concentration raised from 5 to 10% wt., the CH₄ recovery decreased due to a drop in core sample pore capacity induced by the high-density connate water molecule occupying more of the open bubble holes inside the core matrix (Abba et al., 2019). To the best of our knowledge, there have been few experimental findings on CO₂ injections capable of freeing the residual natural gas with a significant volume of injected CO₂ stored due to their miscibility impact (Abba et al., 2018). This prompted a thorough investigation of the use of N₂ as a booster prior to the introduction of CO₂. By doing so, the nascent mixing between the two gases (CO₂ and CH₄) is minimized because injecting a specific volume of N₂ before the CO₂ injection produces a re-pressurization effect that results in more CH₄ recovery and a lower fraction of CO₂ in the core holder's effluent stream before and after the CO₂ breakthrough. It was clear from the gas chromatography (GC) printout that the CO₂ was delayed in reaching the CH₄ boundary, making the process more efficient because less product contamination was observed than with typical CO₂ flooding. Furthermore, calculating the optimal CO₂ injection rate prior to N₂ booster gas inclusion is a precondition for determining the optimum booster gas volume required to ensure maximum CH4 recovery and lowest CH4-CO₂ mixing (dispersion coefficient).

The importance of N₂ as a booster for CH₄ recovery and storage during the EGR process by CO_2 flooding was underlined in this work. The N₂ gas functions as a booster/catalyst, allowing for more CH₄ recovery and storage. Because of the N₂ blanketing effect, it makes it difficult for CO₂ to diffuse faster into CH₄, resulting in a longer CO₂ breakthrough. As a result of gravity, the CO₂ falls downhill and is stored inside the pore spaces. The influence of N₂ as a booster gas for natural gas recovery enhancement and CO₂ storage was explored in this study. Compared to conventional CO₂ flooding, the experimental runs with N₂ as a booster indicate good recovery and CO₂ storage with minimal mixing, as seen from the dispersion coefficient values.

1.3 PROBLEM STATEMENT

Carbon dioxide (CO₂) is a harmful greenhouse gas to the environment and minimising its footprint has become critical. The CO₂ storage approach is one of the most reliable methods of separating and securely storing CO₂ produced into the environment by companies today. However, the practical application of this technology necessitates a detailed grasp of the mechanics involved in the storing process. Discovering the methods will give a means of efficiently implementing this type of CO₂ injection for increased natural gas recovery and storage in depleted gas fields, resulting in cutting costs of carbon emission tax placed on industrialised nations.

The concept of EGR has not been widely accepted due to the excessive mixing of injected CO_2 and nascent CH₄ during the core flooding techniques due to similarities in their thermodynamic and physical characteristics (Al-Abri et al., 2009; Honari et al., 2016, 2015; Honari et al., 2013; Hughes et al., 2012; Khan et al., 2013; Oldenburg & Benson, 2002; Patel et al., 2016; Shtepani, 2006; Sidiq et al., 2011; Sim et al., 2008; Sim et al., 2009; Turta et al., 2007; Zhang et al., 2014). The nascent mixing pollutes the recoverable CH₄ and lowers its specific heat, lowering pipeline quality and incurring extra expenditures during the purification process (Oldenburg & Benson, 2002; Sim et al., 2008; Sim et al., 2009). Because of the unprecedented mixing with the displaced gas, the EGR project has been confined to a few experimental experiments (Pooladi- Darvish et al., 2008) and the method has become uneconomical. As a result, the process is poorly understood (Patel et al., 2016). Thus, using a novel method to reduce nascent mixing during the displacement process might be a beneficial development for the oil and gas sector.

Many authors have conducted substantial research on delaying CO_2 breakthrough time during the EGR process (Gu et al., 2019; Hughes et al., 2012; Janssen et al., 2018; Abba et al., 2018).

Abba et al. (2018) and Gu et al. (2019) made significant progress. Abba et al. (2018) employed different connate water concentrations and delayed CO₂ breakout by 20 minutes at a sodium chloride concentration of 10% wt. (NaCl). Unfortunately, when the salt concentration grew from 5 to 10% wt., the CH₄ recovery decreased due to a drop in core sample pore capacity induced by the high-density connate water molecule filling more of the open bubble holes inside the core matrix (Abba et al., 2019). Another issue with EGR process by CO₂ flooding is inadequate flow mechanism data between the displacing and displaced gases as they transport through the core plug. As a result, the necessity for more study to minimise this in-situ mixing has become critical. To assess displacement efficiency, several writers (Nogueira & Mamora, 2005; Turta et al., 2007) use flue gas to displace CH₄. They observed poor displacement due to the flue gas's low density, which is about the same as that of the in situ CH₄. This unfavourable displacement resulted in quick flue gas breakthrough. As a result, flue gas may be unsuitable for effective CH₄ displacement. To date, no effective known approach for increasing simultaneous natural gas recovery and CO₂ storage has been identified. An in-depth investigation was required to create a unique injection approach to reduce such a complicated phenomenon of gas-gas mixing (Abba et al., 2018), since both gases (CO₂ and CH₄) are miscible in most situations. Investigating the potential of N₂ during natural gas displacement will assist reservoir engineers in better characterising gas systems for efficient EGR adoption and eventual CO₂ sequestration in depleted natural gas reservoirs.

1.4 AIMS AND OBJECTIVES

1.4.1 Aims

Research aims to:

- i. Determine the influence of N_2 as a booster gas during enhanced gas recovery by CO_2 injection and sequestration at 40 ^{0}C and 1500 psig.
- Demonstrate the flow behaviour of the injectate gases within the porous medium during the EGR by CO₂ injection through laboratory experiments at 30-40 ^oC and 1500 psig.

1.4.2 Objectives

The key objectives are to:

- i. ascertain the experimental petrophysical parameters of the core samples using various characterisation procedures.
- ii. investigate the thermodynamic behaviour interaction of gases (CO_2 - N_2 - CH_4) using the FLUIDAT^R simulator under reservoir conditions appropriate to the EGR process.

- iii. assess the effect of injection velocity on recovery efficiency during enhanced gas recovery and their influence on dispersion coefficient and CO₂ storage.
- iv. examine the importance of N₂ as a catalyst for CH₄ recovery and storage during natural gas displacement by CO₂ flooding.
- v. investigate the flow mechanism of CO_2 and N_2 in a porous medium using a core flooding experiment. The findings will explain why CO_2 had a longer breakthrough during the EGR process with N_2 gas as a booster.

1.5 THESIS STRUCTURE

The thesis is divided into six chapters consisting of the following:

Chapter 1: Introduction

The chapter describes the technology of increased gas recovery by CO_2 injection and its significance in reducing greenhouse gas emissions. The concept's disadvantage was also considered, and a possible remedy was proposed. The thesis's scientific impact, as well as its key objectives, were also mentioned.

Chapter 2: Concept of Enhanced Gas Recovery

This chapter discusses the idea and theory of gas flow in porous media as it applies to EGR. It delves into geological CO_2 storage and how EGR may play a role, even maximising storage capacity, when natural gas reserves are employed as sequestration locations. The principles and theories behind dispersion and diffusion in a porous media were highlighted. In addition, the relevant literature on miscible flooding and the impact of physics on mixing between CO_2 and CH_4 was reviewed.

Chapter 3: Materials and Experimental Set-up

The chapter discusses the experimental approach and materials needed to conduct the experiments in this study. The comprehensive design of the work phases is also explained and shown here.

Chapter 4: Results and Discussions

The findings acquired utilising the approach in Chapter 3 and the experimental setup and methods in Chapter 4 are provided, and the observation is reported. All claims made about the data are reviewed and analysed in relation to each experimental phase, as outlined in Chapter 3.

Chapter 5: Conclusions and Recommendations

The findings from the experimental study were drawn here, and the future approach to the technology was underlined.

CHAPTER 2 LITERATURE REVIEW

2.1 OVERVIEW

The concepts and principles of EGR are outlined in this section. A survey of relevant literature is also conducted to support the metaphysical basis for this investigation.

2.2 CONCEPT OF ENHANCED GAS RECOVERY

The reservoir pressure tends to decrease with time. As a result, natural gas production from reservoirs might be hampered, and reservoirs are ignored. Depleted oil and gas fields are the name given to these reservoirs (Abba et al., 2017). Such oil and gas fields are unregulated for a variety of reasons, the most prevalent of which being low production output; other causes might include considerable water incursion (Kalra & Wu 2014). However, these depleted reserves are not exhausted of residual hydrocarbons in-situ, and there is a need for further production and recovery to meet escalating energy demand. This greatly benefits the use of EGR procedures when CH_4 is displaced, and CO_2 is stored. These isolated gas reservoirs' services might be utilized for anthropogenic CO_2 geological storage (Abba et al., 2017). The notion of EGR by CO_2 injection takes use of the availability of residual methane in the reservoir while also storing the injected CO_2 .

Furthermore, dispersion refers to the irreversible mixing that happens during fluid displacement via a miscible process (Adepoju et al., 2013). This mixing happens when two miscible fluids collide and their molecules interact under conditions that promote thermodynamic instability (Abba et al., 2018). According to, the two mechanisms that simultaneously play roles in mixing two miscible fluids are Molecular diffusion and mechanical dispersion (Perkins & Johnston, 1963). They characterized mixing in porous media as a diffusion-like process that is influenced by velocity and concentration gradients.

2.3 GAS TRANSPORT IN POROUS MEDIA

Gas transport via porous media occurs in a variety of applications, including catalytic converters, fuel cells, oil and gas exploration, carbon storage, and the food processing sector, to name a few (Abba et al., 2018). Furthermore, to build and optimize a specialised or planned process that involves the movement of gases through porous media, a complete understanding of the interaction mechanism for such gases when they meet each other is required. As a result,

this gas transport is based on several empirical models that have been established to optimize and assess the design and performance of the operations (Abba et al., 2018). Unless otherwise noted, this study focused on gas movement rather than vapour transport. Based on their physical states at typical temperatures and pressures of 293.15K and 14.7 psi, respectively, the optimal approach to separate gas from vapour was determined (Ho & Webb, 2006). Even though this can only be used if the gas components stay liquid at normal temperature and pressure, such fluid is referred to as a vapour. However, if the gas components stay gaseous and are not condensable at normal temperature and pressure, the fluid is considered a gas. This unique phenomenon is critical because it gives a clear knowledge of the two main transport processes influencing the flow behaviour of gases and vapours across porous surfaces. These parameters are diffusion and dispersion processes, with a particular emphasis on the dispersion dominating porous medium transport mechanism, which is a critical precondition in determining the amount of CO_2 or N_2 with the nascent CH_4 during the EGR process via gas alternating gas injection.

Thus, to properly minimize the overhead cost of investigating residual natural gas during the EGR process, the mechanism of displacing gases must be thoroughly explored to avoid premature mixing. Such abrupt mixing is caused primarily by various core sample property parameters such as longitudinal dispersion coefficient, mobility ratio, porosity, permeability, dispersivity, viscous fingering, gravity, flow velocity, diffusion coefficient, etc. The viscosity ratio, often known as the mobility ratio, is defined as the ratio of displaced gas viscosity to displacing gas viscosity. Because of the high density of CO₂ under condition like the EGR process, the CH₄ to CO₂ ratio is lower than the CH₄ to N₂ ratio. The mobility ratio should be smaller than one for efficient displacement. i.e., $\frac{\mu CH_4}{\mu CO_2} < \frac{\mu CH_4}{\mu N_2} < 1$.

2.4 DISPERSION THEORY AND EQUATION

Based on (Perkins & Johnston, 1963; Newberg & Foh, 1988)'s description of mixing in porous media, the 1D Advection Dispersion equation for gas transport in porous media along the direction of flow is presented in Eq. 2.1.

$$K_1 \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
(2.1)

Critical parameters in the following equation are the effluent composition (C) from the Gas Chromatography (GC) at a distance (x) under time (t), longitudinal dispersion coefficient (K_L), and interstitial velocity (u). Equation 2.1 governs the displacement of methane by supercritical carbon dioxide in cemented rocks. This model is commonly used to mimic the transport of fluids in porous media. However, modelling studies have revealed that this may result in anomalous behaviour known as upstream migration, which happens when the concentration gradient (dC/dx) along the length scale becomes positive. Like supercritical CO_2 flowing through a pollutant following a breakthrough in the porous media, the magnitudes of dC/dx and dispersion coefficient are significant. The longitudinal dispersion (mixing along the axis of transport) coefficient, K_L, in EGR, which measures the rate of mixing between the fluids, is evaluated by the model. As a result, Eq. 2.1 may be stated in dimensionless form as Eq. 2.2.

$$\frac{1}{P_e}\frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2.2)

Where

 $P_e = \frac{uL}{K_l}$, peclet number (ratio of convection to dispersion), L is the length scale of mixing

 $t_D = \frac{tu}{L}$, dimensionless time,

 $x_D = \frac{tu}{L}$, dimensionless distance, $u = \frac{Q}{\pi r^2 \phi}$, interstitial velocity, m/s, Q is superficial velocity (m³/s), ϕ is porosity and K₁ is longitudinal dispersion (m²/s)

The injection of CO_2 and N_2 are at x = 0,

-

Initial condition: C = 0 at $t_D = 0$,

Boundary conditions: C = 1 at $x_D = 0$, $C \rightarrow 0$ as $x_D \rightarrow \infty$

Therefore, the solution to Eq. 2.2 is presented in Eq. 2.3.

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{t_D/P_e}} \right) + e^{P_e x_D} erfc \left(\frac{x_D + t_D}{2\sqrt{t_D/P_e}} \right) \right\}$$
(2.3)

To calculate the relevant dispersion coefficient, the effluent core flooding experimental composition is fitted with the analytical solution to the one differential Advection Dispersion (AD) equation in terms of the Péclet number. The absolute dispersion coefficient of the

experiment is the value that gives the best synergy between the experimental result and the numerical solution.

Perkins and Johnston in (1963) provide a well recognised model for predicting the major displacement mechanism during the EGR process in porous medium. This model equation is written as follows:

$$P_{em} = \frac{u_m d}{D} \tag{2.4}$$

Where Pexp is the experimental medium Péclet number, calculated using the average interstitial velocity (u) in m/s, the molecular diffusion coefficient (D) in m²/s, and (d) is the characteristic length scale of the porous medium, defined as the consolidated rock's medium-grain diameter (Hughes et al., 2012). In general, diffusion dominates the dispersion process at Pem 0.1, but advective mixing dominates the dispersion process for $P_{em} > 10$. To calculate the dispersion coefficient, the analytical solution to Eq. 2.3 was utilized to fit the concentration profiles obtained from the experimental data.

Coats et al, 2009 correlated the dispersion coefficient with molecular diffusion coefficient as shown in Eq. 2.5

$$\frac{K_l}{D} = \frac{1}{\tau} + \alpha \frac{u_m^n}{D} \tag{2.5}$$

Where α is in meter (m), called the porous medium's dispersivity, and n represents an exponent. The tortuosity (τ) can be range from low to as high as 13 or even more for consolidated rocks., reported by (Honari et al., 2013). However, this parameter can be obtained empirically through various methods, and n is primarily determined using the core flooding system (Hughes et al., 2012).

In (2001), Delgado developed a Lambda function by plotting a graph of Lambda for different experimental times versus per cent of displacing fluid in an arithmetic probability paper. The dispersion coefficient was then calculated using Eq. 2.6.

$$K_{L} = u \times L \left(\frac{\lambda_{90} - \lambda_{10}}{3.625}\right)^{2}$$
(2.6)

Where,

 K_L = coefficient of longitudinal dispersion (m²/s)

u = Interstitial velocity (m/s)

L = length or dimeter of porous medium (m)

 λ_{90} and λ_{10} are values of Lambda function obtained from the intersecting equation of line of best fit passing through the effluent concentration profile graph at 90 and 10% concentration.

2.5 DIFFUSION THEORY AND EQUATION

2.5.1 Diffusion Theory

Molecular diffusion is commonly considered to dominate gas-phase diffusion. The onedimensional Fick's second law, provided in Eq. 2.7, describes the uneven widening of a solute over concentration gradients over time.

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{2.7}$$

Where C denotes the gas concentration (mol/m³), t denotes the time (s), Da is the binary molecular diffusion coefficient of air (m²/s), and x denotes the distance along the flow axis (m). When the centre collision occurs within a molecule-molecule interaction without colliding with the container's wall, this is referred to as molecular diffusion. In some cases, more sophisticated gas-phase diffusion processes, such as viscous, Knudsen, and non-equimolar diffusion, can occur (Scanlon et al., 2000). The former two processes are thought to occur because of pore walls and the resulting molecule-wall collisions (Cunningham and Williams, 1980). The latter necessitates the presence of both system walls and a multicomponent gas; such circumstances are typically found in porous media, resulting in a deviation from Fick's law (Sleep, 1998). According to Baehr and Bruell (1990), high vapour pressures, particularly those near organic liquid sources, deviate from Fick's law. Because of the correlations between average kinetic energy, velocity, and molecular mass, diffusion is a solute-dependent component of dispersion (Molly & Mark, 2006). Meanwhile, the average kinetic energy of all gases at a given temperature is equal, as shown in Eq. 2.8.

$$E_k = \frac{3}{2}kT = \frac{1}{2}mv_{rms}^2$$
(2.8)

Where k denotes Boltzmann's constant (J/K), T denotes temperature (K), m denotes solute mass (kg), and vrms is the root-mean-square velocity of the gas particles (m/s). Thus, given thermal equilibrium and equal kinetic energy, lesser molecular weight gases have faster average speeds than higher molecular weight gases (Molly & Mark, 2006). This increased velocity produces

more significant diffusion coefficients, which contributes to total dispersion dominance. In low permeability zones, such as aggregates or fine-textured lenses, diffusion mechanisms often dominate transport.

2.5.2 Diffusion Coefficient

The diffusion coefficient (D) represents the amount or magnitude with which a material or fluid diffuses over a unit surface per unit time at a given or specified unit concentration gradient. Takahashi and Iwasaki presented a mathematical model involving molecular diffusion, temperature, and pressure for empirical measurement of diffusion coefficient in 1970, as described by (Hughes et al., 2012; Liu et al., 2015). This connection was also exploited by other researchers to establish correct diffusivity using Eq. 2.9 under conditions suitable for EGR by CO_2 injection. However, Takahashi and Iwasaki (1970) determined the diffusion coefficient of CO_2 in CH_4 at 298-348K temperature and 5-15MPa pressure for a porous bronze plug. The results were well within the range of EGR-applicable conditions.

$$D_{\rm CO2,CH4} = \frac{(-4.3844 \times 10^{-13} p + 8.55440 \times 10^{-11})T^{1.75}}{p}$$
(2.9)

Where $D_{CO2, CH4}$ is the molecular diffusion coefficient of CO₂ in pure CH₄ estimated in m²/s, P in MPa, and T in K. Over the range of 298-348K and 5–15 MPa, the absolute average deviation (AAD) of this correlation from the experimental data was 1.5 percent. Another model was built in this work to account for the incorporation of Nitrogen (N₂) gas during natural gas displacement and CO₂ sequestration. This model equation is shown in Eq. 2.10. Fuller, Schetter, and Gittings (1966) established a correlation formula from computer-aided correlation of 340 experimental points, which is written as:

$$D_{\text{N2,CH4}} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{(1/\mu_{N_2} + 1/\mu_{CH_4})}}{P[(\Sigma V_{N_2})^{1/3} + (\Sigma V_{CH_4})^{1/3}]^2}$$
(2.10)

Where $(\sum V_{N_2})$ and $(\sum V_{CH_4})$ are the values derived from the summation of atomic diffusion volumes for each component of the binary mixture, i.e., molecules N₂ and CH₄. The values for some atoms and simple molecules as reported by Fuller et al, 1966 are presented in Table 2.1.

C/N	Mologula	Diffusion volume (cm ³)
<u>3/1N</u>	woiecule	Diffusion volume (cm ²)
1	He	2.67
2	Ne	5.98
3	Ar	16.2
4	Kr	24.5
5	Xe	32.7
6	H_2	6.12
7	D_2	6.84
8	N_2	18.5
9	O_2	16.3
10	Air	19.7
11	CO	18.0
12	CO_2	26.9
13	N_2O	35.9
14	NH_3	20.7
15	H_2O	13.1
16	SF_6	71.3
17	Cl_2	38.4
18	Br_2	69.0
19	SO_2	41.8
20	С	15.9
21	Н	2.31
22	Ο	6.11
23	Ν	4.54
24	F	14.7
25	Cl	21.0
26	Br	21.9
27	Ι	29.8
28	S	22.9

Table 2.1: Atomic diffusion contributions for various gas element and molecules (Fuller et al.,1966)

The equation was reduced further when the atomic diffusion volumes and molecular weights of nitrogen and methane were included. The carbon dioxide and methane displacement mechanisms were treated in the same way. Eqs. 2.11, 2.12, and 2.13 showed simpler versions of these equations.

$$D_{\rm N2,CH4} = \frac{10.2 \times 10^{-11} \, T^{1.75}}{P} \tag{2.11}$$

$$D_{\text{CO2,CH4}} = \frac{8.2 \times 10^{-11} T^{1.75}}{P}$$
(2.12)

$$D_{\rm CO2,N2} = \frac{7.69 \times 10^{-11} \, T^{1.75}}{P} \tag{2.13}$$

Where T and P are temperatures in K and pressure in MPa, respectively. The experimental work of Abba et al., 2018 was used to validate the equation. The molecular diffusion coefficient $(D_{CO2,CH4})$ was calculated to be 22.52 x10-8 m²/s rather than 22.56 x10-8 m²/s before. The absolute average deviation (AAD) of this result from Abba et al., 2018 was 0.18 percent, which is well within the experimental error measurement range.

2.6 GAS-PHASE DISPERSION IN POROUS MEDIA

Solute dispersion is the continuous proliferation of a solute plume over time. As seen in Fig. 2.1, spreading is primarily a mixing and further diluting of the solute plume with the occupant fluid (Ho & Webb, 2006). Dispersion analysis is crucial for understanding gas-phase transport in porous media. Several transport principles, such as dispersion, that were first developed to describe gas flow behaviour in saturated porous media and later for unsaturated water flow, may also be applied to the movement of gases in unsaturated systems (Costanza-Robinson & Brusseau, 2006). Any detailed investigation of gas-phase systems, on the other hand, necessitates careful consideration of the specific rigidity of unsaturated systems as well as the features of gases themselves. Unsaturated porous media, for example, exhibit air-filled porosities that change geographically and temporally depending on soil moisture content and grain particle size distribution (Costanza-Robinson & Brusseau, 2006). Gas-phase diffusion coefficients are typically 4-6 orders of magnitude greater than aqueous-phase values. In contrast to water, pressure and temperature changes caused by increased kinetic energy have a significant impact on gases. Furthermore, those gases exhibit slip-flow along pore walls, which is known as the Klinkenberg effect, but water does not (Costanza-Robinson & Brusseau, 2006).



Figure 2.1 Spreading of a solute plume from an instantaneous point source; (A) depicts twodimensional spatial 'snapshots' (concentration versus x-y coordinate) over time (t). Simultaneously, (B) displays a temporal breakthrough curve (concentration against time) as a

function of distance along the flow axis in the x-coordinate (Costanza-Robinson & Brusseau, 2006).

2.6.1 Dispersivity and Peclet Number

In most cases, the longitudinal dispersivity term is assessed using column-scale nonreactive tracer experiments (Costanza-Robinson & Brusseau, 2006). Gas-phase longitudinal dispersivities have been measured in the laboratory using porous medium systems and vary between 0.2 and 2.9 cm (Popovicová and Brusseau, 1997; Garcia-Herruzo et al., 2000; Costanza-Robinson and Brusseau, 2006). Because of increased system heterogeneity, dispersivities determined in the main field tend to be greater. Furthermore, it is solute independent and unaffected by changes in carrier gas velocity or non-equilibrium factors (Costanza-Robinson & Brusseau, 2006). The Peclet number, Pe, is a dimensionless measure of the degree of dispersion experienced by the displacing gas, which can also be characterised as the ratio of advective to dispersive processes or advective to diffusive processes (Rose, 1973). The preceding definition is preferable and will be used throughout the report. This dimensionless number (Pe) is often determined by fitting a displacing fluid (CO₂ or N₂) breakthrough curve to an advective-dispersive solute transport model. The Peclet number's size is inversely proportional to the degree of dispersion. As a result, low Peclet numbers indicate a high degree of solute dispersion (higher molecular diffusion coefficient). The dispersion coefficient stated in Eq. 2.14 can be connected to the Peclet number, commonly known as the Brenner number (Rose and Passioura, 1971).

$$P_{em} = \frac{vL}{D} \tag{2.14}$$

Where L is the system's characteristic length (m), and v is the average velocity (m/s). In grain diameter or column length, the characteristic length can be determined at small or large scales (Rose, 1973). The precise formulation of the Peclet number varies depending on the application and topic of research. In engineering fields such as the EGR process, grain-scale lengths are commonly employed. Dispersivity is independent of fluid velocity, making it a property of the porous medium. According to Coats et al. (2009), the amount of dispersion is quantified by the rock property dispersivity (α), which is on the order of 0.01 ft (3.048 x 10⁻³ m) in consolidated rock and much lower in sand packs based on experimental laboratory measurements.

Coasts and Whitson (2004) reported the link between dispersivity, longitudinal dispersion, and interstitial velocity, which is seen in Eq. 2.15.

$$\alpha = \frac{K_l}{u} \tag{2.15}$$

Where K_l represents longitudinal dispersion and u represents interstitial velocity. Thus, Eq. 2.16 was developed when the ratio of $\frac{K_l}{u}$ in Eq. 2.15 was replaced with $1/P_e$.

$$\alpha = \frac{1}{P_e} L \tag{2.16}$$

The relevance of the Péclet number during a miscible flooding process is seen in Eq. 2.16, which is scale dependent and a function of dispersivity. According to Ekwere (2007), molecular diffusion is more important for transverse dispersion than longitudinal dispersion. This is because the regime dominated by molecular diffusion occurs across a wider range of Péclet numbers for transverse dispersion than for longitudinal dispersion, as shown in Fig. 2.2, modified from the work of Perkins & Johnston (1963).



Figure 2.2 Longitudinal dispersion coefficients in porous media (Perkins & Johnston, 1963) Fig. 2.2 depicts a plot of the longitudinal dispersion and diffusion ratio (K_L/D) vs the porous medium's Péclet number, P_{em} . At low Pem values, molecular diffusion takes precedence over advective dispersion. At large Péclet numbers, the longitudinal dispersion coefficient is invariably greater than the transverse dispersion coefficient. Because the system is dominated by the dispersion process when the reservoir velocity, temperature, and pressure of the Péclet number are more than a value of 6, molecular diffusion may be ignored (Ekwere, 2007).

2.7 SUPERCRITICAL CO₂, N₂, and CH₄ PHASE BEHAVIOUR

The actual flow behaviour of supercritical carbon dioxide as its plume's transverses the pore spaces inside the core sample to displace the in-situ methane is highly complicated, especially when inert nitrogen gas is included. Investigating the complexities of displacing fluids (CO₂ and N₂) to the nascent CH₄ is critical in understanding the trends and expected outcomes of the displacement process, as these gases in their supercritical state exhibit unique behaviour by exhibiting the density of a liquid while retaining the viscosity of a gas (Abba et al., 2018). As shown in Figs. 2.3, 2.4, and 2.5, the critical temperature and pressure values for CO₂, N₂, and CH₄ are 31.05 and 73.80, -146.9 and 33.90, -82.55 ^oC and 46bar, respectively. Thus, the operation parameters for this study are at an average normal reservoir pressure of 0.451 psi/ft gradient, an average reservoir depth of 1km, and an average geothermal temperature of 40 ^oC/km, which are considerably above each gas species.



Figure 2.3 CO₂ vapor pressure line generated from FLUIDAT^R



Figure 2.4 N₂ vapor pressure line generated from FLUIDAT^R



Figure 2.5 CH₄ vapor pressure line generated from FLUIDAT^R

2.8 CO₂ GEOLOGICAL STORAGE

The manmade CO_2 impact is causing an environmental problem that is posing a danger to modern civilisation. Because of its established gas-holding capacity, natural gas reserves offer

the potential to securely store anthropogenic CO_2 (Kalra & Wu 2014). This potential CO_2 storage location must be studied and appraised in terms of both economic and environmental feasibility. When deciding when to begin a geological storage procedure, cost-effectiveness must be considered. It is always important to remember that CO_2 sequestration capability is primarily for the reduction of Green House Gases (GHGs) and global warming (Gu et al., 2019). As Gu et al. (2019) noted, this work revealed the quantity of CO2 sequestrates (V_{stored-CO2}) in sandstone samples during the gas alternating gas displacement process in Eq. 2.17.

$$V_{storage-CO2} = V_{t,injected-CO2} - F_{outlet} \int_0^t C_{t,CO2} dt$$
(2.17)

Where $V_{t,injected-CO2}$ is the volume of injected CO₂ recorded by the high-pressure syringe pump at time t and $C_{t,CO2}$ is the CO₂ mole percent in the effluent at time t measured by the gas chromatography (GC) analyser.

The quantity of CO₂ stored normally increases rapidly at the start of the injection. According to Gu et al. (2019), a large amount of gas must be fed into the adsorption column in the first few minutes to elevate the reservoir pressure from 5.03 to 8.00 MPa. Liu et al. (2015) discovered that injected CO₂ on shale displaced pre-adsorbed CH₄ quicker in the prior 1.5h. As the CO₂ injection continues, the quantity of CO₂ adsorbed falls abruptly (Liu et al., 2018), and the enhanced rate of V_{storage-CO2} begins to diminish.

When the injectant is gradually richer in CO_2 composition, both the amount of stored CO_2 and the rate of storage improve. Injecting CO_2 into the shale reservoir, on the other hand, leads in a simultaneous rise in combined stored CO_2 and rate of storing, which indicates that injecting CO_2 can accelerate and maximise anthropogenic CO_2 storage. Previous study has shown that the difference in CO_2 storage volumes on coal by injection of CO_2 and combination of CO_2 -N₂ is not significant, especially when the permeability of coal falls dramatically during the CO_2 injection (Gu et al., 2019). As a result, when CO_2 is used as a displacing fluid, the rise is rather visible. This indicates that the shale matrix protrusion during the displacement process is substantially smaller, which has a considerable impact on shale permeability and the quantity of CO_2 stored.

2.8.1 An Overview of CO₂ Storage in Depletion Gas Reservoir

Due to their potential, demonstrated storage uprightness, and subsea conditions (Jikich et al., 2003; Raza et al., 2016), depleted oil and gas reserves are among the most certain choices for CO₂ storage projects (Dance, 2013; Wright, 2007). Furthermore, these reservoirs have negligible or low operational expenses, with the ability to encapsulate fluids for decades. Temperature, pressure, porosity, permeability, and the universal storage volume are all known

qualities. However, a significant amount of natural gas is frequently remained in reservoirs after depletion, referred to as trapped gas (Ahmed, 2001; Feather & Archer, 2010), which includes residual and untapped gases. As a result, when injected CO₂ is combined with residual gas during the EGR process, the quality and calorific value of the generated natural gas are significantly lowered (Feather & Archer, 2010; Xiaoling et al., 2012). CO₂ injection, on the other hand, may encourage fault stimulation because to the pressure rise linked with the injection (Mildren et al., 2005; Tenthorey et al., 2012). As a result, as documented by various authors, the development of the EGR and CO₂ sequestration processes in depleted gas reservoirs is linked to strategy, reservoir features, and operating factors. Oldenburg and Benson, for example, investigated the influence of injections on physical parameters during the EGR and CO₂ storage processes in 2002. Reservoir pressure, CH₄-CO₂ advection mixing, dispersion, molecular diffusion, and pressure diffusivity are among these parameters. Due to CO_2 higher density and viscosity than CH_4 , an acceptable amount of CO_2 was injected to collect more natural gases with little in-situ mixing. Jikich et al., in 2003, quantitatively examined the consequences of the following strategic injection scenarios: i) simultaneous CO₂ injection and CH₄ recovery at project inception; and ii) simultaneous CO₂ injection and CH₄ recovery at project completion. iii) primary natural gas production to the economic limit, followed by CO₂ injection for secondary gas recovery. It was determined that injection after field abandon produce a better recovery than the early phases. In addition, in 2005, Al-Hashami and his colleagues conducted comprehensive research on the impacts of mixing, diffusion, and solubility in water formation during EGR and CO₂ sequestration. They observed that CO₂ solubility might have an influence on storage capacity with 8% CH₄ in reservoirs with 85% depletion (Al-Hashami et al., 2005). Finally, Polak and Grimstad developed a computational approach in 2009 to assess the viability of EGR and CO₂ sequestration in Austria's Atzbach-Schwanenstadt gas field. They detected a rapid premature CO₂ breakout, which curtailed natural gas output indirectly owing to product contamination. However, when the injection is stopped, the reservoir pressure stabilises, with just 10% of the total injected CO₂ dissolved in the immobile reservoir water after 1500 years owing to solubility trapping.

2.9 RESERVOIR VOLUMES

Modern 3D seismic surveys create comprehensive interpretations of the reservoir's physical dimensions. Which (along with well-log descriptions) guide the evolution of isopach maps, responsible for determining the volumes, locations (or diffusions) of fluid saturations such as gas, oil, and water in place (Robinson & McCabe, 1997; Sullivan et al., 2000). This map is

used to estimate reservoir capacity by highlighting the boundaries of porosity and permeability (porous-permeable) zones inside unit blocks. They are also seeing changes in which the volume of porosity (ϕ) and permeability (K) for restricting reservoir fluid diminishes (i.e., $\phi < 0.05$; K < 0.10 mD) owing to changes in rock characteristics.

2.9.1 Gas Reservoirs

The volume of original gas in situ (OGIP) is defined as the amount of nascent natural gas initially existing in the reservoir (G) and the amount of gas generated (Gp). If there is no water drive (We and Wp = 0), the gas will expand to its original volume. If the reservoir is connected to an aquifer, the initial volume occupied by the gas (GBgi) will decrease the intruded water volume less water generated along with the gas (We - WpBw) as shown in Fig. 2.6. As a result, water invasion lowers gas pore volume (PV), and lean-to preserves reservoir pressure. Eq. 2.18 shows the link between gas production (GB_{gi}), gas expansion ($(G - G_p)_{Bg}$), water influx (W_e), and the quantity of water generated (W_pW_w).

$$GB_{gi} = (G - G_p)_{Bg} + W_e - W_p W_w$$
(2.18)



Figure 2.6 Gas produced from a reservoir in contact with an aquifer (Djebbar & Erle, 2012). In Fig. 2.6 the gas produced is equal to the expanded gas remaining in (b) plus (water influx - water produced).

To calculate the % recovery of CH_4 and the recovery factor for each injection rate, Eq. 2.19 was used to calculate the Original Gas in Place (OGIP).

$$OGIP = \frac{V_b \phi(1 - s_w)}{B_g}$$
(2.19)
Where V_b is the reservoir's bulk volume in ft³, ϕ is reservoir porosity, S_w is formation water saturation, and Bg is the gas formation volume factor in ft³/scf, which was calculated using Eq. 2.2.

$$B_{g} = \frac{P_{sc}}{T_{sc}} \times z \frac{T}{P}$$
(2.20)

Where z is the gas compressibility factor, P_{sc} and T_{sc} are standard pressure and temperature, and P and T are desired pressure and temperature. Eq. 2.20 was further simplified into Eq. 2.21 by taking P_{sc} and T_{sc} to be 14.696 psia and 18°C (291.15K), respectively.

$$B_g = z \frac{T}{20P} \tag{2.21}$$

2.10 POROSITY AND PERMEABILITY

The quantity of oil and gas contained inside the pore spaces of reservoir rocks, the ability of these fluids to pass through the rocks, and other associated geophysical features are exclusively determined by the reservoir rocks' identity. The porosity of the rock is defined as the estimate of the pore space, whereas the permeability is defined as the measure of the rock's capacity to transmit fluids. However, in addition to these two important reservoir qualities, additional important reservoir parameters include rock texture, resistivity, and the rough quality of the aperture or void channels (Djebbar & Erle, 2012).

Sedimentary rock texture is determined primarily by grain structure, grain size, grain orientation, and chemical content. However, in other cases, the texture gives information on formation permeability and porosity. Fine-grained consolidated sandstones with poorly graded angular grains, for example, would always have lower porosity than coarse-grained cemented sandstones. Thus, differences in permeability may be predicted based on variations in grain size and form, as well as the distribution of pore passage in the rock (Djebbar & Erle, 2012).

2.10.1 Porosity

Because they are all made of sand grains and carbonate particles, sandstone and limestone oil and gas fields do not fit together perfectly. The liquids and gases are obsessed with the pore (void) space formed or constructed throughout the beds linking grains, known as pore space or interstice. The porosity of a reservoir rock is defined as the proportion of the reservoir's bulk volume that is free of the reservoir's solid framework (Djebbar & Erle, 2012). This may be stated mathematically as seen in Eq. 2.22.

$$\Phi = \frac{V_b - V_{gr}}{V_b} = \frac{V_p}{V_b} \tag{2.22}$$

Where φ is the porosity or fraction of uncopied space

V_b is the bulk volume of the reservoir rock, define as $\frac{\pi d^2 L}{4}$ with d and L as the diameter and length of the core sample

 V_{gr} is the grain volume

V_p is the pore volume

The porosity of porous materials can have any value, according to the preceding definition; nevertheless, the porosity of most sedimentary rocks is typically less than 50%. (Djebbar & Erle, 2012). As shown in Table 2.2, the porosity of petroleum oil and gas reservoirs ranges from 5-30% but is most commonly between 10-20%. Any porosity less than 5% is uneconomical for oil and gas exploration, whereas any porosity more than 35% is exceedingly unusual.

Table 2.2: Range	e of porosi	y and possible	e remarks (Djebbar	& Erle, 2012)
------------------	-------------	----------------	--------------------	---------------

% Porosity Ranges	Remark
0-5	Negligible
5-10	Poor
10-15	Fair
15-20	Good
>20	Very good

2.10.2 Permeability

The effective porosity of a rock determines its permeability. This means that a reservoir rock must be able to enable fluids to flow via its jointed pores. Such rocks are porous, but non-permeable rocks are called non-porous because they do not allow fluids to flow through their interconnecting pores. This rock has 0% permeability, especially when freshwater is present, since some clays, notably montmorillonites, swell in freshwater and seem to or completely cover the pore or void spaces.

Henry Darcy, a French engineer, devised a fluid flow equation (Eq. 2.23) in 1856, which became one of the main mathematical methods for assessing permeability in oil and gas fields. As illustrated in Fig. 2.7, this equation was utilised to calculate the permeability of a core sample.

$$v = \frac{q}{A_c} = -\frac{k}{\mu} \frac{dp}{dl}$$
(2.23)

Where,

v is fluid velocity, cm/s

q is flow rate, cm³/s

k is permeability of the porous rock, Darcy (0.986923 μ m²)

A is cross-sectional area of the core sample, cm^2 and μ is the viscosity of the fluid in centipoises (cP)

L is the length of the core sample, cm

dp/dl is pressure gradient in the direction of the flow, atm/cm



Figure 2.7 Core sample (Djebbar & Erle, 2012)

Eq. 2.23 was expressed into its simple form as shown in Eq. 2.23a

$$q = -\frac{A_c k}{\mu} \frac{dp}{dx}$$
(2.23a)

The variables are separated to calculate the permeability (k) over the whole core sample, and equation 2.23a was integrated between a boundary condition of input pressure (P₁) and output pressure (P₂) from x =to L. Eq. 2.23b shows the final solution to Eq. 2.23a.

$$k = -\frac{q\mu L}{A_c(P_1 - P_2)}$$
(2.23b)

Where k is determined by allowing fluid to pass through a clean and dry core sample (plug) of the specified dimensions (Ac and L). Figure 2.8 depicts a symbol for the notion involved in permeability determinations.





A core sample (plug) that was clean and dry was put into a core holder. The manual pressure gauge is used to measure the upstream (P₁) and downstream (P₂) pressures to calculate the differential pressure across the core sample from x = 0 to x = L. Furthermore, the flow rate is measured in cm3/s at 1 atm atmospheric pressure. The steady-state technique is generally used for high permeable rocks, whereas the unsteady-state method is used for low porous rocks because it allows for quick permeability measurement within minutes (Darcy, 1856). Because of their low fluid-rock reactivity and ease of use, dry gas (air) or nitrogen (N2) are often employed as reference fluids for permeability assessment.

Eq. 2.23b is mostly applicable for non or slightly compressible fluids (liquid). However, for compressible fluids (gas) k is obtained from Eq. 2.23c.

$$k = -\frac{2q\mu_g L}{A_c(P_1^2 - P_2^2)}$$
(2.23c)

where μ_g is the gas viscosity in cP

When employing a liquid as the flowing fluid, air permeability testing in a consolidated core sample typically yields larger results than real reservoir permeability. This distinction is because of gas slippage (or Klinkenberg) and overburden pressure.

Klinkerberg established in 1941 that at a low average mean pressure (Pm) of 1 atm, the gas molecules are farther apart, allowing them to "slide" through the pore (void) gaps with no friction loss and a high permeability value. In contrast, with a high average mean pressure, typically 1000 psia, the opposite is true. That is, the gas molecules are close together and encounter considerable drag friction, particularly at the pore walls. This effect becomes more

pronounced as the average mean pressure rises, with the gas acting more like a liquid (Klinkenberg, 1941).

Thus, extrapolating a graph of observed gas permeability versus the inverse of average mean pressure at 1/Pm = 0 (i.e., average mean pressure at infinity), as shown in Fig. 2.9, the permeability would be roughly comparable to the liquid permeability at this stage (k_L). This connection is depicted in Eq. 2.23d.

$$k_a = c \left(\frac{1}{P_m}\right) + k_L \tag{2.23d}$$

where P_m is the average mean pressure, $(P_1+P_2)/2$

c is the gradient of the graph line

 k_L is the identical liquid permeability (absolute permeability, k)

also, according to Klinkenberg the gradient (slope) can be evaluated using Eq. 2.23e

$$c = bk_L \tag{2.23e}$$

Where b is the pore geometry factor, which is inversely proportional to the radius of capillaries and relies on the size of the pore opening.



Figure 2.9 A plot of measured gas permeability versus inverse of mean pressure showing Klinkenberg effect (Klinkenberg, 1941)

2.11 RATIO OF COMPRESSION EQUATION

The term compression ratio can apply to a single compression cycle as well as a multilevel reduction stage. When used to a single device or set of compression, it is characterized as the phase or unit compression ratio; when related to a multiphase compressor, it is described as the total compression ratio. The compression ratio of most gas pipeline compressors is low. A sole

compression cycle in a reciprocating engine and a single entity in a centrifugal compressor can meet low pressure ratios. While pressure ratio is an essential indicator for reciprocating compressors, the pressure ratio that a certain centrifugal compressor can generate is primarily controlled by gas composition and temperature (Mokhatab et al., 2019). For natural gas, a single centrifugal stage may provide a pressure ratio of 1.4 (with a specific gravity of 0.58– 0.70). The compression ratio (CR) is defined as the ratio of actual discharge pressure to absolute suction pressure. Eq. 2.24 shows how this is expressed numerically.

$$CR = \left(\frac{P_2}{P_1}\right)^{\gamma} \tag{2.24}$$

However, the ratio of $\frac{P_2}{P_1}$ represent the pressure ratio (PR). Therefore, Eq. 2.24 can be re-written as:

$$CR = (PR)^{\gamma} \tag{2.25}$$

Where γ is the specific heat ratio for the working gas, which is about 1.4 for N₂ or air and 1.28 for CO₂.

2.12 REVIEW OF CO₂ AND N₂ FLOODING

Using core flooding tests, many researchers have successfully documented the potential of CO_2 at both subcritical and supercritical settings for increased gas recovery. However, it should be highlighted that most of these trials were carried out with the core oriented horizontally, with little thought given to the consequences of such a core orientation. Even though Abba et al. in 2019 were able to identify the role of injection direction in permeability fluctuation of porous medium during EGR by CO_2 injection. He discovered that the coefficient of dispersion increased with decreasing permeability, with Bandera Grey having the greatest dispersion coefficient and, as a result, more mixing between the displacing CO_2 and the displaced CH_4 . Furthermore, with permeability values around 50%, this dispersion phenomena were more prominent in the horizontal injection direction than in the vertical injection. This indicates that the horizontal injection orientation has a 50% higher permeability with the largest dispersion coefficient than the vertical injection orientation (Abba et al., 2019). A core flooding experiment at 1300 psig and 50 $^{\circ}C$ was used in the laboratory.

Seo and Mamora (Mamora and Seo, 2002; Seo, 2004; Seo and Mamora, 2005) carried out a core flooding experiment and measured CO_2 breakthrough profiles for the displacement of nascent CH_4 by CO_2 injection via a clean and dry 305 mm carbonate core sample at temperatures and pressure ranges ranging from 20 to 80 $^{\circ}C$ and 3.5-20.5 MPa, respectively. For the test runs at room temperature, an ideal CO_2 injection rate of 0.25ml per minute was

employed. Furthermore, the dispersion coefficients were calculated using the CO₂ breakthrough profiles. However, because they employed a manually operated backpressure regulator device in their experiment, they were unable to validate the recorded breakthrough profiles because they could not regulate the core pressure during the displacement process (Seo, 2004). However, Seo and Mamora (2005) discovered that as the temperature rises, so do the dispersion coefficients. As the pressure increased from 3.5 to 20.5 MPa, the opposite tendency was seen. As the CO_2 plumes traverse through the core sample, this demonstrates the substantial dependency of the molecular diffusion coefficient on temperature and pressure. Their main constraint was that they were unable to collect and provide data on dispersivities to a specific level of mixing during the core flooding tests; instead, their miscible displacement data for the CO₂–CH₄ displacement was based on historical records for use in simulations. In addition to Seo's study, Nogueira and Mamora (Nogueira & Mamora, 2008; Nogueira, 2005) investigated the influence of gas impurities on CH₄ displacement during EGR. At 10.3 MPa and 70 °C, several breakthrough profiles were examined by injecting CO₂ containing varying degrees of contaminants into a dry, 305 mm long chalk core sample saturated with methane. The best recovery factor (RF) and dispersion coefficient were found (Hughes et al., 2012). Their findings indicate that the lower the impurity level, the less substantial the influence on both dispersion and CH₄ recovery. For example, when CO₂ with fewer than 1% contaminants was injected, the dispersion and recovery were the same as when 100% pure CO₂ was injected (Hughes et al., 2012). When the impurity concentration increased, however, the situation changed. When compared to pure CO_2 injection, injection of (80 percent $N_2 + 15$ percent CO_2) resulted in a 10% recovery reduction and a greater dispersion coefficient. As a result of significant gas slippage and viscous fingering, the mobility ratio of the high impurity content (80% N₂) with CH₄ resulted in reduced displacement efficiency.

In 2009 and 2010, Sidiq and Amin used a core flooding technique to study the CO₂ breakthrough profile across a 194mm sandstone using a 98%CO₂ + 2%CH₄ injection fluid. Prior to the mixed gas injection, the core sample was completely saturated with 25-90% CH₄. In addition, the core sample was pre-saturated with a predetermined brine solution before being reduced to residual water content using the gas combination. The temperature and pressure conditions for the experiment were 160 $^{\circ}$ C and 40.7 MPa, respectively. However, due to the approximation approach used in estimating the individual dispersion coefficient, their observed dispersion coefficient has limited application. This makes identifying the beginning point of the concave slope challenging, resulting in extremely considerable error in the dispersion coefficient extrapolated owing to slight changes in the breakthrough point (Sidiq & Amin,

2009; Sidiq & Amin, 2010). According to many writers, particularly (Al-Abri & Amin, 2012; Al-Abriet et al., 2009; Amin et al., 2010), CH₄ and CO₂ create an 'immiscible' channel interface that is thermodynamically stable. This enables the measurement of interfacial tension via the study of a pendant drop form. Despite this, it was later discovered that the combination of CH₄ + CO₂ is miscible in all proportions with no vapour-liquid equilibria exhibiting under the pressures and temperatures of their tests.

Turta et al. (2007) ran a series of gas-gas displacement operations on Berea grey cores utilising N_2 and CO_2 as injection fluids at 70°C and 6.2 MPa. The runs were carried out in both dry and connate water conditions to investigate the impact of connate water addition on the recovery factor and efficiency. The results of the runs on the consolidated core sample show that the recoveries for pure N_2 and CO_2 , employed as injecting fluids, were comparable. When their mixture in varied proportions was employed to displace the nascent CH₄, however, a delay in CO₂ breakthrough was detected, which corresponded to a time when only a mixture of CH₄ and N_2 was formed. This might be owing to CO₂ great solubility in connate water, as opposed to N_2 , which is only partly soluble. This universally contributes to a greater gas recovery because to a longer residence period, along with the fact that a sweet marketable CH₄ can accept up to 20% N_2 contamination in the generated stream, as opposed to CO₂, which can tolerate just 1% contamination (Turta et al., 2007; Abba et al., 2018). In general, they discovered that the presence of irreducible saturation water (connate water) tended to improve recovery compared to the absence of connate water. This was owing mostly to CO₂ strong solubility and dissolution in brine formation.

As a result of the excessive premature mixing of the injected CO_2 and the nascent displaced CH₄ during the flooding process, EGR promotion is still in its infancy (Oldenburg & Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This contaminates the recovered CH₄ gas, lowering its heating and economic market value, resulting in the high cost of the sweetening procedure to maintain its purity level for consumption (Oldenburg & Benson, 2002; Sim et al., 2009). Because of the unprecedented mixing with the displaced gas, the EGR project has not only been confined to a few pilot experiments (Pooladi-Darvish et al., 2008), but it has also become uneconomical. As a result, the phenomena are poorly understood (Patel et al., 2016). Thus, identifying an appropriate approach for decreasing such in-situ mixing might be beneficial at first by injecting a small amount of nitrogen gas prior to the CO₂ injection.

Several authors (Gu et al., 2019; Hughes et al., 2012; Janssen et al., 2018; Abba et al., 2018) have conducted considerable research on how to prolong CO₂ breakthrough time during the EGR process, but none of them employ the gas alternating gas injection technique. Even though Abba et al., 2018 and Gu et al., 2019 made significant progress. Abba et al., 2018 employed different connate water concentrations and delayed CO₂ breakout by 20 minutes at a sodium chloride concentration of 10% wt. (NaCl). Gu et al., 2019 on the other hand, employed varied mole ratios of CO₂/N₂ mixed gases in coalbed core samples. They discovered that enhanced N₂ mixture injection was responsible for avoiding early CO₂ breakthrough and securely storing substantial amounts of CO₂ in the shale sediment over time.

To this day, such in-situ mixing is compromising EGR acceptability in the oil and gas sectors. This demands a thorough examination to pave the way for limiting the excessive mixing of CO_2 and nascent CH_4 during the EGR process (Abba et al., 2018). Other potential injection gases and procedures might be used to reduce the mixing impact. As a result, a unique gas alternating gas injection scenario utilising N_2 as a booster was developed. This study used consolidated core plugs to conduct an experimental analysis of N_2 alternating CO_2 injection during the EGR process. This is crucial because it will provide reservoir, geological, and production engineers the tools they need to effectively assess the movement of injected supercritical CO_2 plumes as they traverse inside porous medium during EGR and sequestration in natural gas reservoirs.

CHAPTER 3

MATERIALS AND EXPERIMENTAL SET-UP

3.1 SUMMARY

This chapter begins with a thorough examination of the experimental setup, including the stepby-step process for a successful core flooding experimentation, material procurement (such as core samples and high-grade gas cylinders), initial calibration, and physical evaluation required prior to the actual experimental runs.

3.2 MATERIALS

The various core plugs employed as porous media during the core flooding experiments are depicted in Fig. 3.1, together with their physical dimensions and petrophysical parameters, which are listed in Table 3.1. In addition, as previously stated, the Soxhlet extraction process was employed to clean the core plugs following each core flooding experimental test. The porosity and permeability of the sandstone core samples were evaluated and compared to those supplied by the industry where the core plugs were obtained for consistency (Kocurek Industries INC, Hard Rock Division, 8535 State Highway 36 S Caldwell, TX 77836, Texas USA). BOC UK supplied the research-grade CO₂, N₂, and CH₄ with purity better than 99%.



Figure 3.1 (1) Bandera grey, (2) Berea grey, (3) and Bentheimer core samples

Core sample	Length (mm)	Diameter (mm)	^a Porosity (%)	^a Permeability (mD)
Bandera gray	76.02	25.31	19-21	27-47
Berea gray	76.07	25.49	18-21	200-230
Bentheimer	76.23	25.23	23-26	1500-3500
1 0		1 7 1	1 110 1	

Table 3.1: Petrophysical properties and measured dimensions of core plugs

^aMeasured value from supplier (Kocurek Industries Ltd, USA)

3.3 EXPERIMENTAL METHODOLOGY

Figure 3.2 depicts the structure and full advancement of the experimental process. The experimental procedure is divided into five stages. Each of these phases represents the research effort on various objectives. An explicit illustration of each of these stages, however, will be offered in the section 3.6, which will provide an in-depth description of the total experimentation.



Figure 3.2: Experimentation overview

3.3.1 Summary of Methodology

Phase I: The initial part of the experiment was the acquisition, cleaning, and characterization of core samples. Sandstone core samples with similar dimensions and petrophysical parameters were obtained from Kocurek Industries INC, as shown in Table 3.1. Before each core flooding test, the core plugs were properly cleaned, which included drying the core samples in an oven for 8-10 hours at a temperature of 100-120 ^oC. However, at the end of each experimental run, these core plugs were re-cleaned with a Soxhlet extraction device with acetone or methanol as the cleaning solvent to remove any trapped material or fluids within the pore spaces. Permeability, porosity, and pore space configurations are all characteristics of core plugs. The porosities were measured with a specialised Helium Porosimetry instrument, the permeability with a permeameter, and preliminary checks on the pore space layout inside the cemented sandstones using an X-Ray CT scan machine.

Phase II: The thermodynamic characterization of the characteristics needed for a clear and thorough description of N_2 , CO_2 , and CH_4 interactions was the second part of the research. Using the EGR process conditions, an empirical simulation was utilised to forecast CO_2 - N_2 - CH_4 behaviour interaction. This mechanism may be better appreciated if the major thermodynamic features of the CH_4 displacement were considered. Density, viscosity, diffusion coefficient, critical conditions, mobility, and compression ratios are examples of these qualities.

Phase III: The third part of the project includes parametric optimisation to evaluate the impact of injection rates on natural gas recovery and CO_2 storage utilising horizontal orientation. Furthermore, gas chromatography (GC) sequence and technique mitigation for use in EGR was carried out to reduce the residence elution time of the gases of interest (N₂, CO₂, and CH₄). During the experimental runs, the GC and core flooding experimentation rig were co-joined into one unit to offer a coincidence examination of effluent streams from the core flooding system. Several dry tests were conducted to establish control or blank trials for the booster gas sensitivity study in phase IV of the investigation. All the runs were completed in a horizontal configuration, where gravity's effects are more obvious.

Phase IV: Using the CO₂ flooding approach, the potential of N_2 for CH₄ recovery and CO₂ storage will be studied in phase. This will include saturating the core plug with CH₄ at known irreducible water of saturation (S_{wi}), followed by variable volumes of N_2 injection as a booster before CO_2 injection at an ideal rate obtained from phase III.

Phase V: This phase will look at the behaviour of CO_2 and N_2 during core flooding experiments with CO_2 injection. During the core flooding displacement, N_2 would be the continuous phase (saturating fluid), whereas CO_2 would be the scattered phase (displacing). This goal was largely intended to determine why CO_2 has a longer breakthrough time during the EGR process with N_2 gas inclusion. The experiment was constructed with varied injection rates at temperatures of 30 and 40 ^{0}C .

3.4 CORE SAMPLE CHARACTERISATION AND GAS ANALYSIS

Before the core flooding experiment, the petrophysical parameters of the core plugs were evaluated to validate the essential features of the sandstone core samples. This is critical to validate measured values against those given by the provider (Kocurek Industries Ltd, USA). Furthermore, this might be used as a preliminary repeatability test before the principal experimentation.

3.4.1 Porosity and Pore Volume Evaluation

Porosity and pore volume determination are key components of every EGR core flooding experiment. Furthermore, these criteria are commonly utilised to determine the initial gas in situ for any reservoir rocks. The Helium Porosimetry technique was employed in this work to calculate grain volume from effective porosity measurements. The details of these strategies are described in the next chapter of this study.

3.4.2 Permeability Evaluation

Two approaches were utilised in this study to assess the permeability of chosen core plugs. Permeameters and a core flooding mechanism were used in these procedures. Both systems work based on differential pressure and gravity difference (Darcy law). These approaches are described in Chapter 4 of this report, whereas the governing equation was previously published in Section 2.10.2. Using an excel spreadsheet, the main variable values acquired, such as the rate of flow, differential pressure, sample cross-sectional area, and fluid viscosity, were utilised to compute the absolute permeability of the core plugs.

3.4.3 Pore Space Arrangement

The Computed Tomography (CT) scan technology was utilised to inspect the void space layout and fluid linkages during the EGR displacement process. This was accomplished by taking numerous images per second using the CT-scan X-Ray machine at a high magnification sufficient to reflect the average value of the linear attenuation coefficient of core plugs of a certain thickness (Voxel).

3.4.4 Effluent Gas Analysis

In this investigation, an Agilent Gas Chromatography (GC) model 7890A was used to effectively assess the effluent gas composition from the core flooding device's exit stream. This is critical because it tells when the displacing fluids (N_2 and CO_2) combine with the CH₄ gas. This phenomenon is known as breakthrough time, which is the time it takes for the displacing fluids to encounter the nascent CH₄ during the EGR displacement process. For this study, the GC method employed by Abba et al. (2018) was used. In addition, individual pure research-grade N_2 , CO₂, and CH₄ gas were utilised to validate the selected approach prior to the start of the experiment.

3.5 CORE FLOODING EXPERIMENT

The core flooding experiment serves as the foundation for investigating the EGR displacement mechanism. A UFS-200 core flooding equipment from Core Lab Instruments, Oklahoma, USA, was used for the core flooding procedure. It paved the way for the development of an artificial laboratory gas and oil reservoir pertinent to EGR applications. Unwanted contaminants that may contaminate the experimental data were eliminated from the core plugs by drying them in the oven for hours above the boiling point of water. In addition, to decrease the chance of gases infiltrating the Viton sleeve, the core sample was covered with polytetrafluoroethylene (PTFE) film tape and then with foil paper, as shown in Fig. 3.3. As illustrated in Fig. 3.4, after putting the core plug into the Viton sleeve, both sides were fastened using an adjustable screw iron clip.



Figure 3.3 (A) Core plug without protection, (B) with PTFE film tape, and (C) with both PTFE film tape and aluminium foil paper



Figure 3.4 Housed core plug inside Viton sleeve with of its sides clipped with adjustable screw iron clip

The chapter outlines the experimental technique and materials required for this study's investigations. The detailed design of the work stages is also discussed above. The thorough and extensive experimental methodologies will be outlined in Chapter 4 of this report.

3.6 EQUIPMENTAL SET-UP 3.6.1 Summary

This section provides a thorough and extensive discussion of the equipment, methods, and procedures used in this investigation. It continues the same line of thought as Chapter 3, but in a more developed form. The next sections additionally cover the equipment's working principles and experimental setup instructions.

3.6.2 Core Sample Drying and Cleaning

The presence of contaminants inside the core plugs has a general impact on the geological storage process, notably in terms of variations in CO_2 storage capacity or volume. This was related to differences in the phase behaviour of pure CO_2 or N_2 . Furthermore, contaminants have a major impact on gas injectivity via geochemical processes around injected wells. This unfavourable response may also have an influence on gas injectivity, reservoir permeability, and caprock integrity in both well-bore and saline aquifers. To address this impact, the core plugs were dried inside an oven at a temperature above boiling water, as illustrated in Fig. 3.5, since most of those volatile organic contaminants can be removed at a temperature of 100 ^{0}C using an electric oven.



Figure 3.5 Core plugs drying equipment prior to or after gas injectivity

Furthermore, the core sample was re-cleaned after each gas injection into the core plug since much of the CO₂ would be adsorbed on the pore space of the core plug. The Soxhlet device is used to extract the stored CO₂ as well as any foreign material caused by the displacement process. A Pyrex long neck round-bottom flask, a thimble, a condenser (used for water circulation), and an electric control heater that adjusts the temperature to give the required heat to evaporate the toluene or acetone solvent inside the system comprise this device. When the electric control system is adjusted to 70-80 ^oC, the organic solvent (toluene or acetone) normally evaporates upward to the glass condenser. Due to cold-water circulation via the condenser's tube side aperture, the evaporated solvent condenses. The condensed solvent drops into the thimble, which cages the core plug and serves as an end receiver for the trapped fluids (CO₂ and other external contaminants) removed from the used plug. This causes the used core plug to become saturated with the vapour and re-condensed organic cleaning solvent, filling the thimble to the same height as the liquid level within the Soxhlet tube. The Skipton effect then causes it to self-drain and run back into the round bottom Pyrex flask containing the boiling organic solvent. At 100% reflux, this event permits the organic solvent to properly remove any undesired fluid within the core plug. The technique was repeated for 48 hours to reach a specified cleaning outcome. As shown in Fig. 3.6, solvent loss by evaporation was exhibited at a moderate temperature below the organic solvent boiling point.



Figure 3.6 A core cleaning Soxhlet apparatus extraction rig

3.7 POROSITY DETERMINATION

3.7.1 Helium Porosimeter (PORG-200TM)

The PORG-200TM Porosimeter was used to test porosity. The instrument is a manually controlled helium pycnometer with digital technology for determining grain volume within a limited range of sample sizes. This equipment consists of a matrix Cup (1 x 3 inches in diameter) for core samples and a set of steel calibration discs (1 inch in diameter). The core plugs (Bandera grey, Berea grey, and Bentheimer) were properly cleaned and dried. The weight of the dried samples was also measured, and this information was then used to calculate the grain density. Three measurements of the core plug diameter and length were taken using a digital Vernier calliper to get the average value for bulk density determination, as shown in Eq. 3.1.

Pore Volume
$$(P_V)$$
 = Bulk Volume (B_V) – Grain Volume (G_V) (3.1)

where, Bulk Volume = $\frac{\pi d^2}{4} \times L$, and d is the core diameter, and L is core length.

To calculate the core sample grain volume, the apparatus employs the principles of Boyle's law. The volume of a particular mole of gas is inversely proportional to its pressure at constant temperature, according to the law. There are two volume cells in the helium porosimeter: the reference cell and the sample cell. At a pressure of 90-95 psig, the reference cell has a fixed, known volume V_1 , but the sample cell has an unknown volume V_2 (grain volume) at ambient pressure. The helium gas was initially introduced into the reference cell and then expanded into the volume V_2 sample cell. Following the volume's stabilization, the pressures P_1 and P_2 were measured, and the unknown volume V_2 was calculated using Eq. 3.2.

$$G_{V} = V_{c} - V_{r} \left(\frac{P_{1} - P_{2}}{P_{2} - P_{a}}\right) + V_{v} \left(\frac{P_{2}}{P_{2} - P_{a}}\right)$$
(3.2)

Gv, Vc, Vr, and Vv stand for grain, sample cell, reference cell, and valve displacement volume, respectively. P₁, P₂, and Pa represent the reference, expanded, and atmospheric pressures, respectively. Fig. 3.7 depicts the PORG-200TM Porosimeter.



Figure 3.7 PORG-200TM helium porosimeter set-up

3.7.1.1 Measurement procedure

- Prior to the grain volume calibration, a pressure test was performed to check that the system was leak-free. As a result, the system was switched on for 30 minutes to stabilize the system and ensure the pressure transducer achieved equilibrium before connecting the helium gas cylinder to the helium inlet port of the porosimeter and afterwards setting the Helium gas cylinder regulator to 120 psig.
- Following the leak test, the Porosimeter was used to calibrate the system grain volume. With reference, no discs were attached to the instrument in the matrix cup. The valve V₂ was set to vent, while the valve V₁ was set to ON. The Porosimeter's black regulator was then adjusted to 90 psig as the reference pressure P₁; the valve V₁ was turned OFF and the valve V₂ was turned to the EXPAND position to equilibrate the pressure in the chamber until a pressure decrease was stabilized, and a reading was obtained as expanded pressure P₂. The technique was performed for each disc and its combinations. These pressures were entered into an Excel spreadsheet to obtain the regression coefficients and grain volume of the discs. To obtain the calibration line, a plot of the grain volumes was plotted against the ratios of the upstream pressures (P₁/P₂).
- Following the system grain volume calibration, the core plug was solely inserted in the matrix Cup. Valve 2 was set to vent, while Valve 1 (gas inlet) was set to ON, and the system was pressurised to 90 psig using the black front regulator. Valve 1 was then

turned OFF, and the upstream pressure (P_1) was measured. The helium gas was then directed into the matrix Cup by switching Valve 2 to the EXPAND function. The upstream pressure (P_2) was allowed to equilibrate before being measured. These pressures were entered into the Excel spreadsheet, and the volume of the core plug grain was calculated automatically. The process was done for each of the remaining core plugs.

3.8 PERMEABILITY DETERMINATION

3.8.1 Gas Permeameter (PERG-200TM)

The PERG-200TM permeameter is a manually operated gas permeameter with digital technology that provides accurate permeability readings for small sample sizes and permeability ranges. The device is made up of a newly built Fancher core holder. The permeameter contains a digital pressure transducer, flow metre, thermometer, and a valve and flows system for measuring the permeability of one-inch diameter core plugs to air. As indicated in chapter two of this report, the equipment normally operates on the principles of the Darcy equation. The measurements are taken at various flow rates to check that they are within the Darcian area. Furthermore, the Klinkenberg effect was not considered while utilising the PERG-200TM since such changes were minimised by maintaining the mean average pressure as low as feasible. The primary constraint of this apparatus was that the core sample had to be one-inch in diameter and one-inch or less in length, with parallel ends.

3.8.1.1 Air permeability measurement procedure

- Before the measurement, all pressures and air on the lines were removed to avoid contaminating the results. This is known as pressure transducer zeroing (PTZ). It was accomplished by opening the Fancher holder, cutting off the cylinder's gas supply, opening Valve V₁, and twisting the pressure regulator handle clockwise to ensure that any pressure in the lines was drained. As a result, the reading on the digital readout or display screen becomes zero. The operation was repeated until all the pressure on the line was relieved.
- The clean and dry core sample was then inserted in the Fancher core holder, and the device's N₂ source was attached. The N₂ supply was set to 20 psig, V₁ was opened, and the line flow pressure was regulated by rotating the inbuilt device regulator. Following

that, the upstream pressure and gas flow rate are allowed to stabilize for several minutes.

• As a result, the stabilised upstream pressure and temperature were measured. The gas flow rate was then boosted using the device's built-in regulator. Before recording the upstream pressure and gas flow rate, they are permitted to stabilise once more. This procedure was done several times at varied upstream pressures until the Darcian flow was created. It was also discovered that when flow pressure increased, the gas flow rate increased linearly. Because the sample length and cross-sectional area are necessary to calculate the permeability of the core plug, many length and diameter measurements were collected while rotating the core sample, and the average of these data was used to compute the permeability of the core plug. To calculate the final permeability to air/N₂ for the core sample, all of the recorded data were input into an excel spreadsheet that was created. The specifics of these findings are discussed in full in Chapter 4 of this study. Fig. 3.8 depicts the PERG-200TM setup.



Figure 3.8 PERG-200TM air/N₂ permeameter set-up

3.8.2 Pore space and Image Segmentation

As illustrated in Fig. 3.9, the core plugs were scanned using a high magnification CT-scan Xray equipment to study the porous medium's configurations and pore connectivity. The X-ray scan machine is a reliable non-destructive procedure that enables qualitative analysis based on the attenuation of X-ray beams as they travel through the scanned core plug at various inclination angles. The cross-sectional sections of the scanned sample have been obtained, and the 3D pictures may be utilised to investigate the structure, pore size, and grain distribution of the core sample. To prevent long computational residence times and increase picture resolution, the core plug was segmented on the scanned image. The specific processes are.

- **Sample positioning:** The control panel of the system is used to position the core plug so that it may be scanned. The core plug was positioned so that it completely covered the field of vision, allowing for a high resolution.
- Sensor Calibration: Initially, the X-ray energy was adjusted to 200 kW, which was sufficient to provide the core plug particles with a good contrast between void and solid. The voltage was set to 20 kV, while the current was set at 10A. This option allows you to remove any inhomogeneity in the background pictures.
- **Pore Space Imaging:** There are two approaches to creating a 3D picture of the pore space. The first was direct imaging, which generates 3D pictures by mapping the real inner structure of the original sample, like the destructive method of cutting and stacking serial 2D sections. The second includes applying statistical approaches or

geological process modelling to build synthetic 3D rock pictures from high-resolution 2D thin slices using various reconstruction methods.



Figure 3.9 GE Phoenix X-ray CT Scanner

3.9 EFFLUENT ANALYSIS

The effluent gas from the core flooding system's exit stream was analysed with an Agilent GC model 7890A equipped to investigate natural gas in accordance with the American Standard for Material and Testing (ASTM) 1945 and the Gas Processors Association (GPA) 2261. Thermal Conductivity Detector (TCD) gas chromatography was used. The technique is based on the variations in thermal conductivity between the carrier (Helium) gas and the sample components. Agilent Technologies' OpenLab Chemstation software (v.01.19.00) analyses the raw data collected from the separation analysis and component detection in the GC and shows the output results as peaks in the chromatography (Abba et al., 2018). It is simple to use and has an interface for modifying methods and sequences. The elusion time was reduced to a maximum of 5 minutes, as opposed to the standard 30-minute residence period for sour natural gases with high component separation. This was accomplished utilising a modified, widely used approach (Abba et al., 2018) for EGR by initially boosting the oven temperature from 90-130 °C. In addition, to counteract the strong condensation impact at the front entrance, the inlet temperature was raised to 120 °C. This allows the carrier gas flow rate to be increased from 27-40 ml/min, lowering the elusion residence time of N₂, CH₄ and CO₂ to 1.49-1.58, 1.69-1.95 and 2.15-2.5 minutes, respectively, in Fig. 3.10. Furthermore, to avoid CO2 adsorption into the molecular sieves, the molecular sieve column (Column 4) was bypassed by valve 3 isolation.



Figure 3.10 Effluent gas composition measured from the Agilent GC model 7890A3.10 REVIEW ON CH4-N₂-CO₂ FLOW CHARACTERISTICS

A numerical simulation was performed prior to the core flooding experiment to evaluate the flow characteristics of the displacing and displaced fluids interacting under reservoir circumstances. The numerical simulation was carried out using thermodynamic simulation software (FLUIDAT^R) at temperatures and pressures much above the supercritical states (20-120 ^oC and 100-2000 psig, respectively) of the fluids under examination. Density, viscosity, mobility ratio, compression ratio, and molecular diffusion coefficient are the essential characteristics studied. These are critical because they give useful information as well as a wide variety of restricting parameters required for successful experimentation during the CH₄ displacement for the chosen core plugs under examination.

3.11 CORE FLOODING EXPERIMENT

The experimental setup is primarily made up of two distinct units: a Core Lab UFS-200 core flooding system with built-in Smart Flood software and a packed column design Agilent 7890A Gas Chromatography (GC) machine type. The core flooding system, which was built for 2-phase liquid/gas steady or unsteady state condition displacements, was altered to handle the extra N₂ employed in this study's gas alternating gas injection. The GC equipment was used to perform cooperative online concentration measurements of core flooding effluents at every 5-minute sequence. As the experiment continued, these numbers were utilised to plot the injection fluid's concentration profile. Fig. 3.11 illustrate a schematic of the real equipment setup. The UFS-200 core flooding system has overburden and pore pressure ratings of 5,000 and 3,750

psig, respectively. The equipment's injection system consists of a pair of dual ISCO two-barrel metering pump systems (A/B and C/D) for continuous flow for pulseless transition and to maintain an accurate flow rate range of 0 to 200 ml/min with a maximum pressure rating of 3,750 psig. The pumps are connected to a pair of stainless-steel floating piston accumulators, which are similarly rated for 5,000 psig operating pressure and 177°C temperature. They are intended to inject the fluids of interest and can endure test pressures of up to 7,500 psig. The overburden pressure was set using a hydraulic pump with a maximum pressure output of 10,000 psig. The Smart Flood software serves as the foundation for a basic system that connects the UFS system and the computer data-acquisition-control (DAC) system hardware. This produces automated on-screen logging of test data to a computer data file for all measured variables like as pressures, temperatures, volumes, and so on. The differential pressures over the whole Hassler-type core holder, which housed the core sample, were measured using a Rosemount Static DP transmitter. A Viton rubber sleeve held the sample within the core holder. A core holder heat jacket was also used to replicate the desired temperature. The employment of a dome-type back pressure regulator integrated into the flooding system ensured that the requisite pressures remained confined within the core holder. An N₂ cylinder bottle was used to set the desired pressure. Before being analysed by the GC system, the effluents from the back-pressure regulator travel through mass flow controllers, which measure the volume of the actual effluents generated.



Figure 3.11 Online core flooding set-up integrated with GC

3.11.1 Effect of Injection Rate during Natural Gas Displacement by N2 Flooding

The core sample was dried overnight in an oven at 105 °C to remove moisture and other volatile compounds. Before inserting the dried sample into a heat shrink, it was coated in cling film and then foil paper. This is critical to avoid viscous fingering and gas penetration into the ringshaped core holder via the sleeve. It was then put into the core holder and stapled from both ends with clamps. To prevent fracturing the core sleeve, hydraulic oil was fed into the ringshaped core holder to produce the appropriate overburden pressure, which was kept at a minimum of 500 psig above the pore pressures. After installing the heat jacket on the core holder, the temperature step-up (40 °C) was noticed before to methane saturation. Backpressure was then applied, and CH₄ was steadily pumped into the core sample from the CH₄ cylinder through ISCO pumps A/B and accumulator or cell A to saturate the core plug until the GC consistently read methane more than 98%. Pumps A/B were then turned off, and N₂ was supplied at 0.2 ml/min via an accumulator or cell B using ISCO pumps C/D. The experiment ended when either the methane concentration was negligible based on the GC reading or the N₂ concentration was greater than 98%. Additional experiments were performed at increasing N₂ injection rates of 0.4, 0.6, 0.8, and 1.0 ml/min. These flowrates were chosen based on the medium peclet number (Pem) shown in Table 5.14. The time of each GC injection was recorded,

as well as the effluent composition, which was then utilised to evaluate CH₄ recovery efficiency and dispersion coefficient. Based on the percentage recoveries and dispersion coefficients, the best injection rate was determined. The experiment was carried out at a pressure of 1500 psig and a temperature of 40 0 C. This condition was determined using an average gas pressure reservoir with a gradient of 0.451 psi/ft, an average reservoir depth of 1 km, and a geothermal temperature of 35–40 C/km. Figure 4.8 depicts a schematic of the equipment configuration.



Figure 3.12 A Schematics of experimental set-up for N₂ flooding

3.11.2 The Role of N2 as Booster gas by CO2 Flooding

The core sample was dried overnight in an oven at 105 0 C to remove moisture and other volatile chemicals. The dry sample was wrapped in cling film and foil sheets before being placed in a heat shrink. This is critical to prevent leaving viscous fingerprints and penetrating the gases through the sleeve into the ring-shaped core holder. The sample was put into the core holder and clamped from both ends. Hydraulic oil was poured into the ring-shaped core holder to produce the appropriate overburden pressure, which was kept at a minimum of 500 psig above the pore pressures to avoid fracturing the core sleeve. The heat jacket was put on the core holder, and the temperature step-up (40 0 C) was detected before CH₄ saturation. Backpressure was applied, and the core sample was saturated with CH₄ at 10% irreducible water saturation until the GC read methane composition greater than 98% on a consistent basis. Following that,

 CO_2 was supplied at 0.2 ml/min via cell B using ISCO pumps C/D, as illustrated in Fig. 3.13. The experiment was terminated when the CH₄ concentration was determined to be negligible based on the GC reading. Further trials at increasing CO₂ injection rates of 0.4, 0.6, 0.8, and 1.0 ml/min were performed, and the effluent composition was recorded. The best injection rate was chosen and used as the experiment's next stage (with N₂ as booster gas). The sample was cleaned, dried, and re-saturated with CH₄ for a second time. Then, 0.06 HCPV (6% booster) of N₂ was pumped via cell A using ISCO pumps A/B. More runs were performed with increasing N₂ booster gas amounts (13-29% booster) and at the optimum CO₂ rate of injection. The experiment was conducted at a relevant reservoir pressure of 1500 psig and a temperature of 40 °C.



Figure 3.13 CH₄ displacement diagrams with and without cushion gas

3.11.3 Flow Behaviour of CO2 and N2 in Porous Medium

The Bentheimer core plug was oven-dried at 110 ^oC for 24 hours to obtain a minimal moisture content and volatile organic compounds (VOCs). In addition, to ensure smooth and uniform gas molecule distribution and prevent penetration through the Viton sleeve, the core plug was tightly wrapped with thread tape before inserting into the resistant rubber sleeve. To prevent

the core sleeve from rupturing, the overburden pressure was set at 170 bar, slightly higher than the pore pressure. Furthermore, the temperature was fixed and kept at 30 $^{\circ}$ C. The core sample was saturated with N₂ until the final composition was above 98%. Following that, a pressure leak test was performed to guarantee that the system was leak-free. Following that, CO₂ was supplied at 0.4 ml/min using pump C/D and accumulator B. The GC analysed and recorded the endpoint concentration every 5 minutes until CO₂ was dominant relative to N₂ (i.e., CO₂ composition > 98%). The experiment was then called off, and the lines were de-pressurized. Using the same methodology, further experiments were performed at 0.6, 0.8, 1.0, and 1.2 ml/min. To test the influence of temperature, comparable sets of the experiment were performed with a fresh core sample, but this time at a higher temperature of 40 $^{\circ}$ C while retaining the same pressure.

This chapter describes each piece of equipment and its components in depth. Various operating principles and apparatus descriptions, as well as the manner and precautions of operation, were highlighted. The results analysis was presented in chapter 4 of this report.

3.11.4 Original Gas in Place (OGIP) Determination

Before entering the gas chromatography analyser, the mass flow controllers/meters monitored the gas effluents produced during the core flooding trials. The gas effluent production rates were measured in sccm (standard cubic centimetres per minute), and the conversion to actual flowrate was performed under experimental settings of 30°C and 1500 psig using the correlation included in the technical handbook (Honeywell, 2012).

$$Q_x = Q_s \times \frac{P_s}{P_x} \times \frac{T_X}{T_s}$$

Qx is the volumetric flowrate (ccm) under experimental settings; Qs is the volumetric flowrate (sccm) under standard conditions as recorded by the flow metre; and Ps, Px are pressures in atm under standard and experimental conditions, respectively. Ts and Tx are the temperatures under standard and experimental settings, respectively. The flow meter's reference state is 0°C and 14.69 psi. The effluent exit pressure from the backpressure regulator, on the other hand, was 80-100 psig, and the gas flowing temperature was the same as that of the core holder. This was utilised to compute the instantaneous volume created at each timestamp, which in turn determined the cumulative volume produced for each core flooding procedure. The percentage of gas produced by volume acquired from the GC was used to compute the amount of gas

produced in each run. Tables 4.5 to 4.8 illustrate this for each injection rate. The Original Gas in Place (OGIP) was established to calculate CH₄ recovery for each injection rate.

$$OGIP = \frac{V_b \phi(1 - s_w)}{B_g} \tag{3.3}$$

 V_b is the bulk volume of the reservoir ft^3 , ϕ is reservoir porosity, S_w is formation water saturation, and Bg is gas formation volume factor, ft^3/scf .

$$B_g = \frac{P_{sc}}{T_{sc}} \times z \frac{T}{P}$$
(3.4)

Where z is the gas compressibility factor, Psc and Tsc are standard pressure and temperature, and P and T are desired pressure and temperature. Eq. 3.4 was simplified by assuming Psc and Tsc to equal 14.696 psia and 18oC (291.15K).

$$B_g = z \frac{T}{20P} \tag{3.5}$$

The compressibility factor, z, of the gas was used to compute the gas production volume factor under experimental circumstances. The pseudo-reduced properties/conditions of CH_4 at the experimental circumstances was derived to obtain the z factor from the chart. The following is a correlation for the pseudo pressure and temperature.

$$P_r = \frac{P}{P_c}$$
$$T_r = \frac{T}{T_c}$$

Where Pr denotes the pseudoreduced pressure, P and T denote the experimental pressure (1500 psig) and temperature (313.15 K), Pc denotes the critical pressure (46 bar or 676 psig), Tr denotes the pseudoreduced temperature, and Tc is the critical temperature of the gas in K. Using the Standing and Katz (1941) chart, these factors were utilised to estimate the z factor.

$$P_r = \frac{1500}{676} = 2.22$$
$$T_r = \frac{313.15}{190.6} = 1.64$$

Using the parameters, the Standing and Katz chart yielded the gas compressibility factor, z, as 0.86.

The obtained z factor was then used in Eq. 3.4 and Bg was computed as:

$$B_g = 0.87 x \frac{313.15}{20x1500} = 0.00867 \ cm^3 / scm^3$$

The OGIP was calculated by plugging the Bg into Eq. 3.3, the porosity of the core sample (Bandera grey) was 19.68 percent (from Table 5.4), and the bulk volume, Vb, was determined to be 38.27cm³ for the dry core sample, Sw = 0.

$$OGIP = \frac{38.27 \times 0.1968(1-0)}{0.00867} = 868.7 \ cm^3$$

The same procedure was repeated for Berea grey and Bentheimer core samples and the result summary is presented in Table 4.8. The OGIP is mostly determined by the porosity of the rock, as proven by the Bentheimer core sample, which recorded 1002 cm³ gas in placed within it pore spaces. As a result, the more blank spaces inside the reservoir rock, the more gas is required to fill those empty areas.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 INTRODUCTION

This study used three (3) sandstone core plugs (*Grey Berea*, *Bandera Grey*, and *Bentheimer*) with different petrophysical properties. Section 1 of the result entailed cleaning and characterising the core plugs by experimental analyses to determine the permeability and porosity characteristics. Section 2 involved fluids thermodynamic investigation of key properties responsible for mixing and interaction within such gases under study (CH₄-N₂-CO₂). These parameters are mobility ratio, diffusion coefficient, compression ratio, density, and viscosity. The investigation was carried out using an empirical simulation tool called FLUIDATR. Section 3 involved a core flooding experiment simulating methane displacement by nitrogen and carbon dioxide injection at 1500 psig, 40 0C and varying injection rates (0.2, 0.4, 0.6, 0.8 and 1.0 ml/min). This was performed at horizontal orientation as established in literature to determine the best injection rate base on the best CH₄ recovery and CO₂ storage value. Section 4 of the results emphasised the impact of N₂ cushion gas in the mixing and dispersion of CO₂ into nascent natural gas (CH4) during the displacement process at the simulated reservoir condition above during enhanced gas recovery using core flooding experiment with different N₂ booster volumes (6, 13, 19, 29%) at optimum injection rate obtained in section 3. Lastly, the flow mechanism of CO₂ and N₂ in a porous medium using a core flooding experiment was investigated in section 5. The findings explain why CO₂ had a more extended breakthrough during the EGR process with N₂ gas as a booster.

4.1.1 Repeatability and Reproducibility of the Experimental rig and Method

An experiment's iterability is critical since it indicates that the method used, and the experimental setup have ensured repeatability of result outputs. Test runs were carried out prior to the main experiment to check the iterability of the test runs. Experimental runs were performed at an arbitrary injection rate of 0.6 ml/min, temperatures of 40 0 C, and pressures of 1500 psig, respectively. The concentration profile was created using the GC data from the core flooding effluent stream, as shown in Fig. 4.1. The dispersion coefficients for runs 1 and 2 were calculated to be 7.0 x 10-8 and 6.4 x 10-8 m²/s, respectively. Furthermore, the standard deviation of the two sets of data from the repeatability test is less than 11%, indicating that the method used, and experimental setup has guaranteed reproducibility of result outputs; as a

result, all subsequent experimental runs follow the same methodological procedure in carrying out the investigation.





The selection of flow velocity in EGR is critical since greater injection rates may result in early mixing of the fluids. Lower injection rates often result in longer residence periods for the fluids in contact, which indirectly increases gas mixing (Abba et al., 2018). The medium peclet number primarily denotes the optimal injection rate, which corresponds to a smoother displacement with a smaller dispersion coefficient throughout the EGR process and provides an overview of the injection scenarios used in this study. Because the displacement process is driven by a diffusion-like pattern, lesser injection rates will offer unwrinkled concentration profiles for adequate study as contrasted to larger injection rates. The earlier may likely generate higher mixing, and the latter, with high values of medium peclet number, will increase the mixing of the fluids resulting in poor sweep efficiency. Thus, selecting a moderate or optimum gas injection rate is paramount to achieving a sustainable, economic, and efficient EGR process. In this research, CH₄ recovery efficiency, dispersion coefficient, and other selection criteria helped select the best or optimum injection rate. For this work, the core holder orientation was fixed in a horizontal direction for all the core plugs since the effect of gravity on vertical orientation is insignificant, as reported by (Hughes et al., 2012; Liu et al., 2015; Abba et al., 2018).

4.2 CHARACTERISATION

As indicated in chapter three of this study, the porosities of the core plugs were tested using a helium porosimeter. Before the measurement, the instrument was calibrated with several stainless-steel discs, as illustrated in Tables 4.1 and 4.2.

 Table 4.1 Physical dimensions of calibration discs

Disc Volumes Table						
Disc	Length	Volume				
No.	inches	inches	сс			
1	0.124	1.000	1.596			
2	0.373	1.000	4.801			
3	0.498	1.000	6.408			
4	0.747	1.000	9.615			
5	1.248	1.000	16.056			

Table 4.2 Reference and expandable pressure measurements at various discs combinations

Calibration Table						
		Reference	Expanded			
Disc	Volume	Pressure	Pressure	P_1/P_2		
No.	сс	psig (P ₁)	psig (P ₂)			
empty	0	90.22	10.86	8.308		
1	1.596	90.72	11.24	8.071		
2	4.801	90.1	11.94	7.546		
3	6.408	90.49	12.38	7.309		
4	9.615	90.59	13.35	6.786		
5	16.056	90.57	15.61	5.802		
5+1	17.652	90.59	16.31	5.554		
5+3	22.463	90.56	18.88	4.797		
5+4	25.671	90.54	20.92	4.328		
5+4+3	32.079	90.5	27.38	3.305		
5+4+3+2	36.879	90.49	35.25	2.567		

Table 43 shows the results of the evaluation of the unknown model equation coefficients. These numbers were entered into the empirical grain volume equation to calculate the effective grain volume, from which the effective porosity was calculated.

 Table 4.3 Empirical model coefficients for grain volume evaluation

Coefficients Table					
Α	В	С	D		
0.0069	-0.1036	-5.9441	52.642		

The calibration chart was shown in Fig. 4.2 by graphing the measured volume against the pressure ratio. Because the R^2 value is 1, this chart was determined to be completely matched.



Figure 4.2 Calibration chart for grain volume determination

Following the system grain volume calibration, the clean and dried Bandera grey core plugs were put in the matrix cup, and the relevant reference and expandable pressures were recorded. These pressures were entered into an Excel spreadsheet, and the core plug grain volume was automatically calculated. This technique was performed for the remaining two core plugs (Berea grey and Bentheimer), with the results shown in Table 4.4.

Table 4.4 Porosity and pore volume determination for core plugs

Core Plugs	P ₁ , psi	P ₂ , psi	P_1/P_2	G_V, cm^3	P_V , cm ³	B_V , cm ³	Exp.	*Range
Bandera gray	90.42	25.69	3.52	30.74	7.53	38.27	19.68	19-21
Berea gray	90.37	25.83	3.50	30.87	7.97	38.85	20.53	18-21
Bentheimer	90.26	24.25	4.15	29.44	8.69	38.13	22.80	23-26

*Range means porosity values measured by the supplier (Kocurek Industries, Texas, USA)

4.2.1 Permeability Determination

The permeability of the core plug was determined using a state-of-the-art permeameter using N_2 as the carrier gas. The Fancher permeameter cup was inserted with the clean and dry Berea grey core plug. Every increase in flow rate was accompanied by an increase in upstream pressure. The core plug's dimensions were measured with a calibrated digital Vanier calliper. These numbers, together with the N_2 gas viscosity, were entered into the permeability Excel spreadsheet model to calculate the absolute permeability, which is presented in Tables 4.5 and 4.6.
Length (cm)	2.667	Area, cm ²	5.07
Diameter (cm)	2.54	Mean Pres, atm	1.29
Viscosity (cp)	0.0175	Upstream Pres, atm	1.59
Transducer Pres (psig)	8.6	Downstream Pres, atm	1.00
Flow Rate (cc/min)	813.9	Flow Rate, cm ³ /sec	13.57

 Table 4.5 Permeameter model parameters

Table 4.6 Experimental permeability determination for Berea grey core plug

Runs	Flow rate	Pressure (psig)	Temperature $\binom{0}{C}$	Flow rate (cm^{3}/s)	Exp. Permeability	*Range
		(psig)	(()	(CIII / S)		
1	788.9	7.7	22.7	13.15	231.1	200-230
2	800.9	8.0	22.8	13.35	225.8	
3	808.2	8.3	22.8	13.47	219.6	
4	813.9	8.6	22.9	13.57	213.5	
5	816.4	8.9	22.9	13.61	206.9	
					213.5	

*Range means porosity values measured by the supplier (Kocurek Industries, Texas, USA) This technique was performed for the remaining two core plugs (Bandera grey and Bentheimer), with the results shown in Table 4.7.

Core sample	Length (mm)	Diameter (mm)	Porosity (%)	Permeability (mD)
Bandera gray	76.02	25.31	19.68	32
Berea gray	76.07	25.49	20.53	214
Bentheimer	76.23	25.23	22.80	2100

Table 4.7 Permeability results for the core plugs under investigation

The measured porosity and permeability for the core plugs under consideration were found to be comparable to the supplier's values (Kocurek Industries, Texas, USA). This reflects the level of attention and precision used during the laboratory measurement.

Table 4.8 Petrophysical properties and OGIP for the core plugs under investigation

Core sample	Length	Diameter	Porosity	Bulk Volume	Gas in Place
	(mm)	(mm)	(%)	(cm ³)	(cm ³)
Bandera gray	76.02	25.31	19.68	38.27	868.70
Berea gray	76.07	25.23	20.53	38.85	919.94
Bentheimer	76.23	25.49	22.80	38.13	1002.73

4.2.2 Pore Space and Bulk Volume Analysis

The pore space and bulk volume analyses of the Bandera grey core plug were performed utilising a high-resolution CT-scan X-ray scanner. Fig. 4.3 shows the front and top 3D images of the Bandera grey core sample. In addition, as illustrated in Fig. 4.4, a sectional image of the identical views was scanned. As a result, both Figures show how the grain particles are closed, properly ordered, and fastened to one another. This pore space structure size arrangement is like that of solidified sandstone core plugs, as reported by (Abba et al., 2017).



Figure 4.3 Front and top 3D views of Bandera grey core plug



Front View



Figure 4.4 Sectional front and top 3D views of Bandera grey core plug

Meanwhile, the real bulk volume of the Bandera grey core sample was calculated using the CT-scan machine's volume and associated components analysis tool, as shown in Fig 4.5a. The bulk volume (B_V) obtained was 37,186.51mm³ (37.19 cm³), which was comparable to the manual measurement with the Vanier calliper. The 4.46% discrepancy might be because to a parallax error reading during measuring the length and diameter of the Bandera grey sample. The remaining two core plug findings were unavailable due to the CT-Scan equipment was under repair.



Figure 4.5a Bandera grey bulk volume determination using CT-scan machine

4.2.3 Flow Behaviour of Supercritical N2, CO2, and N2-CO2-CH4 Interplay

The actual flow behaviour of supercritical CO₂ plumes as they traverse the pore spaces inside the core sample to displace the in-situ CH₄ is highly complicated, especially when N₂ gas is included. Understanding the trends and expected outcomes of the displacement process requires investigating the complexities of displacing fluids (CO₂ and N₂) concerning the nascent CH₄, knowing that these gases in their supercritical state have unique behaviour by exhibiting the density of a liquid while retaining the viscosity of a gas (Abba et al., 2018). As illustrated in Figs. 4.5b-4.8, the critical temperature and pressure points for CO₂, N₂, and CH₄ are 31.05 and 73.80, -146.9 and 33.90, -82.55 ^oC and 46 bars, respectively. These values are much over the critical points of each individual gas species. The fluids exhibit good behaviour due to their responsiveness of their transport properties to shifting from ambient standard settings to EGR conditions. This is because high recovery and CO₂ storage was recorded when the displacement experiments were carried out at these simulated supercritical conditions.



Figure 4.5b CO₂ vapor pressure line generated from FLUIDAT^R



Figure 4.6 N₂ vapor pressure line generated from FLUIDAT^R



Figure 4.7 CH₄ vapor pressure line generated from FLUIDAT^R

A simulation of their respective characteristics under increased operational circumstances was performed using FLUIDAT^R software to investigate the effects of temperature and pressure on the individual gas densities and viscosities at the settings shown in Figs. 4.8, 4.9, and 4.10. Their characteristics differ significantly, with CO_2 being much greater than N_2 and CH_4

supercritical state. As the gas pressure increased, the density also rises. This was more pronounced with CO₂, particularly at 500-1400 psig range, and later became constant, as seen in Fig. 4.8. This makes CO₂ roughly seven (7) times denser than N₂ or CH₄, indicating more possible storage under supercritical form. However, when the pore pressure increased, N₂ and CH₄ displayed similar behavioural tendencies, explaining why the recovered CH₄ onsite had more traces of N₂ than CO₂ as reported by (Gu et al., 2019). Because of the increasing rate of impact with the container wall, the kinetic energy is proportional to its temperature. The opposite was true for liquid fluids, which were held together by strong intermolecular forces. In general, as pressure rises, so does gas viscosity. However, at higher pressures (1300-2000 psig), CO₂ maintained high viscosity with liquid density, as seen in Figs. 4.8 and 4.9. Furthermore, at lower temperatures (18-50 $^{\circ}$ C), CO₂ showed viscosity decrease comparable to liquid, with approximately 66% reduction at 50 $^{\circ}$ C, as seen in Fig. 4.10. According to the above remark, CO₂ exhibited unusual property behaviour when compared to N₂ and CH₄ under EGR temperature and pressure conditions (40 $^{\circ}$ C and 1500 psig). This validates the experimental parameters chosen, as reported by Abba et al., 2018.



Figure 4.8 CH₄, N₂ and CO₂ densities as a function of pressure at 40 ⁰C (Generated from FLUIDAT^R)



Figure 4.9 CH₄, N₂ and CO₂ viscosity as a function of pressure at 40 ⁰C (Generated from FLUIDAT^R)



Figure 4.10 CH₄, N₂ and CO₂ viscosity as a temperature at 1500 psig (Generated from FLUIDAT^R) At the start of the displacement process, the viscosity rises until the mobility of the displacing phase is less than that of the displaced stage, resulting in a mobility ratio less than one (unity).

Because of the limited premature mixing, this condition maximises gas recovery and sweeps efficiency by creating a strong viscosity gradient at the displacement front while avoiding the viscous fingering effect. A phenomenon in which a mixture of two fluids escapes from a portion of the reservoir as it moves along, resulting in an uneven or fingered profile. Fingering is a common occurrence in reservoirs with gas-injection wells (Al-Abri et al., 2012). Fingering effects primarily result in an inefficient sweeping motion that skips numerous recoverable gas quantities, as well as a premature breakthrough of displacing fluids. Both the N₂ injection (CH₄-N₂) and the CO₂ injection (CH₄-CO₂) have a lower mobility ratio at their respective critical conditions, as shown in Fig. 4.11. At pressures (100-800 psig) below the CO₂ critical limits, the mobility ratio of CH₄-N₂ displacement was lower than that of CH₄-CO₂ (33.9 ⁰C & 1070 psig). As the N₂ plume transverses through the core spaces against CO₂, the effect of viscous fingering was limited. The pressure effect on the CH₄-CO₂ mobility ratio was negligible beyond supercritical conditions and remained almost constant thereafter. Overall, the supercritical state of gases is vital for examining their flow behaviour with optimum recovery efficiency, resulting in an even flood front with little danger of viscous fingering.



Figure 4.11 CH₄-N₂ and CH₄-CO₂ mobility ratios as a function of pressure at 40 0 C

The mobility of CH₄-CO₂ displacement, on the other hand, increased as the temperature climbed due to a rise in density with temperature and pressure down the reservoir. However,

when the temperature rises to 100 0 C, the CH₄-N₂ process exhibits a reversal, as seen in Fig. 4.12. This is because when temperature rises, the diffusion coefficient of the CH₄-N₂ system increases more than that of the CH₄-CO₂ and CO₂-N₂ systems, as seen in Fig. 4.13. As a result, CH₄-CO₂ system mobility is more susceptible to variations in temperature and pressure than CH₄-N₂ system mobility during EGR and storage.



Figure 4.12 CH₄-N₂ and CH₄-CO₂ mobility ratios as a function of temperature at 1500 psig The generated Equations (2.11-2.12), which were obtained from the correlation (Eq. 2.10)

given by Fuller et al. (1966), were utilised to model the influence of pressure and temperature on the N₂-CH₄, CO₂-CH₄, and CO₂-N₂ interaction behaviours. This simulation was run at constant temperatures of 30, 40, and 50 $^{\circ}$ C, with a pressure range of 100-2000 psig for the specified interactions. In Fig. 4.13, the molecular diffusion coefficient increases with a relatively constant value of 1.5 m²/s across the pressure ranges at temperatures of 30, 40, and 50 $^{\circ}$ C. Because CO₂ has a higher density and molecular weight than N₂ in reservoir conditions, these values were more prominent in the CH₄-N₂ interaction than in the CH₄-CO₂ interaction. Meanwhile, above 1500 psig of pressure, the diffusion coefficient trend remained consistent across all temperatures, and the rate of fall was less noticeable.



Figure 4.13: Effect of pressure on diffusion coefficients for CH_4 - N_2 and CH_4 - CO_2 interaction at constant temperature of 30, 40, and 50 ^{0}C

When two fluids, especially those of the same phase, come into contact, temperature has a key influence in determining the degree of diffusion. The higher the temperature, the greater the kinetic energy owing to high impact velocity, resulting in an always high molecular diffusion coefficient. Eq. 2.11-2.13 shows such evidence, with the temperature component (in Kelvin) growing to the order of 1.75. The total diffusion coefficient of binary mixtures is also affected by viscosities and atomic diffusion. Furthermore, greater viscosity and diffusion volume atoms or molecules have lower molecular diffusion coefficient values than lower viscosity and diffusion volume atoms or molecules. Figure 4.14 shows a plot of the diffusion coefficient vs temperature. As the temperature rises to 120 0 C, the CH₄-N₂ binary combination exhibits a strong periodic increase (393.15K). The CH₄-CO₂ combination, on the other hand, experienced a lesser elevation. This was owing to CO₂ higher density, viscosity, and diffusion volume at supercritical temperatures when compared to N₂. A similar pattern was seen for the CO₂-N₂ binary combination.



Figure 4.14 Effect of temperature on diffusion coefficients for CH₄-N₂, CH₄-CO₂, and CO₂-N₂ interaction at constant pressure of 1500 psig

The molecular diffusion coefficients of N₂-CH₄, CO₂-CH₄, and CO₂-N₂ binary mixtures are compared in Fig. 4.15 under the tested experimental conditions of 40 0 C temperature and 1500 psig pressure. These values are 22.99, 18.48, and 17.33 x10-8 m²/s for the binary interactions N₂-CH₄, CO₂-CH₄, and CO₂-N₂, respectively.



Figure 4.15 Comparison chart for N₂-CH₄, CO₂-N₂ and CO₂-CH₄ molecular diffusion coefficients at 40 ⁰C temperature and 1500 psig pressure.

Figure 4.16 shows a plot of the compression ratio vs reservoir pressure. Eq. 2.24 was used to create this data, as indicated in section 2.11. Because the maximum reservoir pressure would not surpass the given value during the CH₄ displacement, a maximum pressure of 2000 psig was evaluated. A comparable study was performed utilising core flooding logging data at 1500 psig, 40 °C, 0.4 ml/min injection rate, and various N₂ cushion gas quantities. The results showed that when the booster gas volume increased from 8 to 36 cm³, the head load decreased. This was obvious in the decreased percentage heat load when compared to pure CO₂ injection, with the greatest result observed at 24 cm³, equating to a 25% power loss due to heat reduction. When the pressure ratio (PR) was plotted against the experimental time for traditional N₂ and CO₂ injection, a similar pattern was found in Fig. 4.17. A decline in PR was detected prior to both injections (N₂ or CO₂) following methane saturation, which might be attributed to changes in thermophysical characteristics of the displacing fluids (N₂ and CO₂) and the displaced gas (CH₄). This decrease was more severe in CO2 than in N₂ due to the behaviour of CO2 in a supercritical state. As a result, the PR of CO₂ was discovered to be 4% higher than that of N₂ at the end of the displacement experiment. Overall, the CO₂ compression ratio deviates parallelly as reservoir pressure increases, with CO₂ witnessing around 33 climbs (from 13 to 47) within the pressure range (400-2000 psig) studied. This appears to be a significant increase over N₂ with 22, suggesting a 50 percent increase. CO₂ compression is a critical step in the development of carbon capture and storage (CCS) technology (Honari et al., 2016). A full CCS system necessitates safe, dependable, and cost-effective CO₂ conveyance choices from the capture rig to a permanent storage location. CO2 compression varies from N2 compression due to its large molecular mass and highly compressible processes. During the compression process, the CO₂ volume is greatly reduced, resulting in a huge impeller diameter (Honari et al., 2016). In general, CO_2 compression is highly costly due to the high-pressure ratio (100:1) caused by the presence of water vapour during compression (Honari et al., 2016). In contrast, N₂ may be recovered almost entirely from ambient air through an air separation unit. As a result, it has a lower compression ratio than CO₂, hence less of it was required to generate high pressure in the CH₄ reservoir during displacement.



Figure 4.16 The plot of compression ratio (CR) against reservoir pressure generated from Eq. 2.11



Figure 4.17 The plot of pressure ratio (PR) against experimental time at 1500 psig, 40 0 C, 0.4 ml/min injection rate, and 8-36 cm³ booster volumes.

4.2.4 Effect of Injection Rates by N₂ Flooding

Based on the excellent CH₄ recovery and minimal dispersion (mixing), the optimal N₂ injection rate was chosen. Considering Table 4.9, at lower velocities, flow transport in porous media is largely diffusion, but at higher velocities, dispersion is always dominate (Huysmans & Dassargues, 2005; Yu, Jackson, & Harmon, 1999). Identifying the displacement phenomena in fluid transport in porous media is critical, particularly when studying solute transport in sandstone rocks. Choosing precise and accurate input variables is a prerequisite for obtaining accurate findings reasonable enough to give the framework for the pilot and field displacement processes relevant to the EGR process in numerical and empirical simulation. As a result, underestimating or overestimating the injection rate may result in an incorrect forecast, jeopardising the integrity of the idea goal and rendering the entire process uneconomical and inefficient.

According to Table 4.9, all the medium Peclet number values, P_{em} , within the suggested range of injection rate selected (0.2-1.0 ml/min) fall below 0.1 utilising the grain diameters (94.66 and 57.15 µm) as the mixing length scale provided by Abba et al., (2018) for Berea and Bandera grey. This suggests that diffusion is dominating within the experiment's injection rate range. However, for Berea grey, the peclet number (P_{exp}) calculated from the assumed dispersion coefficient (Ka) at maximum injection (1.0 ml/min) first suggested dominating diffusion flow but afterwards revealed large P_{exp} values at higher injection (0.8-1.0 ml/min). As a result, it slipped into a zone of transition between molecular diffusion and mechanical dispersion displacement processes. The injection rate is important in both cases when the displacement is dominated by diffusion because it influences parameters that impact the mixing of the displacing and displaced fluids. Furthermore, for lower P_{exp} values, when diffusion is the major displacement mechanism, flow is controlled by the concentration gradient, and mobility ratio affects transport via flow velocity (Abba et al., 2019).

Core Samples	Q (ml/min)	Interstitial Velocity (10 ⁻⁵ m/s)	Diffusion Coefficient (10 ⁻⁸ m ² /s)	Dispersion Coefficient (10 ⁻⁸ m ² /s)	$P_{em} = \frac{u_m d_p}{D}$	$P_{exp} = \frac{u_m d}{K_{Lmax}}$
Berea gray						
	0.2	3.18	22.99	9.12	0.013	0.033
	0.4	6.36	22.99	9.12	0.026	0.066
	0.6	9.54	22.99	9.12	0.039	0.099
	0.8	12.72	22.99	9.12	0.052	0.132
	1.0	15.90	22.99	9.12	0.066	0.165
Bandera gray						
	0.2	3.36	22.99	13.13	0.008	0.015
	0.4	6.72	22.99	13.13	0.017	0.029
	0.6	10.08	22.99	13.13	0.025	0.044
	0.8	13.44	22.99	13.13	0.033	0.059
	1.0	16.80	22.99	13.13	0.042	0.073

 Table 4.9 Peclet number comparison as injection rate selection criteria

K_{Lmax} is the maximum dispersion coefficient for each of the core samples

Tables A1 and A2 in the appendix show the composition of the core flooding effluent for each run as determined by gas chromatography for each plug. Tables A3 and A4 show the percentages by volume of N_2 at each injection location at about 5-minute intervals to construct a concentration profile. Using Eq. 2.3, this was utilised to get the longitudinal dispersion coefficient. Tables 4.10 and 4.11 show the effect of different injection rates on breakthrough, methane recovery, and dispersion coefficient. The concentration profile graphs for Berea and Bandera core samples were presented in Figs 4.18 and 4.19, while Figs. 4.20 and 4.21 provide a plot of CH₄ recovery efficiency vs experimental time.



Figure 4.18 Concentration profile for Berea gray at varying injection rate (0.2-1.0 ml/min)



Figure 4.19 Concentration profile for Bandera gray at varying injection rate (0.2-1.0 ml/min)

Core	Q	Breakthrough	CH ₄	CH ₄ Preduced
Samples	(ml/min)	(min)	Produced	$KF = \frac{OGIP}{OGIP}$
			(cm ³)	× 100
Berea gray				
	0.2	93.33	640.59	69.63
	0.4	73.32	819.09	89.04
	0.6	42.15	559.45	60.81
	0.8	40.15	476.28	51.77
	1.0	39.99	478.06	51.97
Bandera gray				
	0.2	76.32	550.53	63.37
	0.4	82.49	652.20	75.08
	0.6	35.65	495.76	57.07
	0.8	26.82	402.13	46.29
	1.0	35.32	313.69	36.11

 Table 4.10 Effect of injection rates on CH4 recovery and breakthrough

Table 4.11 Dispersion coefficient determination for different N_2 injection rates

Core	Q	Interstitial	Dispersion Coefficient	Diffusion Coefficient
Samples	(ml/min)	Velocity (10 ⁻⁵ m/s)	$(10^{-8} \text{ m}^2/\text{s})$	$(10^{-8} \text{ m}^2/\text{s})$
Berea gray				
	0.2	3.18	1.47	22.99
	0.4	6.36	4.21	22.99
	0.6	9.54	5.32	22.99
	0.8	12.72	7.84	22.99
	1.0	15.90	9.12	22.99
Bandera gray				
	0.2	3.36	5.36	22.99
	0.4	6.72	7.80	22.99
	0.6	10.08	10.10	22.99
	0.8	13.44	10.35	22.99
	1.0	16.80	13.13	22.99



Figure 4.20 Graphical representation of CH₄ volumes produced from all the experiments on Berea grey



Figure 4.21 Graphical representation of CH₄ volumes produced from all the experiments on Bandera grey

The selection of the fluid flow velocity during EGR becomes crucial as greater injection rates generally result in early mixing of the fluids. Lower injection rates, on the other hand, primarily result in prolonged resident durations (breakthrough) for the fluids in contact during the CH₄

displacement process. As a result, it indirectly enhances the mixing of these gases. The P_{exp} values, as shown in Table 4.9, represent the ideal injection rates, which translate into more displacement and smaller dispersion throughout the displacement process. The total volume of effluents generated at the end of the core flooding experiment was used to calculate the CH₄ recovery. These quantities represented portions of the original gas in the core samples. Tables 5.12, 5.17, and 5.18 show the recorded findings.

The results of the core flooding tests utilising varied injection rates at the same reservoir conditions are shown in Figs. 4.20a and 4.20b. These figures are shaped like a parabolic ellipse. The vertical axis indicates the total amount of CH₄ created in pore volumes (PV) from time t=0 to time t=tx, where x is the period when the CH₄ recovery becomes minor, as observed by the online GC machine. The experiment concludes at time tx because the majority of the CH₄ that was initially present has been retrieved. The objective is to recover 100 percent of the original 115 PV of gas with little pollution. The system was fully saturated with CH₄ prior to N₂ injection. N₂ was gently delivered at a preset rate via cell B using the ISCO pump C/D. As additional pore volume of N2 is introduced into the system, free contaminant CH4 is created till the system breaks down owing to phase shift and gravity action due to pressure rise. The greater the proportion of N₂ produced, the greater the amount of CH₄ recovered. The ratio of CH₄ generated to the original gas in situ is used to calculate recovery efficiency. Following the breakthrough, the proportion of N₂ in the exit stream continues to climb, whereas CH₄ recovery begins to decline until it is almost nil at t =tx due to product contamination. At breakthrough, the highest CH₄ recovery efficiency was obtained. The breakthrough is set at maximum product contamination of 15%. In other words, the time it took for the GC to record 0.15 mole fraction of N₂, as indicated in Tables 4.15 and 4.16. The recovery was significant compared to the experimental run at 0.2 ml/min. However, because the combined breakthrough time was high, a stream of N₂-contaminated CH₄ was recovered, as shown in Table 4.10.

Given their similarities in property and miscibility, there was a possibility of a significant length scale of mixing between N₂ and CH₄ despite their low dispersion coefficient values (1.47 x 10-8 and 5.36 x 10-8 m²/s) in Table 4.11. According to Abba et al. (2018), a similar pattern was seen with CO₂ injection at varied injection rates. This is not a cost-effective imitation because additional CH₄ will be produced, which will be severely polluted by the injected N₂, weakening the recovery idea, and rendering the EGR process uneconomical. As a result, the 0.4 ml/min trial run shows a new situation with the maximum methane recovery and efficiency. There was significant CH₄ recovery, and a lower longitudinal dispersion coefficient compared to the runs with 0.6-1.0 ml/min injections, which demonstrated a deficient recovery efficiency, breakthrough time, and dispersion coefficient trends due to higher interstitial velocity (9.54- 16.80×10^{-5} m/s) as the N₂ plumes transverses through the core sample during the core flooding experiment. Furthermore, high mean interstitial velocities (um) significantly enhance molecular kinetic energy by generating turbulence or eddy current, which effects molecular agitation of the gas and so alleviates the contact between the displacing displaced gases. Finally, Table 4.12 shows that the best (optimum) injection rate for N₂ injection for both Bandera and Berea grey occurs at 0.4 ml/min.

Core Samples	Q	Breakthrough	CH ₄ Produced	$BE = CH_4 Produced$	Dispersion Coefficient (10 ⁻
	(ml/min)	(min)	(cm ³)	$RF = \frac{OGIP}{OGIP} \times 100$	⁸ m ² /s)
Berea gray					
	0.2	93.33	646.55	70.28	1.47
	0.4	73.32	819.09	89.04	4.21
	0.6	42.15	559.45	60.81	5.32
	0.8	40.15	476.28	51.77	7.84
	1.0	39.99	478.06	51.97	9.12
Bandera gray					
	0.2	76.32	550.53	63.37	5.36
	0.4	77.16	652.20	75.08	7.80
	0.6	35.65	495.76	57.07	10.10
	0.8	26.82	402.13	46.29	10.35
	1.0	35.32	313.69	36.11	13.13

Table 4.12 Effect of injection rates on CH₄ recovery and breakthrough

4.2.5 Effect of Injection Rates on Dispersivity

According to Eq. 2.5, precise and reliable modelling of dispersion in an enhanced recovery process requires a thorough understanding of molecular dispersion (D), tortuosity (τ) , and dispersivity (α) under the conditions relevant to natural gas displacement in porous media. The latter factors are the core plug's key qualities as determined by a set of experimental data. At suitable intervals, such as those presented in this work, the flow velocity across the medium rises. Although the pressure and temperature dependence of the longitudinal dispersion coefficient (K_L) is mostly gained using the molecular dispersion model (D). As a result, precise estimates of the molecular diffusion coefficient are required for a good dispersion correlation. Fuller, Schetter, and Gittings (1966) constructed a numerical model based on a computer-aided correlation of 340 experimental points, which was described in Eq. 2.7 and was used to calculate the molecular diffusion coefficient of N2-CH4 under circumstances relevant to EGR and miscible displacements. The equation was simplified further by substituting the atomic diffusion volumes and molecular weights of N₂ and CH₄, as stated in Eq. 2.8. As a result, using Eq. 2.8, the molecular diffusion coefficients, D, for experimental pressure and temperature conditions of 1500 psig and 40 °C were calculated and are shown in Table 4.19. Furthermore, the dispersivity was evaluated by applying Eq. 2.5 to the plots of K_L/D vs u/D, a straight-line graph as seen in Figs. 4.22 and 4.23. Also, the effect of injection rates on the longitudinal dispersion coefficient was presented in Figs. 4.24 and 4.25 for Berea and Bandera grey, respectively.



Figure 4.22 Plot of dispersion to diffusion coefficient ratio against interstitial velocity for Berea grey



Figure 4.23 Plot of dispersion to diffusion coefficient ratio against interstitial velocity for Bandera grey



Figure 4.24 Relationship of coefficient of longitudinal dispersion with flow injections for Berea grey



Figure 4.25 Relationship of coefficient of longitudinal dispersion with flow injections for Bandera grey

According to several research, the dispersivity (α) in consolidated porous rocks is typically less than 0.003m (Coats & Whitson, 2004; Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012; Abba et al., 2018). Hughes et al. (2012) measured dispersivity in a range of 0.0001 m to 0.0011 m using a Donnybrook core sample with petrophysical parameters like those addressed in this study. Furthermore, precise dispersivity determination is critical as an experimental attribute of a porous medium that analyses the medium's distinctive dispersion by linking the components of pore velocity to the dispersion coefficient. This parameter is quite sensitive to invigorating fluid flow in the reservoir rock model. The dispersivity, as determined by the slopes in Figs. 4.22 and 4.23, was 0.0005m for both the Berea and Bandera grey core samples. This is within the range of values, as seen in Table 4.7. The observed dispersivity (0.0005m) was used as the mixing characteristic length scale. This was then used in Eq. 2.4 to recalculate the medium peclet (P_{em}) and experimental peclet (P_{exp}) counts at different injection rates. Tables 4.13 and 4.14 show these values.

Core Samples	Q (ml/min)	u_m (10 ⁻⁵ m/s)	D (10 ⁻⁸ m ² /s)	K _L (10 ⁻⁸ m ² /s)	$P_{em} = \frac{u_m \alpha}{D}$	$P_{exp} = \frac{u_m \alpha}{K_L}$
Berea gray						
	0.2	3.18	22.99	1.47	0.069	1.081
	0.4	6.36	22.99	4.21	0.138	0.755
	0.6	9.54	22.99	5.32	0.207	0.896
	0.8	12.72	22.99	7.84	0.278	0.811
	1.0	15.90	22.99	9.12	0.346	0.872
Bandera gray						
	0.2	3.36	22.99	5.36	0.074	0.313
	0.4	6.72	22.99	7.80	0.146	0.431
	0.6	10.08	22.99	10.10	0.219	0.499
	0.8	13.44	22.99	10.35	0.292	0.649
	1.0	16.80	22.99	13.13	0.365	0.640

Table 4.13 Peclet numbers determination using α as characteristic length scale of mixing

K_L is the respective dispersion coefficient for each injection rate across the core samples.

Both Bandera and Berea grey samples had almost the same average medium peclet number of 0.219 and 0.208, respectively. Because α and D are the same for the core plugs, the interstitial velocity is the determining factor. However, when the interstitial velocity equation, $u = \frac{Q}{\pi r^2 \phi}$, is considered, it can be shown that porosity (ϕ) is the sole dependant variable. Since both plugs were injected at the same rate (Q), the smaller the porosity, the greater the injection flow velocity (inversely proportional). As a result of their nearness porosity values, it is critical that both have around the same medium peclet number. This demonstrates that the displacement mechanism, which is driven by concentration and velocity, exists at the transition zone between molecular diffusion and mechanical dispersion in both core plugs.

In contrast, using measured grain diameter of 94.66 and 57.15 μ m for Berea and Bandera grey, reported by Abba et al. (2018) as the characteristic length scale of mixing, the medium peclet number was evaluated using Eq. 2.4, taking (u) as the average interstitial velocity of the runs as an input variable. The P_{em} recorded were 0.03 and 0.04, which indicates that the flow mechanism is dominated by diffusion within the entire experimental tests for both core plugs since both values are < 0.1, as earlier stated. With this, the selection of gas injection rates based on dispersivity value was quite misleading, and this could result in over or underestimation of transport parameters in porous medium. Table 4.14 summarises the influence of injection rates on the longitudinal dispersion coefficients of Berea and Bandera grey.

Q	Pressure	Temperature	Interstitial Velocity	Dispersion Coefficient
(ml/min)	(psig)	(⁰ C)	(10 ⁻⁵ m/s)	$(10^{-8} \text{ m}^2/\text{s})$
Berea gray	1500	40		
0.2			3.18	1.47
0.4			6.36	4.21
0.6			9.54	5.32
0.8			12.72	7.84
1.0			15.90	9.12
Bandera gray				
0.2			3.36	5.36
0.4			6.72	7.80
0.6			10.08	10.10
0.8			13.44	10.35
1.0			16.80	13.13

Table 4.14 Summary of the effect of interstitial velocity on longitudinal dispersion coefficient

As shown in Table 4.14, the longitudinal dispersion coefficient generally rises with increasing flow velocity owing to turbulence or eddy current generation. As a result, Bandera grey with the lowest permeability (32 mD) had a much larger dispersion coefficient than Berea grey (214 mD). Furthermore, because interstitial velocity is a function of porosity, the core plug with the greatest porosity will have the lowest interstitial velocity with the least significant dispersion coefficients at lower injection rates. However, the dispersion coefficient rises dramatically at higher injection rates in both core samples, with Bandera grey recording the highest value of 13.13 x 10-8 m²/s compared to Berea grey, which recorded 9.12 x 10-8 m²/s at maximum injection rate (1.0 ml/min). That represents a 44% increase. Pore volume (PV) is commonly used to quantify producing reservoirs. This is the ratio of the original gas in place or residual CH₄ recovered to the grain volume measured with the Helium Porosimeter. Pore volumes for Bandera and Berea grey core plugs were 7.53 and 7.97 cm³, respectively. The greatest CH₄ recoveries for Bandera and Berea grey, respectively. As a result, the PV values (103 and 87) were derived as a ratio of 819 to 7.97 and 652 to 7.53, respectively.

4.2.6. The Potential of N2 during EGR by CO2 Injection

The standard or traditional strategy for CH₄ recovery by CO₂ injection is depletion development, however such recovery (about 35 percent) is judged insufficient to balance the CO₂ storage expense (Wang et al., 2018). The nascent mixing of the injected CO₂ and displaced CH₄ invariably results in early CO₂ breakthrough in the production well. The goal was to recover a significant amount of CH₄ that was free of CO₂, allowing additional injected CO₂ to be stored. However, employing the traditional EGR-CO₂ injection strategy proved less efficient. The value of X₀ at the intersection point (1) in Fig. 4.27 shows a high injected CO₂ proportion at breakthrough. As a result, a new EGR strategy is needed to lower the mole fraction of CO₂ in the recovered CH₄. The N₂ gas functions as a booster, repressurizing the reservoir pressure prior to the CO₂ breakthrough, allowing for more CH₄ recovery without contamination. It also serves as a retardant by forming a thin barrier between the CO₂-CH₄ phase area seen in Fig. 4.26b. This makes it harder for CO₂ to disperse into CH₄, resulting in a longer CO₂ breakthrough, with most of the injected CO₂ falling downhill for storage inside the pore spaces owing to gravity. In this section, N₂ was used as a booster gas to delay CO₂ breakout with minimum mixing. More CH₄ recovery and CO₂ storage were realised when the generated CO_2 proportion decreased, as indicated in Fig. 4.27 by junction points (2) and (3), X₁, and X₂ representing the mole fraction of CO₂. To improve both CH₄ recovery and CO₂ storage, (1) the percentage of generated CO₂ (X_0 , X_1 , and X_2) was reduced ($X_2 < X_1 < X_0$), and (2) the change in the proportion of produced CO₂ (ΔX) and slope (S₁ and S₂) were also minimised ($\Delta X_2 > \Delta X_2$ and $S_2 > S_1$). The plot of generated CO₂ fractions against displaced CH₄ at 0.4ml/min optimal conventional CO₂ injection, 1500 psig pressure, and 40 ^oC temperature is shown in Fig. 4.27. The effluent stream compositions recorded by the GC machine are represented by these mole fractions. Based on the factors listed above, the appropriate booster gas volume was determined.



Figure 4.26a Schematics of conventional CO_2 injection to displace CH_4 without N₂ booter gas (Wang et al., 2018)

Figure 4.26b Schematics of conventional CO_2 injection to displace CH_4 with N₂ booster gas (Wang et al., 2018)



Figure 4.27 The plot of generated CO_2 fractions against displaced CH_4 at 0.4ml/min optimal conventional CO_2 injection, 1500 psig pressure, and 40 ^{0}C temperature (Mohammed et al., 2020).

4.2.6.1 Effects of CO₂ injection on CH₄ recovery

The Original Gas in Place (OGIP) was calculated using Eq. 4.3 to evaluate the CH₄ recovery effectiveness of each injection rate based on the gas production measured. The compressibility factor (Z), determined numerically from models in the works provided by (Abba et al., 2018), was used to assess the porosity acquired from Helium Porosimetry, the gas formation volume factor, at experimental circumstances (Shabani and Vilcaez, 2017; Ziabakhsh-Ganji and Kooi, 2012). The generation of CH₄ gas was monitored online using a gas flow metre, and its composition was determined on a regular basis (every 5 minutes) using the GC equipment. In real-time, the displacing gas movement and breakthroughs were recorded, and the dispersion coefficient, recovery sweep efficiency, and CO₂ storage were calculated. The experiment was terminated when the amount of CO₂ produced exceeded the amount injected (the produced gas contained an insignificant amount of CH₄). The experimental results for CO₂ produced at various injection rates (0.2-1.0 ml/min) are shown in Appendix A. At the front of supercritical CO₂, miscible displacement occurs (ScCO₂). The injection of CO₂ up to 0.21 HCPV resulted in lower CO₂ concentrations at the exit and little natural gas contamination. The initial CH₄ recovery rose linearly during the operation. When 0.22 HCPV was injected, the CO₂ content

of the effluent stream increased by roughly 5%, and the percentage recovery climbed by 3% to its maximal value of 35%. The point might be seen as a watershed moment. For injections following breakthrough, a significant increase in the CO₂ output composition was seen until 0.3 HCPV of CO₂ was injected, resulting in a substantial CH₄ recovery drop. Further injections into 0.372 HCPV had little influence on the proportions of CO₂ generated and the efficiency of CH₄ recovery remained nearly constant. This signifies that the displacement has come to an end. At 0.2ml/min injection, the same graph pattern was seen. However, the presence of CO₂ in the exit stream appeared sooner than that for 0.4ml/min, and the greatest CH₄ recovery was reported when 0.3 HCPV of CO₂ was injected into the system. This is seen in Figures 4.28 and 4.30, respectively. A similar pattern was seen at various injection rates, however the drop in CH₄ recovery was greater at higher injection rates (0.6-1.0 ml/min), with an average 20% decline, as shown in Fig. 4.30. The breakthrough graphs in Figs. 4.30, 4.31, and 4.32 at higher injection rates (0.6-1.0ml/min) exhibit a steep slope due to the rigidity of the curves after the CO₂ breakout. This indicates that there is a substantial chance of CO₂ and CH₄ miscibility during the displacement process. Overall, lower injection rates (0.2-0.4ml/min) resulted in more methane recovery than higher injection rates (0.6-1.0 ml/min). Due to the greater interstitial velocity at these rates, low recovery and sweep efficiency were found. According to Abba et al. (2018), high interstitial velocity tends to create turbulence and eddy current in the flow profile and agitate the molecules of the gas species, enhancing the interaction collision between the displacing and displaced gases. As seen in Table 4.15, this results in a high dispersion coefficient.



Figure 4.28 CH₄ recovery against HCPV of total CO₂ injected at 0.2ml/min using Bandera gray



Figure 4.29 CH4 recovery against HCPV of total CO2 injected at 0.4ml/min using Bandera gray



Figure 4.30 CH4 recovery against HCPV of total CO2 injected at 0.6ml/min using Bandera gray



Figure 4.31 CH4 recovery against HCPV of total CO2 injected at 0.8ml/min using Bandera gray



Figure 4.32 CH4 recovery against HCPV of total CO2 injected at 1.0ml/min using Bandera gray

4.2.6.2 Effects of CO₂ injection on dispersion

To establish the best injection rate from the range of interest, several injection rates were used. By using the longitudinal dispersion coefficient K_L as the fitting parameter, the CO₂ compositions obtained were utilised to examine the mixing rate of CO₂-CH₄ interaction. Table 4.15 shows the values of the dispersion coefficients for various injection rates. The mixing characteristics length scale (L) was adjusted in the OriginPro software regression tool to provide a better fit as recommended by (Hughes et al., 2012; Liu et al., 2015; Abba et al., 2018), with the interstitial velocity remaining constant for each run as assumed in the 1D advectiondispersion equation. The greater injection rates, as predicted, resulted in an early CO₂ breakthrough; this accords with the study described by (Liu et al., 2015; Abba et al., 2018). The molecular diffusion coefficients, D, were measured under experimental conditions of 1500 psig pressure and 40 ⁰C temperature. Using Abba et al. (2018) determined grain diameter of 57.15µm as the characteristic length scale of mixing, the medium Peclet numbers were calculated, with (u) as the average interstitial velocity of the runs as an input variable. The Pem values were 0.02, 0.03, 0.04, and 0.05. All results were 0.1, indicating that diffusion was the dominant flow mechanism during the whole experimental tests. Furthermore, the dispersivity (α) was obtained constructively by using Eq. 2.5 to the graphs of K_L/D vs u/D, as shown in Fig. 4.33. According to (Coats, K.H & Whitson, 2004; Keith H. Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012), the values of dispersivity (α) in consolidated porous medium are generally less than 0.01 ft (0.003 m). Hughes et al. (2012) measured dispersivity in the range of 0.0001 to 0.0011 m using the Donnybrook core. Abba et al. (2018) found 0.0006m dispersivity and tortuosity of 29 in a Bandera grey core plug with parameters like those utilised in this study. In general, as flow velocity rises owing to turbulence or eddy current generation, the longitudinal dispersion coefficient increases. As shown in Fig. 4.34, the largest and smallest dispersion coefficients were obtained at maximum and minimum injection rates, respectively. When the dispersion coefficients were plotted versus tests, injection rates invariably showed a linear relationship.



Figure 4.33 Plot of dispersion to diffusion coefficient ratio against interstitial velocity



Figure 4.34 Plot of longitudinal dispersion coefficient ratio against injection rates

Injection at a low rate primarily leads in a longer breakthrough (resident) time for gases in contact, as well as increased mixing of the gases (Abba et al., 2018). Because of this embryonic mixing, using standard CO_2 injection without an additional component to achieve better CH_4 recovery and CO_2 storage at the same time is difficult. To address this issue, the next section discusses the use of N₂ as a booster during CH_4 displacement by CO_2 injection. Due to the considerable combined CH_4 recovery and a significant amount of injected CO_2 saved, a 0.4 ml/min injection rate was used for additional CO_2 injection on this occasion.

Q (ml/min)	Interstitial Velocity (10 ⁻⁵ m/s)	Total CO ₂ Injected (HCPV)	CO ₂ Breakthrough (HCPV)	CO ₂ Injected Stored (%)	CH ₄ Recovery (%)	Dispersion Coefficient (10 ⁻⁸ m ² /s)
0.2	3.36	0.36	0.20	35.62	59.63	2.64
0.4	6.72	0.37	0.22	58.03	39.97	3.49
0.6	10.08	0.56	0.33	56.82	26.61	6.06
0.8	13.44	0.81	0.54	66.10	24.59	7.63
1.0	16.80	0.90	0.53	68.51	27.74	10.99

Table 4.15 Results summary for all the experimental runs at diffusion coefficient of 18.48 10⁻⁸ m²/s

4.2.6.3 Effect of N2 as a booster gas during CO2 flooding

During the experiment, the breakthrough represents the initial contact between the injected gas species (CO₂ or N₂) and the displaced CH₄ gas over the length scale of the core sample. The longer the breakthrough for traditional CO₂ flooding, the lower the sweep recovery efficiency owing to nascent mixing of CO₂ and CH₄, as seen by increased dispersion coefficients. As a result, natural gas generation has a poor calorific value and significant purifying expenses, rendering the process uneconomical. When N₂ was used as a booster gas, however, there was a delay in breakthrough. At 1500 psig, 40 $^{\circ}$ C, and varied booster gas volumes of 0.06-0.29 HCPV, four sets of tests were performed. Fig. 4.35 depicts the fluctuation in effluent components with total gas injection (HCPV). Simultaneously, Fig. 4.36 demonstrated the effect of N₂ booster gas on CO₂ breakthrough when compared to ordinary CO₂ injection at 0.4 ml/min. For all the booster gas quantities used, the CO₂ residence duration was delayed. Due to its high conductivity, the injected amount of N₂ before to the CO₂ injection has a repressurization effect, producing maximum amounts of CH₄ and a minimal percentage of CO₂ in the effluent stream of the core holder before the CO₂ breakthrough. This validated N₂ utility in reservoir maintenance applications. The rise in booster gas volume was related to the delay

in CO₂ breakthrough, with the greatest at 0.3 PV fraction. The GC equipment was used to check the booster composition throughout the studies. As shown in Fig. 4.38, the greater the booster gas in the system, the more N₂ gas was recorded in the product stream. At larger injection rates, a similar result was observed during the CO₂ flooding. However, lesser booster gas volume resulted in lower product contamination with higher CH₄ recovery and CO₂ storage as compared to 0.4ml/min optimal CO₂ flooding. This means that infusing a modest quantity of N₂ into the reservoir before injecting CO₂ promotes effective CH₄ recovery and allows for significant amounts of CO₂ storage inside the pore spaces of the core plug. The addition of N₂ displaces a greater quantity of the CH₄ until it achieves its breakthrough, allowing most of the CO₂ afterwards injected to be trapped inside the rock space without mixing with the nascent CH₄. When the CO₂ reaches its breaking point, a significant amount of pure CH₄ is recovered. In the presence of N₂, which operated as a barrier wall between the CO₂ and CH₄ interphases, CO₂ found it difficult to disperse into CH₄.

To improve CH₄ recovery and CO₂ storage, the fraction of CO₂ and N₂ created at the exit stream (X) must be reduced, while the change in the produced CO₂ fraction (Δ X) must be maximised. The concentration profile curve might flatten, resulting in increased CH₄ recovery and CO₂ storage, as shown in Fig. 4.28. Because most natural gas exploration sites accept greater nitrogen contamination than CO₂ based impurities, natural gas products based on N₂ contaminants are more environmentally friendly than CO₂ based impurities. Because of the high compression energy cost and depressurizing technique used, the sweetening process of CH₄-N₂ contamination is less expensive than CH₄-CO₂.



Figure 4.35 Concentration profile at 0.4ml/min optimum conventional CO₂ injection using Bandera gray



Figure 4.36 Effects of booster gas on CO₂ breakthroughs



Figure 4.37 Concentration profile comparison at 6% booter gas



Figure 4.38 Concentration profile comparison at 29% booster gas
When a total proportion of 0.348 HCPV of CO₂ was injected, significant CO₂ storage was seen at the highest booster dosage. This was within the range of total CO₂ injected during traditional CO₂ flooding at 0.2 and 0.4 ml/min. The latter, on the other hand, observed more CO₂ storage than the most recent 0.2 and 0.4ml/min injections. The extra N₂ injected served as a retardant, forming a thin barrier between the CO₂-CH₄ interface, and encouraging the CO₂ to fall for storage owing to gravity. The generated CH₄ was significantly polluted with N₂ rather than CO₂, as seen by the N₂ and CO₂ curves crossing the CH₄ curve in Fig. 4.38. As a result of the excessive amount of booster gas utilised, the most minimal recovery was reported. The low dispersion coefficient value reported resulted in a decrease in nascent CO₂-CH₄ mixing. Furthermore, the experimental runs at 0.06, 0.13, and 0.19 fractions of HCPV inject a comparable quantity of total CO₂ as the 0.6ml/min conventional CO₂ flooding. Table 4.16 shows that the test with 0.13 HCPV of N₂ booster resulted in the maximum CO₂ storage. The large differential pressure drops (dp) illustrated in Fig. 4.43 characterised this value. When the least amount of booster gas was utilised, the maximum recovery occurred. This value was distinguished by having the lowest N₂ product contamination and differential pressure (dp). However, it produced the largest mole fraction of CO₂, as seen in Fig. 4.37. As a result, the presence of N₂ as a booster or contaminant produces enormous changes in the behaviour of supercritical CO₂, as documented by (Xidong et al., 2019; Hughes et al., 2012; Janssen et al., 2018; Abba et al., 2018). Various authors advocated that a longer residency (breakthrough) time for gas injection be considered to lower gas separation costs (Xiangchen et al., 2018), provided that excessive CO₂-CH₄ mixing can be minimised. This will allow for a substantial amount of CO₂ storage while also recovering most of the leftover natural gas. It is worth mentioning that better displacement efficiency may be accomplished with a smaller booster volume.



Figure 4.39 A plot of differential pressure drops against experimental time with and without booster gas

Table 4.16 Results summary for all the experimental runs at diffusion coefficient of 18.48 10⁻⁸ m²/s

Case Study	Q	Interstitial	CO ₂ Injected	CO ₂ Injected	CH ₄ Recovery	Dispersion Coefficient
-	(ml/min)	Velocity (10 ⁻⁵ m/s)	(HCPV)	Stored	(%)	$(10^{-8} \text{ m}^2/\text{s})$
		-		(%)		
Without N ₂						
booster						
	0.2	3.36	0.36	35.62	59.63	2.64
	0.4	6.72	0.37	58.03	39.97	3.49
	0.6	10.08	0.56	56.82	26.61	6.06
	0.8	13.44	0.81	66.10	24.59	7.63
	1.0	16.80	0.90	68.51	27.74	10.99
With N ₂						
booter						
	(HCPV)					
	0.06	6.72	0.492	57.91	89.17	3.59
	0.13	6.72	0.486	68.67	64.81	2.78
	0.19	6.72	0.504	49.06	75.95	3.27
	0.29	6.72	0.348	63.47	44.39	2.59

4.2.7 Flow Behaviour of CO2 and N2 in Porous Medium

Experiments were carried out on Bentheimer core samples to evaluate the temperature dependency of diffusion and dispersion coefficients. The experiment was carried out at temperatures of 30 and 40 °C, at a pressure of 102 bars, and at various CO₂ injection rates (0.4, 0.6, 0.8, 1.0, and 1.2 ml/min). According to Fig. 4.40, the diffusion coefficient is linearly related to temperature, which is consistent with the findings of other studies (Mamora and Seo, 2002; Liu et al., 2015; Mohammed et al., 2019; Abba et al., 2018). As a result of the increase in activation energy, the molecular mobility of the gas species is directly proportional to temperature. Due to the obvious higher temperatures within the pore matrix, the gas species gradually exceed the natural force of attraction between them as they migrate down the core. Because of the increased kinetic energy associated with temperature increases, it allows them to flow across a larger area. As a result, it encourages the free diffusion of CO_2 and N_2 molecules, resulting in more displacing and displaced gas molecules entering each other and confirming greater mixing scales. The plot of dispersion coefficient vs injection rate in Fig. 4.42 provided evidence, with larger dispersion coefficient values at 40 °C than at 30 °C for the same range of CO_2 injection velocities. When the temperature went from 30 to 40 $^{\circ}C$, a combined average of 25% rise was noted. This indicates that when the temperature rises, both the dispersion and diffusion coefficients increase. At simulated reservoir conditions, it can be concluded that high temperatures aided in the mixing of gases in motion within the pore channels. As a result, higher-temperature gas resources are unlikely to be suited for the CO₂ enhanced gas recovery procedure for basic production operations. Due to increasing flow velocities, the turbulence effect is probably responsible for substantial diffusion and dispersion over the core length. The largest dispersion was obtained in this portion at 1.2 ml/min, while the lowest was reported at 0.4 ml/min, as shown in Fig. 4.41.



Figure 4.40 Effect of injection rates on the longitudinal dispersion coefficient at 30 & 40 0 C



Figure 4.41 Relationship between diffusion coefficient and temperature at 102 bars using Eq. (2.13)

4.2.7.1 Effect of temperature on dispersivity

Using Eq. (2.4), the experimental results at 30 and 40 $^{\circ}$ C were used to calculate the dispersivity (a) of the Bentheimer core plug at $\tau = 3, 2$, and n = 1. The dispersivities of the core plug at 30 and 40 °C are well suited by the experimental data shown in Figs. 4.43 and 4.44. At 40 °C, the medium peclet number P_{em} was determined to be 0.964 – 2.894. Furthermore, at lower injection velocities (0.06-0.09 mm/s), corresponding to the 0.964 - 1.448 medium peclet number range, a modest convection impact was found, with diffusion being the primary mechanism. The convection effect becomes more pronounced as the injection velocity increases, with a corresponding mean peclet number range of 1.448 - 2.89. As a result, diffusion and convection predominated the process, leading to early CO₂ breakthroughs. As a result, choosing the proper injection rate is critical for simultaneous CO₂ storage and the EGR process. The dispersivity (α) for the core plug at 30 ^oC was 0.00265 m, which was smaller than that reported by (Mohammed et al., 2020; Abba et al., 2018) and within the range described by (Gist et al., 1990; Schulze-Makuch, 2005; Honari et al., 2013). In summary, using Eq. (2.4) to the experimental findings allows the dispersivity (α) for the two temperatures investigated for the Bentheimer sandstone plug to be calculated. For temperatures of 30 and 40 0 C, $\alpha = 0.00222$ and 0.002265 m, respectively, and these results are within the range reported for sandstones by (Coats et al., 2009; Schulze-Makuch, 2005; Liu et al., 2020), though for the 40 ^oC temperature, the dispersivity recorded was slightly higher, though lower than that presented according to (Brigham et al., 1974). As a result, higher temperatures have a greater influence on dispersion and diffusion coefficient, which finally leads to more significant mixing of CO₂ and N₂ (Liu et al., 2018).



Figure 4.42 Plot of dispersivity determination at 30 ⁰C



Figure 4.43 Plot of dispersivity determination at 40 ^oC

4.2.7.2 CO₂ breakthrough

The breakthrough is defined by the detection of the displacing gas (CO₂ or N₂ gas) at the exit product stream. In this investigation, the breakthrough was defined as 1-3% CH₄ contamination by CO₂, or when the GC result revealed a CO₂ concentration within a range of 1-3%. CO₂ breakthrough curves (S-shape curves) were calculated by graphing CO₂ mole fractions against the PV of injected CO₂ at the outflow stream. The experiment was conducted at two distinct temperatures (30 and 40 °C) to evaluate the effect of temperature change on CO₂ breakthrough at varied injection velocities. The CO₂ breakthrough decreased as reservoir temperature increased, indicating that diffusion and dispersion coefficients are temperature dependent. In all cases, the experiment at 30 °C reported a longer breakthrough time than the experiment at 40 0C. At 30 °C and the lowest injection velocity, the greatest breakthrough at 0.52 PV was recorded. When the temperature was raised from 30 to 40 °C, the breakthrough reduced to 0.17 PV. The breakthrough curves measured at 30°C are less steep than those measured at 40°C. The CO₂ breakthroughs at varied injection rates for 30 and 40 ^oC experimental settings are shown in Figs. 5.49a-e. These graphs were created by graphing the CO₂ exit composition from GC equipment downstream of the core holder versus the injected PV of CO₂. As seen by the vertical distance difference between the two graphs, the temperature impact was rather considerable at a reduced injection rate. Thus, at lower injection rates, the temperature impact was more important than the injection rates. However, when the injection rates increase from 0.4 to 1.2 ml/min, such vertical variations become small until the two graphs (30 and 40 0 C) coincide at 1.2 ml/min. The injection rate impact surpassed the dominating temperature effect and took over as the primary driving force. The trials were conducted at 102 bar constant pressure and an interstitial velocity range of 0.06 - 0.18 mm/s. The longest CO₂ breakthrough at 0.52 PV was seen at 0.06 mm/s and 30 °C, which afterwards dropped by half when the interstitial velocity rose to 0.18 mm/s. At 0.06 mm/s and 40 °C temperature, the smallest CO₂ breakout was reported at 0.17 PV. During the displacement experiment, the greatest injected CO_2 (0.8 PV) via the system was ostensibly observed at these settings. These findings corroborate the findings of the research (Mesfer et al., 2020). Overall, the gas injection velocity has a large impact on the CO₂ breakthrough threshold, and this affect is stronger at lower rates. As seen in Figs. 4.44a-e, the difference in the breakthrough periods between the two temperature sets drops from 0.35 PV to virtually nil. The two graphs in Fig. 4.44e overlap, indicating the same 0.24PV breakthrough time. As a result, a longer CO₂ breakthrough indicates decreased mixing and increased storage at lower system temperatures when diffusion reigns supreme. In contrast, at larger injection rates, the gas molecules obtain more kinetic energy, resulting in a turbulent flow regime. As a result, advection takes precedence over diffusion inside the porous material.



Figure 4.44a-e CO₂ breakthrough at varying injection rate (0.4-1.2 ml/min) for 30 & 40 $^{\circ}$ C temperatures using Bentheimer core sample.

Diffusion is temperature-dependent, which means that the greater the temperature, the faster the diffusion rate. Because the kinetic energy of the gas species rises at higher temperatures, they travel quicker within the porous media. This indicates that fewer molecules of CO_2 would have the kinetic energy to touch the N₂ in the core holder's outflow stream, explaining why a lesser quantity of CO_2 was measured before breakthrough at lower injections. As a result, CO_2 injected settles to the bottom section of the porous medium, indirectly affecting increased storage in the context of geological sequestration and, presumably, less effluent contamination. The lower the temperature, the less mixing (lower dispersion coefficient), the longer the CO_2 breakthrough and, consequently, better storage with little product contamination.

4.2.7.3 Concentration profile

During the core flooding experiment, the concentration profile plots demonstrate the pattern between displacing and displaced gas. These plots are shown in Figs. 4.45a-e. According to Fig. 4.46a, when the PV of total injected CO₂ reaches 0.17 PV, a CO₂ reading was recorded at the exit stream, indicating the presence of a displacement front. Following then, the exit CO₂ concentration rises linearly with the total CO₂ injected (PV) until it reaches a high at roughly 0.3 PV, equal to 0.99 CO₂ mole fraction. At this time, a negligible concentration of N₂ was measured downstream of the core holder, which is indicated by the green curve in Fig. 4.46a. This shows that there has been a large recovery of N₂. When the experiment was carried out at a higher temperature of 40 °C, a similar trend was seen. At 30 and 40 °C, a point of junction was detected at about 50% of the CO₂ exit concentration. Furthermore, the curves at 30 ^oC were steeper than those at 40 °C, indicating increased mixing of N₂ and CO₂. This was clear, with many of the runs at 40 °C registering a larger dispersion coefficient under the identical injection situations. The distance between the two curve crossings diminishes as the injection rate rises from 0.4 to 1.2 ml/min, until it becomes less noticeable, especially at the maximum injection rate of 1.2 ml/min; at this point, the N₂ and CO₂ curves overlap, as seen in Fig. 4.45e. This plot corresponded to the breakthrough plot in Fig. 4.44e. When a result, given reservoir circumstances, both N₂ and CO₂ exhibit comparable phase shift behaviour as the interstitial velocity rises throughout the EGR process.



Figure 4.45a-e Concentration profile at varying injection rate (0.4-1.2 ml/min) for 30 & 40 0 C temperatures.

4.2.7.4 CO₂ sequestration

The law of mass conservation, as proved by Abba et al., was used to study CO_2 sequestration (2018). Consequently, the total quantity of CO_2 injected and generated was calculated to investigate each injection rate, storage efficiency, and temperature, as shown in Eqs. (5.4a) and (5.4b).

$$\Sigma V_{CO2, in} = \Sigma (V_{CO2, Accumulated} + V_{CO2, Produced})$$
(4.4a)

% CO₂ Storage =
$$\frac{\Sigma V_{CO2, Accumulated}}{\Sigma V_{CO2, in}} \times 100$$
 (4.4b)

Most CO₂ sequestration methods are impacted at CO₂ critical temperatures and pressures of 31.5 ^oC and 74 bar, respectively, since CO₂ becomes more compressible as reservoir conditions increase (Hoteit, Fahs and Soltanian, 2019; and Godec et al., 2011). The fraction of CO₂ stored was calculated using Eq. (4.4b) as the ratio of total CO₂ accumulated to total injected.

Furthermore, CO_2 gas displays a considerable discrepancy in density in its supercritical stages, allowing it to drop lower due to gravity while displacing the residual N₂ inside the accessible pore spaces. As a result, a considerable percentage of total injected CO₂ remained trapped inside the lengthy core, resulting in a large sequestration volume. Table 4.18 shows that when the injection rate increases from 0.4 to 1.2 ml/min, the proportion of CO₂ stored increases. Higher storage volumes were obtained at higher injection rates during the 30 ^oC testing cycles. The ratio of total CO₂ injected to N₂ saturation was low for large injections compared to low doses. As the CO₂ flow stream travelled longitudinally in the core sample, most of the CO₂ within the core plug was able to move downhill and be stored. Furthermore, the largest CO₂ storages were achieved at injection rates of 1.0 and 1.2 ml/min, resulting in 89.2 - 89.6 and 71.89 - 79.17% for 30 and 40 ^oC, respectively. It is reasonable to assume that CO₂ storage will be more desirable at lower temperatures, as seen by the percentage storability. Furthermore, the differential pressure plots in Figs. (4.51d) and (4.51e) indicate a similar pattern for both temperatures, which explains why both tests showed a proximal range of value parameters. The injection at 0.4 ml/min, on the other hand, was unable to overcome the capillary forces within the pore matrix's smaller pore gaps. This is due to its density and flow progression, which were seen during the core flooding experiment, as well as its distinctive differential pressure (Δp) and high permeability (k). At greater injections, more of the flow pathways become accessible for continuous flow without limitation or curtailment, as shown

in Eq. (2.23b). As a result, the flow profile was continuous, which explains the decreased longitudinal dispersion coefficient and significant CO_2 storage with little mixing, as predicted. This corresponded to the works described by (Abba et al., 2018; Honari et al., 2016; Liu et al., 2018; Mohammed et al., 2020).





Figure 4.46a-e Differential pressure comparison for 0.4-1.2ml/min injection at 30 and 40 0 C

Q (ml/min)	Interstitial Velocity (10 ⁻⁵ m/s)	CO ₂ Breakthrough (HCPV)	CO ₂ Injected (HCPV)	CO ₂ Injected Stored (HCPV)	CO ₂ Stored (%)	Dispersion Coefficient (10 ⁻⁸ m ² /s)
Temp. 30 ⁰ C						
0.4	5.96	0.52	0.78	0.56	71.80	8.23
0.6	8.95	0.39	0.58	0.44	74.81	14.03
0.8	11.93	0.37	0.56	0.43	76.39	21.09
1.0	14.91	0.31	0.39	0.35	89.06	24.13
1.2	17.89	0.24	0.42	0.38	89.02	42.53
Temp. 40 ⁰ C						
0.4	5.96	0.17	0.31	0.14	46.73	12.52
0.6	8.95	0.21	0.32	0.20	61.43	17.25
0.8	11.93	0.23	0.32	0.21	66.59	25.06
1.0	14.91	0.24	0.41	0.29	71.89	33.62
1.2	17.89	0.24	0.37	0.30	79.17	39.41

Table 4.17 General results summary at 30 and 40 0 C runs

4.3 CHAPTER SUMMARY

From Chapter 3 it was found that the maximum CH_4 recovery was achieved at 0.4 ml/min for both Berea and Bandera grey core samples. It was identified that the Berea recovered 18% more CH_4 than Bandera grey at the same injection. The main findings from this chapter show that:

- i. The coefficient of longitudinal dispersion declines with raises in booster gas volume, hence the higher the amount of booster the less the dispersion of CO₂ into CH₄.
- ii. The higher the booster volume, the higher the sequestered CO_2 , especially at higher CO_2 injection rates (1.0-1.2 ml/min).
- iii. The maximum CO_2 storage was obtained at 0.13 PV of N₂ booster. The large differential pressure drops (dp) characterised this value. The maximum CH_4 recovery occurred when the least amount of booster gas was employed and was marked by the least amount of N₂ product impurity.
- iv. The core flooding experiment at 30 °C, recorded an extendable breakthrough time over that at 40 °C. The maximum breakthrough of 0.52 PV was recorded at 30 °C at the lowest injection velocity.
- v. It was found that the displacement efficiency of the current research outperforms traditional CO₂ floods. When N₂ was employed as a booster gas, there was a 62 & 18% improvement in CH₄ recovery and CO₂ storage, respectively, and a 20% reduction in dispersion coefficient when compared to standard CO₂ flooding.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The objective of this study is to investigate the role of N_2 as a booster gas during enhanced gas recovery and CO_2 sequestration using core flooding experiment. The key findings are as follows:

- The experiments with N₂ as a booster recorded higher natural gas recovery and CO₂ storage. This value is 37% higher when compared with the traditional CO₂ flooding at supercritical conditions of temperature (30-40 ⁰C) and pressure 1500 psig).
- In their supercritical state, CO₂, CH₄, and N₂ gases display the density of a liquid while retaining the viscosity of a gas. This phenomenon was more in CO₂ than N₂ and CH₄. At 50 ^oC, CO₂ had a viscosity drop equivalent to liquid, with a 66% reduction. Because of the high-pressure ratio (100:1) induced by the presence of water vapour during compression, CO₂ compression is extremely expensive. N₂, on the other hand, may be recovered totally from ambient air. As a result, it has a smaller compression ratio than CO₂, requiring less of it to create high pressure in the CH₄ reservoir during displacement process.
- The OGIP is mostly determined by the porosity of the rock, as proven by the Bentheimer core sample, which recorded 1002 cm³ gas in placed within it pore spaces. As a result, the more blank spaces inside the reservoir rock, the more gas is required to fill those empty areas. The P_{exp} measurement using the grain diameter as the length scale of mixing for the complete core samples utilised revealed that the major displacement mechanism during EGR was diffusion like with Pe < 0.1, and the concentration gradient regulates the flow. The dispersivity of the Berea and Bandera grey core samples was 0.0005m. The similarities can be attributed to the similarity of their porosity levels. The P_{em} values observed were 0.03 and 0.04, indicating that the flow mechanism is dominated by diffusion during the whole experimental testing for both core plugs, as previously indicated, because both values are < 0.1. While the dispersivity of the Bentheimer plug was 0.00222 and 0.00227 at 30 and 40 $^{\circ}$ C, indicating that temperature has minimal influence on its dispersivity. At a maximum injection rate of 1.0 ml/min, the dispersion coefficient increases considerably in both

core samples, with Berea grey recording the least dispersion of 9.12 x 10^{-8} m²/s compared to Bandera grey and Bentheimer with 13.13 x 10^{-8} and 33.62 x 10^{-8} m²/s, respectively. The most effective injection rate was 0.4 ml/min.

- The addition of N₂ as a booster gas before the CO₂ injection into the reservoir impacted CH₄ recovery and CO₂ storage. The displacement efficiency outperforms traditional CO₂ floods results. Overall, there was better CH₄ recovery, more CO₂ storage, and less miscibility impact compared with traditional CO₂ flooding. The best results were obtained at lower booster gas volumes, with the optimum at 0.13% of PV. This indicates N₂ possible involvement as a booster gas during the EGR and CO₂ storage processes.
- The experiment at 30 °C observed a longer breakthrough time than the experiment at 40 °C. At 30 °C and the slowest injection velocity, the greatest breakthrough was 0.52 PV. During the core flooding experiment, the concentration profile plots illustrated the pattern between displacing and displaced gas. The N₂ and CO₂ curves overlapping at the 1.2 ml/min injection rate, and this figure was in synergy with the breakthrough plot. Under reservoir conditions, both N₂ and CO₂ exhibit comparable flow behaviour as the interstitial velocity increases during the EGR process. The proportion of CO₂ stored rises as the injection rate increases from 0.4 to 1.2 ml/min over the range of injections and temperatures evaluated. Because of the flow resistance inside the flow channels, the total CO₂ stored was more promising at higher rates, corresponding to greater differential pressure.
- The selection of the flow velocity in EGR is thus critical, as larger injection rates may result in premature mixing of the fluids. Lower injection rates often allow longer residence durations for the fluids in contact and, as a result, indirectly improve gas mixing. Furthermore, medium peclet numbers primarily represent the optimal injection rates, which translate to smoother displacement with a smaller dispersion coefficient during the EGR process. As a result, as compared to conventional CO₂ injection, N₂ injection into natural gas reservoirs has the potential for better recovery efficiency with less mixing. The study highlights the importance of N₂ gas during the EGR. This significantly increased the displacement phase. This research sought to provide information for the field-scale implementation of EGR via computer simulations by including these systematic effects for a more accurate portrayal of the process.

5.2 CONTRIBUTION TO KNOWLEDGE

This study demonstrates that using N_2 as a booster gas can increase both CH₄ recovery and CO₂ sequestration, thus can be suitable for pilot application within the oil and gas. When compared to traditional CO₂ flooding, there was a 62 and 18% in natural gas recovery and CO₂ storage, respectively, and a 20% drop in dispersion coefficient when N_2 was used as a booster gas. Knowledge

5.3 RECOMMENDATIONS

Despite the significant advances in this study, it is worth noting that there are still paths to investigate beyond the scope of this research endeavour. The following are some suggestions:

- More advanced imaging techniques, such as Nuclear Magnetic Resonance (NMR), might be used to examine the pore distribution before and after core flooding to analyse any dynamics caused by the injection process.
- To further investigate the potential of N₂ as a booster during natural gas displacement and CO₂ sequestration, a pilot study should be undertaken.
- Connate water saturation might be used to assess the influence of connate water saturation and salinity on displacement efficiency and dispersion coefficient during EGR with N₂ as booster.

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Appendix A: Resource Tables

Injection a	at 0.2ml	Injection a	t 0.4ml	Injection at	t 0.6ml	Injection at	0.8ml	Injection at 1.0ml	
Time	N ₂	Time	N2	Time	N2	Time	N2	Time	N2
(min)	(yN ₂)	(min)	(yN ₂)	(min)	(yN ₂)	(min)	(yN ₂)	(min)	(yN ₂)
0.16	0.001	0.15	0.001	0.15	0.001	0.15	0.001	0.16	0.001
6.33	0.001	6.32	0.001	6.32	0.001	5.98	0.001	6.83	0.001
11.99	0.001	12.15	0.001	12.15	0.001	11.32	0.001	12.49	0.001
17.49	0.001	18.48	0.001	18.15	0.001	18.65	0.011	18.16	0.001
23.32	0.001	24.15	0.001	24.48	0.031	24.15	0.018	21.82	0.001
28.82	0.001	32.98	0.001	30.32	0.051	29.48	0.040	29.17	0.002
34.49	0.001	38.65	0.001	35.98	0.083	34.82	0.081	34.49	0.020
40.82	0.011	44.32	0.001	42.15	0.132	40.15	0.146	39.99	0.115
46.66	0.015	50.32	0.001	47.82	0.200	46.98	0.232	45.32	0.343
52.99	0.02	55.82	0.016	53.32	0.286	53.48	0.332	50.66	0.618
58.66	0.026	61.98	0.020	58.82	0.391	58.98	0.436	55.99	0.826
64.32	0.034	67.65	0.021	64.48	0.523	64.32	0.541	61.49	0.925
70.32	0.043	73.32	0.122	69.98	0.653	69.98	0.651	66.83	0.958
76.16	0.053	78.82	0.153	75.65	0.767	75.32	0.745	72.33	0.980
81.99	0.065	84.48	0.186	81.65	0.855	81.15	0.804	77.83	0.986
87.66	0.079	90.32	0.222	87.48	0.912	86.82	0.858	83.32	0.987
93.33	0.144	95.98	0.262	93.15	0.943	92.32	0.894		
99.16	0.245	101.66	0.305	98.65	0.965	98.65	0.918		
104.82	0.353	108.32	0.349	104.32	0.974	103.99	0.934		
110.66	0.462	113.98	0.395	110.32	0.981	110.48	0.945		
116.5	0.559	119.65	0.442	116.65	0.983	115.82	0.958		
122.49	0.648	125.32	0.489			121.48	0.959		
127.99	0.763	130.98	0.556			126.98	0.962		
133.99	0.776	136.65	0.604			133.32	0.968		
139.99	0.873	142.32	0.650			139.15	0.973		
145.82	0.932	148.15	0.696			144.49	0.978		
151.49	0.954	153.65	0.742			149.82	0.979		
157.67	0.964	161.15	0.783			155.15	0.981		
163.32	0.969	167 15	0.820			160.65	0.985		
168.83	0.000	173 15	0.853			165.00	0.000		
17/ 82	0.975	178.66	0.881			100.00	0.000		
180 /0	0.079	18/1 32	0.001						
186 92	0.970	104.52	0.303						
100.02	0.30	106 22	0.321						
192.50	0.982	190.32	0.937						
199.00	0.984	201.82	0.950						
205.32	0.985	207.48	0.961						
210.99	0.985	212.99	0.970						
216.49	0.986	218.82	0.976						

Table A1 Berea gray effluent mole fraction of N_2 produced recorded from the GC for the experimental runs

222.16	0.986	230.66	0.979
228.49	0.987	237.15	0.983
236.82	0.988		
242.32	0.990		
248.16	0.994		

 $\label{eq:constraint} \textbf{Table A2} \ Bandera \ gray \ effluent \ mole \ fraction \ of \ N_2 \ produced \ recorded \ from \ the \ GC \ for \ the \ experimental \ runs$

Injection	at 0.2ml	Injection	at 0.4ml	Injection	at 0.6ml	Injection	at 0.8ml	Injection	at 1.0ml
Time	N ₂	Time	N ₂	Time	N ₂	Time	N2	Time	N ₂
(min)	(yN ₂)								
0.16	0.001	0.16	0.001	0.15	0.001	0.17	0.001	0.15	0.001
3.99	0.001	5.49	0.001	3.48	0.001	5.83	0.001	2.48	0.001
9.32	0.001	11.99	0.001	8.82	0.001	11.33	0.001	7.98	0.001
14.66	0.001	18.16	0.001	14.16	0.001	15.49	0.001	13.82	0.001
19.99	0.001	23.49	0.001	19.48	0.001	21.29	0.013	19.32	0.001
25.65	0.001	28.82	0.001	24.82	0.001	26.82	0.153	24.65	0.015
32.48	0.001	34.16	0.001	30.48	0.001	31.99	0.383	29.98	0.029
38.48	0.001	39.66	0.001	35.65	0.054	37.99	0.609	35.32	0.100
43.82	0.001	44.99	0.001	41.16	0.169	43.5	0.79	40.82	0.227
49.16	0.001	50.32	0.001	46.48	0.322	48.82	0.884	46.32	0.378
54.48	0.001	55.82	0.001	51.82	0.491	54.15	0.934	51.66	0.524
59.82	0.001	61.16	0.001	57.15	0.649	59.49	0.96	57.16	0.656
65.15	0.001	66.49	0.001	62.99	0.777	65	0.971	63.98	0.753
70.82	0.001	71.82	0.001	68.32	0.857	70.32	0.977	69.32	0.839
76.32	0.032	77.16	0.018	73.82	0.907	75.66	0.98	74.83	0.884
82.15	0.708	82.49	0.057	79.15	0.937	81.15	0.982	80.15	0.914
87.65	0.957	87.82	0.512	84.65	0.957	86.65	0.984	85.83	0.935
95.15	0.98	93.16	0.845	90.32	0.97	92.5	0.984	91.15	0.95
100.98	0.982	98.66	0.937	95.82	0.976	98	0.985	96.48	0.959
106.32	0.983	103.99	0.963	101.15	0.981	104	0.985	101.82	0.965
112.98	0.983	109.32	0.969	106.65	0.982	109.3	0.986	107.32	0.97
118.82	0.984	114.66	0.97	111.99	0.984			112.65	0.973
								117.98	0.976

0.2ml Injection 0.4	Iml Injection	0.6ml Injection	0.8ml Injection	1 0ml
Table A3 Berea gray CH	4 production in p	pore volumes for a	Ill the experimental	runs

_	Tuble 113 Dereu gruy erit production in pore volumes for un the experimental runs											
	0.2ml Injection		0.4ml Injection		0.6ml Injection		0.8ml Injection		1.0ml Injection			
	Time (min)	CH ₄ Prod	Time (min)	CH ₄ Prod	Time (min)	CH ₄ Prod	Time (min)	CH ₄ Prod	Time (min)	CH ₄ Prod		
	0.16	4.17	0.15	4.48	0.15	7.81	0.15	4.65	0.16	6.61		
	6.33	5.58	6.32	6.14	6.32	12.10	5.98	9.36	6.83	12.31		
	11.99	9.82	12.15	10.72	12.15	18.08	11.32	14.13	12.49	19.20		
	17.49	14.06	18.48	15.40	18.15	22.31	18.65	18.80	18.16	26.37		

23.32	18.34	24.15	20.11	24.48	26.02	24.15	23.24	21.82	33.71
28.82	22.65	32.98	22.00	30.32	29.85	29.48	27.54	29.17	40.51
34.49	27.00	38.65	26.86	35.98	36.89	34.82	31.06	34.49	45.99
40.82	31.06	44.32	31.79	42.15	39.28	40.15	33.29	39.99	47.97
46.66	35.25	50.32	36.75	47.82	40.49	46.98	34.00	45.32	39.49
52.99	39.43	55.82	41.15	53.32	40.15	53.48	33.18	50.66	24.94
58.66	40.80	61.98	45.95	58.82	37.72	58.98	31.11	55.99	11.63
64.32	44.65	67.65	47.01	64.48	34.39	64.32	27.87	61.49	5.45
70.32	48.56	73.32	50.19	69.98	28.65	69.98	23.17	66.83	3.15
76.16	52.32	78.82	52.84	75.65	21.76	75.32	18.40	72.33	1.55
81.99	56.00	84.48	55.05	81.65	15.17	81.15	15.30	77.83	1.12
87.66	59.41	90.32	56.73	87.48	10.02	86.82	11.94	83.32	1.08
93.33	56.82	95.98	57.75	93.15	7.00	92.32	9.56		
99.16	53.64	101.66	58.22	98.65	4.66	98.65	7.91		
104.82	48.54	108.32	58.09	104.32	3.73	103.99	6.80		
110.66	42.91	113.98	57.31	110.32	2.91	110.48	6.02		
116.50	37.09	119.65	55.96	116.65	2.79	115.82	4.87		
122.49	27.98	125.32	54.12			121.48	5.03		
127.99	22.09	130.98	49.55			126.98	4.89		
133.99	21.93	136.65	46.47			133.32	4.29		
139.99	12.82	142.32	43.14			139.15	3.76		
145.82	7.20	148.15	39.26			144.49	3.19		
151.49	5.09	153.65	34.86			149.82	3.17		
157.67	4.08	161.15	30.63			155.15	2.97		
163.32	3.67	167.15	25.53			160.65	2.42		
168.83	3.25	173.15	21.23			165.98	2.00		
174.82	3.06	178.66	17.49						
180.49	2.74	184.32	14.53						
186.82	2.60	190.15	12.04						
192.50	2.42	196.32	9.77						
199.00	2.19	201.82	7.90						

205.32	2.09	207.48	6.28
210.99	2.12	212.99	4.93
216.49	2.01	218.82	4.01
		230.66	3.57
		237.15	2.95

Table A4 Bandera gray CH_4 production in pore volumes for all the experimental runs

0.2ml I	njection	0.4ml	Injection	0.6ml	Injection	0.8ml	Injection	1.0ml	Injection
Time	CH ₄ Prod	Time	CH ₄ Prod	Time	CH ₄ Prod	Time	CH ₄ Prod	Time	CH ₄ Prod
(min)	(PV)	(min)	(PV)	(min)	(PV)	(min)	(PV)	(min)	(PV)
0.16	0.02	0.16	0.02	0.15	0.02	0.17	0.02	0.15	0.02
3.99	0.53	5.49	0.73	3.48	0.46	5.83	0.77	2.48	0.33
9.32	1.24	11.99	1.59	8.82	1.17	11.33	1.51	7.98	1.06
14.66	1.95	18.16	2.41	14.16	1.88	15.49	2.06	13.82	1.84
19.99	2.66	23.49	3.12	19.48	2.59	21.29	2.83	19.32	2.57
25.65	3.41	28.82	3.83	24.82	3.30	26.82	3.56	24.65	3.27
32.48	4.31	34.16	4.54	30.48	4.05	31.99	4.25	29.98	3.98
38.48	5.11	39.66	5.27	35.65	4.73	37.99	5.05	35.32	4.69
43.82	5.82	44.99	5.98	41.16	5.47	43.5	5.78	40.82	5.42
49.16	6.53	50.32	6.68	46.48	6.17	48.82	6.48	46.32	6.15
54.48	7.24	55.82	7.41	51.82	6.88	54.15	7.19	51.66	6.86
59.82	7.94	61.16	8.12	57.15	7.59	59.49	7.90	57.16	7.59
65.15	8.65	66.49	8.83	62.99	8.37	65.00	8.63	63.98	8.50
70.82	9.41	71.82	9.54	68.32	9.07	70.32	9.34	69.32	9.21
76.32	10.14	77.16	10.25	73.82	9.80	75.66	10.05	74.83	9.94
82.15	10.91	82.49	10.95	79.15	10.51	81.15	10.78	80.15	10.64
87.65	11.64	87.82	11.66	84.65	11.24	86.65	11.51	85.83	11.40
95.15	12.64	93.16	12.37	90.32	11.99	92.50	12.28	91.15	12.10
100.98	13.41	98.66	13.10	95.82	12.73	98.00	13.01	96.48	12.81
106.32	14.12	103.99	13.81	101.15	13.43	104.00	13.81	101.82	13.52
112.98	15.00	109.32	14.52	106.65	14.16	109.30	14.52	107.32	14.25
118.82	15.78	114.66	15.23	111.99	14.87			112.65	14.96
								117.98	15.67

Core	Q	u	K∟	D	u/D	K∟/D
Samples	(ml/min)	(10 ⁻⁵ m/s)	(10 ⁻⁸ m²/s)	(10⁻ ⁸ m²/s)	(m ⁻¹)	
Berea gray						
	0.2	3.18	1.47	22.99	138.28	0.100
	0.4	6.36	4.21	22.99	276.56	0.183
	0.6	9.54	5.32	22.99	414.83	0.231
	0.8	12.72	7.84	22.99	553.28	0.341
	1.0	15.90	9.12	22.99	691.61	0.397
Bandera gray						
	0.2	3.38	5.36	22.99	146.15	0.233
	0.4	6.72	7.80	22.99	292.30	0.339
	0.6	10.08	10.10	22.99	438.45	0.439
	0.8	13.44	10.35	22.99	584.60	0.450
	1.0	16.80	13.13	22.99	730.75	0.571

Table A5 Dispersion coefficients of N2-CH4 as functions of concentration profiles

Table A6 Flow properties and cumulative CO₂ storage of the experimental run at 0.2 ml/min

Time (min)	Qs (cm ³)	Qx (cm ³)	Cum Vol. (cm ³)	yCO ₂	CO ₂ out (cm ³)	CO ₂ in (cm ³)	CO ₂ stored (cm ³)
0.16	112	1.258	1.2583	0.0001	0.0001	0.032	0.0319
6.49	199	2.236	3.4941	0.0001	0.0003	1.298	1.2977
12.49	198	2.225	5.7186	0.0001	0.0006	2.498	2.4974
18.32	199	2.236	7.9544	0.0001	0.0008	3.664	3.6632
24.49	225	2.528	10.482	0.0001	0.0010	4.898	4.8970
30.33	204	2.292	12.774	0.0001	0.0013	6.066	6.0647
36.49	205	2.303	15.077	0.0001	0.0015	7.298	7.2965
42.99	261	2.932	18.010	0.0001	0.0018	8.598	8.5962
49.16	102	1.146	19.156	0.0001	0.0019	9.832	9.8301
54.99	209	2.348	21.504	0.0001	0.0022	10.998	10.996
60.83	213	2.393	23.897	0.0001	0.0024	12.166	12.164
67.16	207	2.326	26.222	0.0001	0.0026	13.432	13.429
73.16	213	2.393	28.616	0.0001	0.0029	14.632	14.629
79.16	216	2.427	31.042	0.0001	0.0031	15.832	15.829
84.99	216	2.427	33.469	0.0001	0.0033	16.998	16.995
90.83	376	4.224	37.693	0.0001	0.0038	18.166	18.162
96.83	223	2.505	40.199	0.0001	0.0040	19.366	19.362
102.99	241	2.708	42.906	0.0001	0.0043	20.598	20.594

108.83	240	2.696	45.603	0.0001	0.0046	21.766	21.761
114.66	257	2.887	48.490	0.0001	0.0048	22.932	22.927
120.49	238	2.674	51.164	0.0001	0.0051	24.098	24.093
126.66	235	2.640	53.804	0.0001	0.0054	25.332	25.327
132.66	272	3.056	56.860	0.0001	0.0057	26.532	26.526
138.49	257	2.887	59.748	0.0001	0.0060	27.698	27.692
144.33	377	4.236	63.983	0.0001	0.0064	28.866	28.860
150.83	379	4.258	68.241	0.0001	0.0068	30.166	30.159
157.16	114	1.281	69.522	0.0026	0.0101	31.432	31.422
162.99	344	3.865	73.387	0.0026	0.0203	32.598	32.578
168.66	345	3.876	77.263	0.0027	0.0307	33.732	33.701
174.66	116	1.303	78.566	0.0028	0.0343	34.932	34.898
180.99	351	3.943	82.510	0.0029	0.0458	36.198	36.152
187.16	351	3.943	86.453	0.0031	0.0578	37.432	37.374
192.99	358	4.022	90.475	0.0031	0.0704	38.598	38.528
198.99	358	4.022	94.498	0.0033	0.0834	39.798	39.715
204.82	359	4.033	98.531	0.0034	0.0972	40.964	40.867
210.83	361	4.056	102.59	0.0036	0.1119	42.166	42.054
217.16	74	0.831	103.42	0.0042	0.1154	43.432	43.317
222.83	369	4.146	107.56	0.0058	0.1393	44.566	44.427
228.66	370	4.157	111.72	0.0091	0.1771	45.732	45.555
234.49	372	4.179	115.90	0.0157	0.2428	46.898	46.655
240.33	365	4.101	120.00	0.027	0.3535	48.066	47.712
246.33	84	0.944	120.94	0.0447	0.3957	49.266	48.870
252.32	369	4.146	125.09	0.0705	0.6878	50.464	49.776
258.16	364	4.09	129.18	0.1025	1.1069	51.632	50.525
263.99	96	1.079	130.26	0.1419	1.2600	52.798	51.538
270.16	358	4.022	134.28	0.1891	2.0207	54.032	52.011
275.99	352	3.955	138.24	0.2402	2.9708	55.198	52.227
281.99	355	3.988	142.22	0.2964	4.153	56.398	52.245

287.99	324	3.64	145.86	0.3543	5.4427	57.598	52.155
293.99	297	3.337	149.20	0.4132	6.8214	58.798	51.977
299.82	310	3.483	152.68	0.4667	8.4469	59.964	51.517
305.66	226	2.539	155.22	0.5162	9.7576	61.132	51.374
311.49	249	2.798	158.02	0.5622	11.33	62.298	50.968
317.49	311	3.494	161.51	0.6054	13.446	63.498	50.052
335.66	268	3.011	164.53	0.7072	15.575	67.132	51.557
342.66	272	3.056	167.58	0.8039	18.032	68.532	50.500
348.99	275	3.09	170.67	0.8253	20.582	69.798	49.216
354.83	285	3.202	173.87	0.9646	23.670	70.966	47.296
360.49	284	3.191	177.06	0.9788	26.793	72.098	45.305
366.99	235	2.64	179.70	0.9888	29.404	73.398	43.994

Table A7 Flow properties and cumulative CO_2 storage of the experimental run at 0.4 ml/min

Time (min)	Qs (cm ³)	Qx (cm ³)	Cum Vol. (cm ³)	yCO ₂	CO ₂ out (cm ³)	CO ₂ in (cm ³)	CO ₂ stored (cm ³)
0.15	333	3.741	3.7413	0.0001	0.0004	0.06	0.0596
6.46	330	3.708	7.4488	0.0001	0.0007	2.584	2.5833
10.49	334	3.752	11.201	0.0001	0.0011	4.196	4.1949
16.48	333	3.741	14.943	0.0001	0.0015	6.592	6.5905
22.16	343	3.854	18.796	0.0001	0.0019	8.864	8.8621
27.99	350	3.932	22.728	0.0001	0.0023	11.196	11.194
33.83	352	3.955	26.683	0.0001	0.0027	13.532	13.529
39.99	356	4.000	30.683	0.0001	0.0031	15.996	15.993
45.66	358	4.022	34.705	0.0001	0.0035	18.264	18.261
51.65	363	4.078	38.783	0.0001	0.0039	20.660	20.656
57.66	367	4.123	42.906	0.0001	0.0043	23.064	23.060
63.32	376	4.224	47.131	0.00061	0.0069	25.328	25.321
69.15	136	1.528	48.659	0.00071	0.0080	27.66	27.652
75.32	302	3.393	52.052	0.00086	0.0109	30.128	30.117

80.98	332	3.730	55.782	0.00096	0.0145	32.392	32.378
86.82	403	4.528	60.309	0.00098	0.0189	34.728	34.709
92.98	428	4.809	65.118	0.00098	0.0236	37.192	37.168
99.15	400	4.494	69.612	0.00098	0.0280	39.660	39.632
105.48	399	4.483	74.095	0.00099	0.0324	42.192	42.160
111.82	86	0.966	75.061	0.00099	0.0334	44.728	44.695
117.48	420	4.719	79.780	0.00099	0.0381	46.992	46.954
123.32	454	5.101	84.880	0.00099	0.0431	49.328	49.285
129.15	441	4.955	89.835	0.00117	0.0489	51.66	51.611
134.82	442	4.966	94.801	0.01628	0.1298	53.928	53.798
140.65	402	4.516	99.317	0.12502	0.6944	56.26	55.566
146.48	139	1.562	100.88	0.40024	1.3195	58.592	57.273
152.32	327	3.674	104.55	0.65576	3.7286	60.928	57.199
157.99	304	3.415	107.97	0.78445	6.4079	63.196	56.788
163.98	309	3.472	111.44	0.84820	9.3525	65.592	56.240
169.65	315	3.539	114.98	0.88200	12.474	67.860	55.386
175.48	405	4.550	119.53	0.90365	16.586	70.192	53.606
181.32	417	4.685	124.21	0.92952	20.94	72.528	51.588
187.48	147	1.652	125.87	0.95933	22.525	74.992	52.467
193.82	394	4.427	130.29	0.97322	26.833	77.528	50.695
205.48	394	4.427	134.72	0.97519	31.15	82.192	51.042
211.32	135	1.517	136.24	0.97440	32.628	84.528	51.900
218.98	139	1.562	137.8	0.97856	34.156	87.592	53.436
228.83	384	4.314	142.11	0.99296	38.44	91.532	53.092

 Table A8 Flow properties and cumulative CO2 storage of the experimental run at 0.6 ml/min

Time	Qs	Qx	Cum Vol.	yCO ₂	CO ₂ out	CO ₂ in	CO ₂ stored
(min)	(cm ³)	(cm ³)	(cm ³)		(cm ³)	(cm ³)	(cm ³)
0.16	285	3.202	3.202	0.0001	0.0003	0.096	0.0957

7.99	217	2.438	5.640	0.0001	0.0006	4.794	4.7934
14.66	224	2.517	8.157	0.0001	0.0008	8.796	8.7952
20.32	228	2.562	10.718	0.0023	0.0066	12.192	12.185
27.66	249	2.798	13.516	0.0023	0.0129	16.596	16.583
33.49	310	3.483	16.999	0.0029	0.0229	20.094	20.071
39.32	290	3.258	20.257	0.0031	0.0331	23.592	23.559
44.99	144	1.618	21.875	0.0032	0.0382	26.994	26.956
50.82	135	1.517	23.391	0.0032	0.0431	30.492	30.449
56.66	186	2.090	25.481	0.0033	0.0499	33.996	33.946
62.32	190	2.135	27.616	0.0033	0.0571	37.392	37.335
67.99	472	5.303	32.919	0.2369	1.3135	40.794	39.481
73.83	166	1.865	34.784	0.7533	2.7184	44.298	41.580
80.49	168	1.887	36.671	0.9365	4.4861	48.294	43.808
86.82	205	2.303	38.974	0.9728	6.7266	52.092	45.365
92.66	25	0.281	39.255	0.9912	7.0050	55.596	48.591

Table A9 Flow properties and cumulative CO₂ storage of the experimental run at 0.8 ml/min

Time (min)	Qs (cm ³)	Qx (cm ³)	Cum Vol. (cm ³)	yCO ₂	CO ₂ out (cm ³)	CO ₂ in (cm ³)	CO ₂ stored (cm ³)
0.15	337	3.786	3.786	0.0001	0.0004	0.12	0.1196
6.48	355	3.988	7.775	0.0001	0.0008	5.184	5.1832
12.82	72	0.809	8.584	0.0022	0.0026	10.256	10.253
18.82	383	4.303	12.887	0.0026	0.0136	15.056	15.042
24.82	112	1.258	14.145	0.0026	0.0169	19.856	19.839
30.82	387	4.348	18.493	0.003	0.0299	24.656	24.626
36.48	384	4.314	22.807	0.003	0.0429	29.184	29.141
42.82	361	4.056	26.863	0.003	0.0552	34.256	34.201
48.65	390	4.382	31.245	0.0031	0.0686	38.92	38.851
54.48	120	1.348	32.593	0.0031	0.0727	43.584	43.511
60.32	394	4.427	37.019	0.0032	0.0869	48.256	48.169

66.15	364	4.090	41.109	0.0032	0.1001	52.92	52.820
72.48	453	5.089	46.1983	0.0036	0.1182	57.984	57.866
78.32	559	6.280	52.479	0.0037	0.1413	62.656	62.515
84.48	167	1.876	54.355	0.3149	0.7321	67.584	66.852
90.48	147	1.652	56.007	0.8468	2.1306	72.384	70.253
96.32	407	4.573	60.579	0.9434	6.4446	77.056	70.611
102.32	461	5.179	65.759	0.9724	11.481	81.856	70.375
108.32	173	1.944	67.702	0.9784	13.382	86.656	73.274
113.98	198	2.225	69.927	0.9809	15.564	91.184	75.620

Table A10 Flow properties and cumulative CO₂ storage of the experimental run at 1.0 ml/min

Time (min)	Qs	Qx	Cum Vol.	yCO ₂	$CO_2 \text{ out}$	CO_2 in (cm^3)	CO ₂ stored
(IIIII)	(cm)	(cm)	(cm)		(cm)	(cm)	(cm)
0.16	144	1.618	1.6178	0.0001	0.0002	0.16	0.1598
7.50	174	1.955	3.5727	0.0001	0.0004	7.50	7.4996
13.32	132	1.483	5.0558	0.0001	0.0005	13.32	13.319
18.99	201	2.258	7.314	0.0006	0.0018	18.99	18.988
24.99	154	1.730	9.0442	0.0006	0.0028	24.99	24.987
30.66	154	1.730	10.774	0.0006	0.0038	30.66	30.656
36.49	173	1.944	12.718	0.0006	0.005	36.49	36.485
42.16	334	3.752	16.471	0.0007	0.0075	42.16	42.153
47.82	97	1.090	17.56	0.0007	0.0082	47.82	47.812
53.49	390	4.382	21.942	0.0007	0.0113	53.49	53.479
61.33	582	6.539	28.481	0.0012	0.0191	61.33	61.311
66.99	602	6.763	35.244	0.217	1.4869	66.99	65.503
72.82	148	1.663	36.907	0.8871	2.9619	72.82	69.858
78.66	205	2.303	39.21	0.9654	5.1854	78.66	73.475
84.66	214	2.404	41.614	0.9743	7.5280	84.66	77.132
90.49	209	2.348	43.963	0.9764	9.8206	90.49	80.669

96.16	195	2.191	46.153	0.9782	11.964	96.16	84.196	
101.99	548	6.157	52.310	0.979	17.991	101.99	83.999	
107.82	198	2.225	54.535	0.9796	20.170	107.82	87.650	
113.49	607	6.820	61.354	0.9804	26.856	113.49	86.634	

Table A11 Dispersion coefficient determination for different CO₂ injection

Q	Pressure	Temperature	Interstitial Velocity	Lambda Constants	Dispersion Coefficient	Diffusion Coefficient
(ml/min)	(psig)	(⁰ C)	(10⁻⁵ m/s)	(λ90/λ10)	(10 ⁻⁸ m ² /s)	(10 ⁻⁸ m ² /s)
0.2	1500	40	3.36	2.6872/2.0472	2.64	18.48
0.4	1500	40	6.72	2.2876/1.7676	3.49	18.48
0.6	1500	40	10.08	1.9313/1.3713	6.06	18.48
0.8	1500	40	13.44	1.9990/1.4550	7.63	18.48
1.0	1500	40	16.80	1.9336/13496	10.99	18.48

Table A12 Dispersion coefficient determination for different N_2 injection rates

ure Interstitial Velocity	Lambda Constants	Dispersion Coefficient	Diffusion Coefficient
(10^{-5} m/s)	$(\lambda_{90}/\lambda_{10})$	$(10^{-8} \text{ m}^2/\text{s})$	$(10^{-8} \text{ m}^2/\text{s})$
3.36	1.9749/1.0629	5.36	22.99
6.72	2.0323/1.4803	7.80	22.99
10.08	1.9700/1.4099	10.10	22.99
13.44	1.8230/0.9270	10.35	22.99
16.80	1.9414/1.1174	13.13	22.99
-	Interstitial Velocity (10 ⁻⁵ m/s) 3.36 6.72 10.08 13.44 16.80	tureInterstitial Velocity (10^{-5} m/s) Lambda Constants $(\lambda_{90}/\lambda_{10})$ 3.361.9749/1.06296.722.0323/1.480310.081.9700/1.409913.441.8230/0.927016.801.9414/1.1174	ureInterstitial VelocityLambda ConstantsDispersion Coefficient (10^{-5} m/s) $(\lambda_{90}/\lambda_{10})$ $(10^{-8} \text{ m}^2/\text{s})$ 3.36 $1.9749/1.0629$ 5.36 6.72 $2.0323/1.4803$ 7.80 10.08 $1.9700/1.4099$ 10.10 13.44 $1.8230/0.9270$ 10.35 16.80 $1.9414/1.1174$ 13.13

Table A13 Core flooding effluent composition by N2 alternating CO2 injection at 5min intervals

Booster Volume (0%)		Booster Volume (6%)		Booster Volume (13%)		Booster Volume (19%)		Booster Volume (29%)	
Time (min)	Conc. (Vol.%)	Time (min)	Conc. (Vol.%)	Time (min)	Conc. (Vol.%)	Time (min)	Conc. (Vol.%)	Time (min)	Conc. (Vol.%)
0.15	0.096	0.16	0.449	0.15	0.069	0.15	0.205	0.15	0.200
6.46	0.098	5.98	0.465	5.98	0.067	5.82	0.205	5.82	0.192
10.49	0.092	11.49	0.482	11.98	0.064	11.32	0.205	12.48	0.19
16.48	0.095	17.32	0.501	17.65	0.063	17.65	0.204	17.98	0.186
22.16	0.093	22.65	0.485	22.98	0.061	23.15	0.193	23.48	0.181
27.99	0.089	28.15	0.560	28.65	0.059	28.65	0.197	28.82	0.180
33.83	0.085	33.98	0.587	34.15	0.057	33.98	0.199	34.48	0.177
39.99	0.084	39.65	0.614	39.65	0.056	39.32	0.200	40.48	0.174
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45.66	0.082	45.15	0.501	45.32	0.067	44.82	0.200	45.98	0.171
51.65	0.091	50.48	0.421	50.82	0.060	50.32	0.197	51.32	0.167
57.66	0.092	55.98	0.510	56.15	0.058	55.82	0.191	56.82	0.164
63.32	0.093	61.65	0.615	61.65	0.057	60.98	0.186	62.32	0.160
69.15	0.095	67.15	0.674	67.15	0.056	66.48	0.185	67.65	0.156
75.32	0.095	72.82	0.710	72.48	0.056	71.98	0.179	72.98	0.151
80.98	0.096	78.32	0.739	77.82	0.053	77.48	0.173	78.48	0.143
86.82	0.098	83.98	0.764	83.32	0.052	82.82	0.169	83.98	0.141
92.98	0.099	89.65	0.790	88.65	0.051	88.62	0.169	89.32	0.136
99.15	0.099	95.65	0.819	94.15	0.049	93.98	0.162	94.98	0.149
105.48	0.098	101.15	0.841	99.48	0.048	99.82	0.162	100.65	0.143
111.82	0.086	106.65	0.856	104.98	0.046	105.32	0.164	105.98	0.138
117.48	0.071	112.15	0.856	110.32	0.044	110.65	0.157	111.48	0.134
123.32	0.061	117.82	0.824	115.82	0.042	116.15	0.142	116.82	0.135
129.15	0.117	123.32	0.757	121.65	0.04	121.48	0.131	122.32	0.128
134.82	1.628	128.98	1.166	126.98	0.038	127.65	0.118	127.82	0.125
140.65	12.502	134.48	7.107	132.65	0.034	132.98	0.137	133.15	0.122
146.48	40.024	140.15	27.371	137.98	0.03	138.32	0.387	138.48	0.115
152.32	65.576	145.82	56.115	143.48	0.025	144.65	1.141	143.98	0.108
157.99	78.445	151.32	75.681	148.98	0.018	150.15	3.269	149.65	0.099
163.98	84.82	156.98	87.422	154.48	0.018	155.48	21.793	154.98	0.0085
169.65	88.2	162.65	94.339	159.82	2.145	161.15	60.864	160.66	0.071
175.48	90.365	168.32	96.827	165.15	26.814	166.65	82.816	166.15	0.055
181.32	92.952	173.98	98.946	170.65	72.473	172.15	91.405	171.65	0.047
187.48	95.933	180.32	99.226	175.98	90.375	177.48	94.774	177.15	3.406
193.82	97.322	186.15	99.317	181.48	96.228	183.15	96.533	182.98	60.648
205.48	97.519			186.82	98.66	188.65	97.503	188.48	88.588
211.32	97.44			192.15	99.152	194.32	97.995	193.82	97.136
218.98	97.856					199.82	98.154	199.32	98.501

228.83	98.122	205.32	98.247	204.65	99.045
		211.15	98.378	209.98	99.237
		217.48	98.533		

Time Qs Qx yCO₂ **CO₂ Produced** (cm^3) (min) (cm^3) (cm^3) 0.16 352 3.9547 0.0045 0.0178 5.98 385 4.3255 0.0042 0.036 11.49 352 3.9547 0.0047 0.0544 17.32 4.2244 0.0747 376 0.004822.65 426 4.7861 0.0049 0.0979 28.15 379 4.2581 0.005 0.1193 33.98 388 4.3592 0.005 0.1411 39.65 388 4.3592 0.0051 0.1633 45.15 430 4.8311 0.0056 0.1904 50.48 368 4.1345 0.0059 0.2147 4.303 55.98 383 0.0061 0.2411 61.65 396 4.4491 0.0062 0.2684 67.15 358 4.0221 0.0067 0.2955 72.82 4.1907 0.0071 373 0.3253 78.32 3.7862 0.0074 337 0.3533 83.98 401 4.5052 0.0076 0.3877 89.65 0.0079 0.4202 366 4.112 95.65 0.0082 358 4.0221 0.4531 101.15 4.3929 0.0084 0.4901 391 106.65 4.3592 0.0086 388 0.5274 112.15 421 4.7299 0.0086 0.5679 117.82 0.0086 407 4.5726 0.6071 123.32 462 5.1906 0.0088 0.6525 128.98 448 5.0333 0.0117 0.7112 134.48 415 4.6625 0.0711 1.0426

Table A14 Flow properties and cumulative CO_2 produced at 6%

140.15	103	1.1572	0.2737	1.3593
145.82	375	4.2131	0.5612	3.7235
151.32	364	4.0895	0.7568	6.8185
156.98	394	4.4266	0.8742	10.688
162.65	432	4.8535	0.9434	15.2670
168.32	440	4.9434	0.9683	20.0540
173.98	529	5.9433	0.9895	25.2840

Table A15 Flow properties and cumulative CO_2 produced at 13%

Time	Qs	Qx	yCO ₂	CO ₂ Produced
(min)	(cm ³)	(cm ³)		(cm ³)
0.15	115	1.292	0.0002	0.0002
5.98	370	4.157	0.0002	0.0010
11.98	372	4.179	0.0003	0.0020
17.65	371	4.168	0.0003	0.0033
22.98	123	1.382	0.0003	0.0037
28.65	114	1.281	0.0004	0.0042
34.15	132	1.483	0.0004	0.0048
39.65	384	4.314	0.0004	0.0066
45.32	113	1.27	0.0004	0.0072
50.82	117	1.314	0.0005	0.0078
56.15	112	1.258	0.0005	0.0084
61.65	126	1.416	0.0005	0.0091
67.15	125	1.404	0.0005	0.0098
72.48	136	1.528	0.0005	0.0106
77.82	378	4.247	0.0005	0.0129
83.32	382	4.292	0.0006	0.0153
88.65	344	3.865	0.0006	0.0174
94.15	349	3.921	0.0006	0.0197
99.48	352	3.955	0.0006	0.0219
104.98	357	4.011	0.0006	0.0242
110.32	104	1.168	0.0006	0.0249
115.82	371	4.168	0.0006	0.0274
121.65	124	1.393	0.0006	0.0283
126.98	152	1.708	0.0006	0.0294
132.65	399	4.483	0.0006	0.0322
137.98	165	1.854	0.0007	0.0335
143.48	184	2.067	0.0007	0.0349
148.98	174	1.955	0.0007	0.0362
154.48	183	2.056	0.0007	0.0376

159.82	191	2.146	0.0215	0.0837
165.15	153	1.719	0.2681	0.5446
170.65	408	4.584	0.7247	3.8667
175.98	411	4.618	0.9038	8.0398
181.48	226	2.539	0.9623	10.483
186.82	222	2.494	0.9866	12.944
192.15	550	6.179	0.9915	19.071

Table A16: Flow properties and cumulative CO₂ produced at 19%

Time (min)	Qs	Qx	yCO ₂	CO ₂ Produced
0.15	407	(CIII) 4 573	0.0012	0.0054
5.82	407	4.575	0.0012	0.0034
J.82	404	4.339	0.0015	0.0115
11.52	132	1.485	0.0014	0.0157
17.65	143	1.607	0.0014	0.0157
23.15	126	1.416	0.0016	0.0179
28.65	414	4.651	0.0016	0.0254
33.98	413	4.64	0.0016	0.0329
39.32	140	1.573	0.0016	0.0355
44.82	134	1.505	0.0017	0.0381
50.32	141	1.584	0.0017	0.0407
55.82	148	1.663	0.0017	0.0436
60.98	303	3.404	0.0018	0.0497
66.48	409	4.595	0.0019	0.0582
71.98	436	4.898	0.0019	0.0673
77.48	414	4.651	0.0019	0.0762
82.82	416	4.674	0.0019	0.0852
88.62	417	4.685	0.002	0.0944
93.98	398	4.472	0.002	0.1033
99.82	418	4.696	0.002	0.1126
105.32	136	1.528	0.002	0.1157
110.65	435	4.887	0.002	0.1254
116.15	459	5.157	0.002	0.136
121.48	452	5.078	0.0021	0.1464
127.65	172	1.932	0.0021	0.1503
132.98	158	1.775	0.0021	0.154
138.32	142	1.595	0.0039	0.1601
144.65	410	4.606	0.0114	0.2127
150.15	363	4.078	0.0327	0.346
155.48	339	3.809	0.2179	1.176
161.15	358	4.022	0.6086	3.6241
166.65	352	3.955	0.8282	6.8992
172.15	353	3.966	0.9141	10.524

177.48	163	1.831	0.9477	12.26
183.15	160	1.798	0.9653	13.995
188.65	178	2	0.975	15.945
194.32	173	1.944	0.98	17.85
199.82	148	1.663	0.9815	19.482
205.32	376	4.224	0.9825	23.632
211.15	381	4.281	0.9838	27.843
217.48	384	4.314	0.9853	32.094

Table A17 Flow properties and cumulative CO_2 produced at 29%

Time (min)	Qs (cm ³)	Qx (cm ³)	yCO ₂	CO ₂ Produced (cm ³)
0.15	130	1.461	0.0005	0.0007
5.82	128	1.438	0.0006	0.0015
12.48	133	1.494	0.0007	0.0025
17.98	144	1.618	0.0009	0.0039
23.48	147	1.652	0.001	0.0055
28.82	149	1.674	0.0011	0.0074
34.48	153	1.719	0.0012	0.0093
40.48	138	1.55	0.0012	0.0112
45.98	142	1.595	0.0013	0.0132
51.32	117	1.314	0.0013	0.0149
56.82	122	1.371	0.0013	0.0167
62.32	122	1.371	0.0014	0.0186
67.65	123	1.382	0.0014	0.0205
72.98	131	1.472	0.0014	0.0225
78.48	139	1.562	0.0014	0.0247
83.98	134	1.505	0.0014	0.0269
89.32	422	4.741	0.0014	0.0336
94.98	113	1.27	0.0015	0.0355
100.65	120	1.348	0.0015	0.0376
105.98	132	1.483	0.0016	0.0399
111.48	156	1.753	0.0016	0.0427

116.82	130	1.461	0.0016	0.0451
122.32	132	1.483	0.0017	0.0476
127.82	129	1.449	0.0017	0.05
133.15	388	4.359	0.0017	0.0576
138.48	380	4.269	0.0018	0.0652
143.98	132	1.483	0.0018	0.0678
149.65	130	1.461	0.0018	0.0705
154.98	133	1.494	0.0019	0.0733
160.66	136	1.528	0.0019	0.0762
166.15	138	1.55	0.0019	0.0791
171.65	121	1.359	0.002	0.0819
177.15	342	3.842	0.0341	0.2127
182.98	393	4.415	0.6065	2.8906
188.48	149	1.674	0.8859	4.3735
193.82	519	5.831	0.9714	10.038
199.32	537	6.033	0.985	15.98

Appendix B: Resource Figures



Figure B1 Effluent N_2 and CH_4 composition recorded from the GC as a function of displacement time for Bandera grey



Figure B2 Effluent N_2 and CH_4 composition recorded from the GC as a function of displacement time for Berea grey



Figure B3 Effluent concentration as a function of pore volumes injected observed during a core flooding experiment with N_2 and CH_4 as displacing and displaced gases at the rate of 0.6ml/min

Appendix C: GC output at 5min sequence for CO₂ injection and booster volumes



Figure C1 0.15min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C2 5.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C3 11.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C4 17.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C5 22.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C6 28.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C7 34.15min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C8 39.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C9 45.32min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C10 50.82min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C11 56.15min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C12 61.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C13 67.15min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C14 72.48min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C15 77.82min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C16 83.32min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C17 88.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C18 94.15min GC output for CO_2 injection at 0.4ml/min and 6% booster



Figure C19 99.48min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C20 104.98min GC output for CO2 injection at 0.4ml/min and 6% booster



Figure C21 110.32min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C22 115.82min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C23 121.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C24 126.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C25 132.65min GC output for CO_2 injection at 0.4ml/min and 6% booster



Figure C26 137.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C27 143.48min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C28 148.98min GC output for CO_2 injection at 0.4ml/min and 6% booster



Figure C29 154.48min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C30 159.82min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C31 165.15min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C32 170.65min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C33 175.98min GC output for CO₂ injection at 0.4ml/min and 6% booster



Figure C34 181.48min GC output for CO_2 injection at 0.4ml/min and 6% booster



Figure C35 186.82min GC output for CO2 injection at 0.4ml/min and 6% booster



Figure C36 192.15min GC output for CO_2 injection at 0.4ml/min and 6% booster

Appendix D: Journals and Conferences

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Investigating the flow behaviour of CO2 and N2 in porous medium using core flooding experiment



Nuhu Mohammed^{a,*}, Abubakar J. Abbas^a, Godpower C. Enyi^a, Muhammad Kabir Abba^a, Onukak Imeh Etim^b, Bello Saidu^a, Salihu M. Suleiman^a, Hassan Kabiru Yar'adua^a

⁸ Department of Petroleum and Gas Engineering, University of Salford Manchester, M4 5WT, United Kingdom
^b Department of Research and Development, Nigerian Institute of Leather and Science Technology, Kaduna-Zaria, Nigeria

ARTICLEINFO	ABSTRACT
Keywords: Diffusion coefficient Pore volume OC ₂ sequestration Mixing Dispersion coefficient	Several researchers employed N ₂ to augment CH4 recovery efficiency and CO ₂ sequestration during the Enhanced Gas Recovery (EGR) process in consolidated rocks. To our knowledge, there has been limited data backing the reason why CO ₂ experienced a more extended breakthrough during the EOR process in the presence of N ₂ gas. This study investigated CO ₂ and N ₂ behaviour during the core flooding experiment by CO ₂ injection in Ben- theimer core plug. N ₂ was used as the continuous phase during the core flooding process, while CO ₂ was the dispersed phase. The experiment was designed with varying injection rates at 30 and 40 °C temperature points. The experimental findings showed that the dispersion and diffusion coefficient, CO ₂ atorage, concentration profile and breakthroughs were highly influenced by temperature change, especially at lower injection rates. However, at high injections, those properties are less sensitive to change in temperature, with most of the curves overlapping in the concentration profile. The highest and most negligible dispersion and diffusion coefficients were recorded at the highest and lowest injection rates respectively. These results agree with those reported by several researchers for sandstone rocka. Thus, higher temperatures have a more substantial effect on dispersion and diffusion coefficient, which eventually led to higher mixing between CO ₂ and N ₂ . The breakthrough time decreases with an increase in reservoir temperature, confirming the diffusion and dispersion coefficients are temperature dependent. The experiment at 30 °C recorded an extended breakthrough time over that at 40 °C. The maximum breakthrough time at 0.52 PV was recorded at 30 °C at the lowest injection rate. The concen- tration profile highlighted the trend between the displacing and displaced gas during the core flooding experi- ment. From the range of injections and temperatures tested, the CO ₂ PV stored decreases as the rate of injection increases from 0.4 to 1. 2m/min. However, the CO ₂ s

1. Introduction

Gas transport in porous media occurs in different applications, including catalytic converters, fuel cells, oil and gas exploration, carbons storage, and the food processing industry, to mention a few (Abba et al., 2018). More so, to design and optimize a specific process that involves the transport of gases in porous media, there is a need to thoroughly understand the interplay mechanism for such gas as they meet each other. This gas transport is based on various empirical models developed to optimize and evaluate the design and performance of the processes (Abba et al., 2018). This research emphasized more on gas transport as against vapour transport unless otherwise stated therein. The best way

to separate gas from vapour was based on their physical states at the standard condition of temperature and pressure of 20 °C and 1 bar, respectively, (Molly and Mark, 2006). The analytical conditions of CO2, N2 and CH4, are 31.05 and 73.80, -146.9 and 33.90, 82.55 °C and 46 bars for temperature and pressure respectively. Although this can only be applied if the gas components remain liquid at normal temperature and pressure, such fluid is considered a vapour or condensate. However, if the gas components remain as gaseous and not condensable at standard temperature and pressure, such fluid is regarded as a gas. This distinct phenomenon is essential as it provides a clear understanding of the two primary transport mechanisms affecting the flow behaviour of gases and vapours through the porous media. These factors are diffusion

* Corresponding author.

E-mail address: n.mohammed5@edu.salford.ac.uk (N. Mohammed).

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and dispersion processes with more focus on the dispersion dominant porous media transport mechanism, being critical in determining the extent of CO_2 or N_2 with the nascent CH_4 during the EGR process by gas alternating gas injection.

Thus, in turn, to successfully optimize and reduce the overhead cost of exploring residual natural gas during the EGR process, the mode of displacing gases needs to be comprehensively investigated in other to avoid premature mixing. Such premature mixing primarily arises from several core sample property parameters. These are longitudinal dispersion coefficient, mobility ratio, porosity, permeability, dispersivity, viscous fingering, gravity, flow velocity, diffusion coefficient, and the likes. The viscosity ratio measures mobility. This is similar to the case of supercritical carbon dioxide displacing methane. The CO₂ is denser than either N₂ or CH₄ at conditions relevant to the EGR process, i. e. $\frac{\mu CH_4}{\mu CO_2} < 1$.

The flow mechanism of supercritical carbon dioxide as it moves transverses the pore sizes of the Bentheimer core plug to displace the continuous natural phase is quite complicated, particularly in the presence of nitrogen as booster gas. Studying such a complex phenomenon is vital to understanding the patterns and expected outputs of the displacement process. These gases mostly exhibit liquid density while still retaining the gas viscosity at their supercritical state.

Several researchers have studied the dispersion and diffusion mechanism during the EGR process in a porous medium. For example, in (1988), Newberg used an explicit variety of sandstone plugs to measured the CH4 and N2 scale of mixing. The experiment was conducted at varying flow velocities of 0.02-0.3 mm/s and 34.5-68.9 bars of pressure. In addition, an enhanced gas recovery by CO2 flooding in dry carbonate sandstone plugs was investigated (Seo, 2004; Seo and Mamora, 2005). The distribution of CH4 and CO2 molecules at the breakthrough time was examined using Computed Tomography (CT). The dispersion coefficient was also measured, and 73–87% CH4 recovery was recorded. Furthermore, Hughes et al. (2012) studied the reaction of different CH4 and CO2 longitudinal dispersion coefficient elements using consolidated sandstones. The experiment was carried out under a wide range of permeabilities. A lower displacement velocity in the horizontal direction shows a significant gravitational effect on the rocks with higher permeability. At the same time, the dispersion coefficient was 63% more than the nascent value due to the gravitational effect. More so, Abba et al. (2018), at 95 bars and 40 °C of pressure and temperature, studied the impact of connate-water salinity on the Berea grey core dispersion mechanism.

The novelty of this work was the use of inert N₂ gas as external support for simultaneous CH₄ recovery and CO₂ storage improvement. The experimental results have proven that N₂ can be used as third-party gas to improve natural gas recovery and CO₂ storage during the EGR process. However, the mechanism behind such improvement is limited, which was this study focus solely to investigate that effect. Furthermore, to our knowledge, there have been limited data backing the EGR process in the presence of N₂ gas using consolidated sandstone rocks. Therefore, this study is designed to establish why CO₂ experience a more extended breakthrough during the EGR process is booster gas.

To date, there are limited experimental data on how the displacing and displaced fluids interact during the core flooding displacement process. This paper investigates CO_2 and N_2 behaviour during core flooding experiments by CO_2 injection in a *Bentheimer* core plug. N_2 was used as the continuous phase (saturating fluid) during the core flooding process, while CO_2 was the dispersed phase (displacing). This study was primarily designed to establish why CO_2 experiences a more extended breakthrough time during Enhanced Gas Recovery (EGR) process (Mohammed et al., 2021) with N_2 as the displaced gas. The experiment was designed with varying injection rates at 30 and 40 °C temperature points. Thus, for this study, the operation conditions are at average normal reservoir pressure of 0.1 bar/m gradients, 1000 m depth, and 30-40 °C/1000 m temperature gradient, which is well above each single gas species criticality.

2. Advection vs diffusion

Transport systems in the environment may be classified into two types. These are advection and diffusion. Advection refers to movement with the mean fluid flow. In contrast, diffusion assigns to the bulk transfer of compounds through the means of random motions. In addition, diffusion isolates sharp discontinuities in concentration and results in smoother, flatter, and precise concentration profiles (Pages.mtu.edu, 2021).

In this paper, Eqs. (1)-(8) was developed to model and evaluate the dispersion driving mechanism. These fundamental equations were originated based on several works of literature as outlined by (Abba et al., 2017, 2018, 2019; Takahashi and Iwaaaki, 1970; Fuller et al., 1965; Newberg and Foh, 1968; Hughes et al., 2012; Mamora and Seo, 2002; Liu et al., 2015; Perkins and Johnston, 1963; Coats et al., 2009; Honari et al., 2013). More information can be obtained in our initial publications (Mohammed et al., 2019, 2020).

$$K_{L}\frac{\partial^{2}C}{\partial x^{2}} - u\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
(1)

Also, Eq. (1) was further simplified into a dimensionless form, presented in Eq. (2).

$$\frac{1}{P_{\star}}\frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2)

where.

Parameter	Symbol	Expression
Peclet number	P.	nL
		KL
Dimensionless time	t _D	tu
		L
Dimensionless distance	xp	x
		L
Interstitial velocity	24	Q
		sr ² w

The solution of Eq. (2) was shown in Eq. (3) under a known initial (C = 0 at $t_D = 0$) and boundary conditions (C = 1 at $x_D = 0$, C \rightarrow 0 as $x_D \rightarrow \infty$)

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{t_D/P_{en}}} \right) + e^{P_{en}x_D} erfc \left(\frac{x_D + t_D}{2\sqrt{t_D/P_{en}}} \right) \right\}$$
(3)

The final longitudinal dispersion coefficient was determined by curve fitting the CO_2 exit composition (C) measured by the online GC into the 1AD equation. However, to forecast the dominant mechanism of displacement, the model equation governing the medium peclet number (P_{em}), the characteristic length scale of mixing (d), molecular diffusion coefficient (D) and mean interstitial velocity (um) was used as presented in Eq. (4).

$$P_{un} = \frac{u_n d}{D}$$
(4)

In general, when Pem <0.1, the dominant mechanism within the porous medium is diffusion like, while the advective mixing becomes dominant at Pem>10 (Perkins and Johnston, 1963). Also, an intermediate zone co-exists when the value of Pem ranges between 0.1 and 10.0. Thus, the model equation developed by Coats et al. (2009) was used to evaluate the dispersivity of the Bentheimer core sample.

$$\frac{K_l}{D} = \frac{1}{\tau} + \alpha \frac{u_m^*}{D}$$
(5)

Here α represent the Bentheimer core plug dispersivity in meters in the presence of an exponential constant (n). However, most consolidated sandstones have a tortuosity (r) ranges between 1 and 13 (Honari et al., 2013). Thus, the tortuosity (r) of the Bentheimer was evaluated as an intercept point (Hughes et al., 2012) obtained from the linear plot of Eq. (5).

Gas-phase diffusion is often assumed to be dominated by molecular diffusion. However, the irregular broadening of a solute along concentration gradients over time is described here by the one-dimensional Fick's second law presented in Eq. (6).

$$\frac{\partial C}{\partial t} = D_a \frac{\partial^2 C}{\partial x^2} \tag{6}$$

where C is the gas concentration (mol/m³), t is time (s), Da is the binary molecular diffusion coefficient of air (m²/s), and x is the distance along the axis of flow (m). When the main collision is within moleculemolecule interaction without colliding with the wall of the container, such a process is called molecular diffusion. More complex gas-phase diffusion processes can also occur in some situations, such as viscous, Knudsen, and non-equimolar diffusion (Scanlon et al., 2000). The former two processes are said to occur due to pore walls and resultant molecule-wall collisions (Cunningham and Williams, 1980). The latter requires both the presence of system walls and a multicomponent gas, and such conditions are primarily present in porous media and lead to digression from Fick's law (Sleep, 1998). Baehr and Bruell (1990) report that high vapour pressures, especially those near organic liquid sources, results in divergence from Fick's law. Diffusion is a solute-dependent component of dispersion due to the relationships among average kinetic energy, velocity, and molecular mass (Molly and Mark, 2006). Meanwhile, at a given temperature, the average kinetic energy of all gases is equal and presented in Eq. (7).

$$E_k = \frac{3}{2}kT = \frac{1}{2}mv_{row}^2$$
(7)

where k is Boltzmann's constant (J·K-1), T is the temperature (K), m is the solute mass (kg), and vrms is the root-mean-square velocity of the gas particles (m/s). Thus, lower molecular weight gases are said to exhibit higher average velocities than those with a higher molecular weight under given thermal equilibrium and consequent equal kinetic energy (Molly and Mark, 2006). This higher velocity results in more significant diffusion coefficients, which grossly contributions to overall advection (dispersion) domination.

The widely accepted model equation, developed by Takahashi & Iwasaki, 1970 for diffusion coefficient evaluation, was used. Unfortunately, this model is primarily applicable for CO_2 and CH_4 systems. This necessitates the use of an alternative model equation developed by Fuller et al. (1966). This model can be relevant for CO_2 and N_2 displacement, as shown in Eq. (8a).

$$D_{N2CO2} = \frac{1.0110 \times 10^{-4} T^{1.73} \sqrt{(1/\mu_{N_2} + 1/\mu_{CO_2})}}{P \left[(\sum V_{N_2})^{1/3} + (\sum V_{CO_2})^{1/3} \right]^2}$$
(8a)

The model equation was further simplified and expressed as equation (8b) substitution.

$$D_{\text{CO2,N2}} = \frac{7.69 \times 10^{-11} \, T^{1.75}}{P} \tag{8b}$$

In equation (8b) T and P are the experimental temperature and pressure in Kelvin (K) and MPa, respectively.

3. Materials and methods

In this paper, N_2 and CO_2 behaviour were investigated using core flooding experiments with Bentheimer core plug. N_2 was used as the

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Table 1

The	e characteristics	of	Bentheimer	core	plug	at	conditions	relevant	to	the	EGR
pro	cess.										

Core plug	Length	Diameter	Porosity	Gas Permeability
	(m)	(m)	(%)	(D)
Bentheimer grey	0.076	0.025	22.80	2.10

Table 2

The initial experimental conditions relevant to the EGR process.

Components	Value		
Saturation gas	N ₂		
Injection gas	002		
Fluid composition, wt. %	99.9		
Initial pressure, bars	102		
Initial temperature, °C	30-40		
Injection pressure, bars	100-102		
Injection composition, wt. %	98-99		
Production constraints, wt. %	Breakthrough @ 2–5% CO ₂ product contamination		
Dispersion coefficient range, m ² /s	$8-50 \times 10^{-6}$		
Diffusion coefficient range, m ² /s	15-30 × 10 ⁻⁰		

continuous phase during the core flooding process, while CO₂ was the dispersed phase. The experiment was designed with varying injection rates at temperatures of 30 and 40 °C and 102 bars pressure. The general properties of the Bentheimer core plug used and the initial experimental conditions were shown in Tables 1 and 2.

3.1. Procedure

To achieve a negligible moisture content and volatile organic compounds (VOCs), the Bentheimer core plug was oven-dried at a temperature of 110 °C for 24 h. Also, to maintain smooth and uniform gas molecule distribution and avoid permeation through the vitton sleeve, the core plug was securely wrapped with a thread tape followed by aluminium foil before inserting into the resistance rubber sleeve. The overburden pressure was set at 170 bar, reasonably above the pore pressure to prevent the core sleeve from rupturing. More so, the temperature was set and maintained at 30 °C. The equipment lines were flooded with N_2 until the final composition attained was \geq 98% from the GC spectrum. A pressure leak test was carried out to ensure the system was leak-free. CO2 was later injected at 0.4 ml/min using pump C/D and accumulator B, as shown in Fig. 1. At every 5 min sequential interval, the GC analyzed and recorded the endpoint concentration until CO2 was dominant relative to N2 (i.e. CO2 composition >98%). The experiment was terminated, and the lines were de-pressurized. Additional tests were further carried out at 0.6, 0.8, 1.0, and 1.3 ml/min using the same protocol as already described. Thus, to investigate the effect of temperature, similar sets of the experiment were conducted using a fresh core sample, but this time at a higher temperature of 40 °C while maintaining the same 102 bars pressure. The experimental flow diagram is presented in Fig. 1.

4. Results

4.1. Temperature effect on dispersion and diffusion coefficient

Sets of experiments were carried out in Bentheimer core samples to investigate the diffusion and dispersion coefficient dependence on temperature. The study was performed at 30 and 40 °C temperatures, 102 bar of pressure, at a specific CO_2 injection rate (0.4, 0.6, 0.8, 1.0, and 1.2 ml/min). Fig. 2 shows that the diffusion coefficient is directly proportional to temperatures, which conforms with the findings

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Fig. 1. Experimental flow diagram of N2 displacement by CO2 flooding.



Fig. 2. Effect of injection rates on the longitudinal dispersion coefficient at 30 & 40 °C.

outlined by other researchers (Mamora and Seo, 2002; Liu et al., 2015; Mohammed et al., 2019; Abba et al., 2018). Thus, the molecular movement of the gas species is directly proportional to temperature due

to the rise in activation energy. As the gas species move along the core, they slowly exceed the natural force of attraction between them as a result of elevated temperatures within the pore matrix. It gives them

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Fig. 3. Relationship between diffusion coefficient and temperature at 102 bars using Eq. (8b).



Fig. 4. Plot of dispersivity determination at 30 °C.

substantial liberation to flow over more significant space due to increased kinetic energy associated with temperature rise. Thus, it later promotes the free diffusion of CO₂ and N₂ molecules, resulting in more displacing and displaced gas molecules entering each other, affirming ocales. A piece of evidence was the plot of dispersion coefficient against injection rate in Fig. 3, with higher dispersion coefficient values at 40 than at 30 °C under the same range of CO₂ injection velocities. A combined average of 25% rise was recorded when the temperature increased from 30 to 40 °C. Therefore, the dispersion addiffusion coefficient increase due to temperature rise. It can be drawn that high temperature encouraged the mixing of gases under motion

within the pore channels at simulated reservoir conditions. Therefore, gas fields with higher temperatures are likely unsuitable for the CO₂ enhanced gas recovery process for fundamental production operations. In general, the turbulence effect is undoubtedly responsible for high diffusion and dispersion along the core length due to increased flow velocities. In this study, the highest dispersion occurred at 1.2 ml/min while the least was recorded at 0.4 ml/min, as shown in Fig. 2.

4.2. Effect of temperature on dispersivity

The experimental data at 30 and 40 °C were applied to evaluate the

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Fig. 5. Plot of dispersivity determination at 40 °C.

dispersivity (a) of the Bentheimer core plug using Eq. (4), at $\tau = 3, 2$ and n = 1. From Figs. 4 and 5, the dispersivities of the core plug were well fitted by experimental results at 30 and 40 °C. More so, the medium peclet number Pem at 40 °C was calculated to be 0.964-2.894. In addition, a moderate convection effect was observed at lower injection velocities (0.06-0.09 mm/s), corresponding to 0.964-1.448 medium peclet number range, with diffusion being the dominant mechanism. As the injection velocity further rises with a corresponding medium peclet number range of 1.448-2.89, the convection effect intensifies. Thus, both diffusion and convection dominated the process, resulting in early CO2 breakthroughs. Therefore, selecting the correct injection rate is vital for simultaneous CO₂ storage and the EGR process. The dispersivity (α) for the core plug at 30 °C was recorded as 0.00265 m, less than those mmed et al., 2020; Abba et al., 2018) and within the reported by (Mo range written by (Gist et al., 1990; Schulze-Makuch, 2005; Honari et al., 2013). In summary, the application of Eq. (4) to the experimental results permit the dispersivity (α) to be evaluated for the two temperatures considered for the Bentheimer sandstone plug. For 30 and 40 OC of temperature, $\alpha = 0.00222$, and 0.002265 m, and these results are within the range reported for sandstones by (Coats et al., 2009; Schulze-Makuch, 2005; Liu et al., 2020), although for the 40 °C temperature, the dispersivity recorded was slightly higher, though lower than that presented according to (Brigham, 1974). Thus, higher temperatures have a more substantial effect on dispersion and diffusion coefficient, which eventually led to mixing CO2 and N2 from a more significant perspective (Liu et al., 2018).

4.3. CO2 breakthrough

The breathrough is considered as a point at which the displacing gas (CO₂ or N₂ gas) was noticed at the exit product stream. In this study, the breakthrough was characterised within 1-3% CH₄ contamination by CO₂, in other words, when the GC output indicated CO₂ concentration within a range of 1-3% concentration. The CO₂ breakthrough curves (Sshape curves) were obtained by plotting CO₂ mole fractions at the exit stream against the PV of injected CO₂. The experiment was carried out at two temperature regimes (30 and 40 °C) to investigate the influence of temperature variation on CO2 breakthrough at different injection velocities. The CO2 breakthrough tailed off with reservoir temperature rise, signifying the dependence of diffusion and dispersion coefficients on temperature. The experiment at 30 °C recorded an extendable breakthrough time than that at 40 °C in all cases. The maximum breakthrough at 0.52 PV was recorded at 30 °C and the lowest injection velocity. The breakthrough, however, decreased to 0.17 PV when the temperature increases from 30 to 40 °C. The breakthrough curves recorded at 30 °C are less steep compared with those measured at 40 °C. Fig. 6a-e presents the CO₂ breakthroughs at varying injection rates for 30 and 40 °C experimental conditions. These graphs were obtained by plotting the CO2 exit composition from the downstream of the core holder by GC equipment against the injected PV of CO2. At a lower injection rate, the temperature effect was quite significant, as observed from the vertical distance difference of the two plots. Thus, at lower injection, the temperature effect was the driving factor compared to the injection rates. However, as the injection rates increase from 0.4 to 1.2 ml/min, such vertical differences become minimal until at 1.2 ml/min when the two plots (30 and 40 °C) overlap. At this point, the injection rate effect overcomes the dominant temperature effect and became the dominant driving factor. The experiments were carried out at constant pressure of 102 bar and an interstitial velocity range of 0.06-0.18 mm/s.

The most extended CO₂ breakthrough at 0.52 PV was noticed at 0.06 mm/s and 30 °C, which later tailed off by 50% when the interstitial velocity increase to 0.18 mm/s. The least CO₂ breakthrough at 0.17 PV was observed at 0.06 mm/s and 0° C temperature. Ostensibly, at this conditions, the highest injected CO₂ (0.8 PV) through the system was recorded during the displacement experiment. These results are in agreement with the study reported by (Mesfer et al., 2020). Overall, the gas injection velocity has a strong influence in determining the CO₂ breakthrough point and are more significant at lower rates. As evidenced in Fig. 6a–e, when the change in the breakthrough periods between the two sets of temperature decreases from 0.35 PV to nearly zero. The two plots in Fig. 6e overlap with each other, recording the same breakthrough period at 0.24 PV. Thus, a prolonged CO₂ breakthrough

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Fig. 6. a-e. CO2 breakthrough at varrying injection rate (0.4-1.2 ml/min) for 30 & 40 °C temperatures.

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Fig. 7. a-e. Concentration profile at varrying injection rate (0.4-1.2 ml/min) for 30 & 40 °C temperatures.

Table S

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Q (ml/ min)	Interstitial Velocity (10 ⁻⁵ m/ s)	CO ₂ Breakthrough (HCPV)	CO ₂ Injected (HCPV)	CO ₂ Injected Stored (HCPV	CO ₂ Stored (%)	Dispersion Coefficient $(10^{-8} m^2/s)$
Temp. 30	°C			200 - 200 Hors	to and the second	100000
0.4	5.96	0.52	0.78	0.56	71.80	8.23
0.6	8.95	0.39	0.58	0.44	74.81	14.03
0.8	11.93	0.37	0.56	0.43	76.39	21.09
1.0	14.91	0.31	0.39	0.35	89.06	24.13
1.2	17.89	0.24	0.42	0.38	89.02	42.53
Temp. 40	°C					
0.4	5.96	0.17	0.31	0.14	46.73	12.52
0.6	8.95	0.21	0.32	0.20	61.43	17.25
0.8	11.93	0.23	0.32	0.21	66.59	25.06
1.0	14.91	0.24	0.41	0.29	71.89	33.62
1.2	17.89	0.24	0.37	0.30	79.17	39.41

signifies lower mixing and higher storage at reduced system temperature where diffusion dominates. In contrast, the gas molecules gain higher kinetic energy at higher injections rates sufficient enough to create turbulent flow regime. Hence, making advection dominant as against diffusion within the porous medium.

Diffusion is highly temperature-dependent, meaning the higher the temperature, the higher the rate of diffusion. Higher temperatures promote faster movement of the gas species within the porous medium due to the increase in their respective kinetic energies. This means only fewer molecules of the CO_2 would have sufficient kinetic energy to contact the N_2 in the outlet stream of the core holder, which is why lower amount of CO_2 was recorded before breakthrough at lower injections. Thus, CO_2 injected sinks to the lower part of the porous medium, indirectly influencing higher storage in the context of geological sequestration and apparently, less effluent contamination. In summary, the lower the temperature, the lower the mixing (lower dispersion coefficient), the longer the CO_2 breakthrough and invariably better storage with little product contamination.

4.4. Concentration profile

The concentration profile plots highlight the trend between the displacing and displaced gas during the core flooding experiment. These plots were presented in Fig. 7a-e. According to Fig. 7a, as the PV of the total injected CO₂ reaches 0.17 PV, a current of CO₂ was detected at the exit stream, which invariably indicates the presence of a displacement front. After this, the exit CO₂ concentration increases linearly with the total CO₂ injected (HCPV) until it reaches the peak at nearly 0.3 PV, corresponding to approximately 0.99 CO₂ mole fraction. At this point, an insignificant concentration of N₂ was recorded at the downstream of the core holder depicted by the green curve in Fig. 7a. Thus, indicating a significant recovery of the N₂ has occurred.

A similar trend was observed when the experiment was carried out at a higher temperature of 40 °C. Thus, a point of intersection was observed at almost 50% of the CO₂ exit concentration at 30 and 40 °C. Furthermore, the curves at 30 °C were steeper than at 40 °C, indicating higher extent of mixing between the N₂ and CO₂. This was evident later in Table 2, with most of the runs at 40 °C recording a higher value of dispersion coefficient under the same injection scenarios. More so, when the injection rate increases from 0.4 to 1.2 ml/min, the distance between the two intersection of curves decrease until it becomes less visible, especially at the maximum injection of 1.2 ml/min. At this point, the N₂ and CO₂ curves overlapped, as shown in Fig. 7e. Such plot was in synergy with the breakthrough plot in Fig. 6e. Thus, it can be deduced that as the interstitial velocity increases during the EGR process, both N₂ and CO₂ experienced similar phase change behaviour under reservoir conditions.

4.5. CO₂ sequestration

The CO₂ sequestration was examined using the law of mass conservation as demonstrated by Abba et al. (2018). As a result, the total amount of CO₂ injected and produced can be determined to study each injection rate's, storage efficiency and temperature as presented in Eqs. (9a) and (9b).

$$\Sigma V_{CO2, in} = \Sigma (V_{CO2, Accumulated} + V_{CO2, Produced})$$
 (9a)

$$% CO_2 \text{ Storage} = \frac{\Sigma V_{CO2}}{\Sigma V_{CO2}} \xrightarrow{\text{Accumulated}} \times 100$$
(9b)

The higher the reservoir conditions, the more compressible CO₂ becomes, which is why most CO₂ sequestration processes are affected at CO₂ critical temperature and pressure of 31.5 oC and 74 bar, respectively (Hoteit et al., 2019; and Godec et al., 2011). Eq. (9b) defined the proportion of CO₂ stored as the ratio of total CO₂ accumulated to that of total injected. Also, the N₂ and CO₂ gases are in their supercritical states and thus a sharp disparity in density will exist (CO₂ will have higher density owing to the special behaviour of supercritical CO₂, making it possible for the CO₂ to descend downward due to the gravity effect and simultaneously displacing the residual N₂ within the available pore spaces. Thus, a significant amount of total injected CO₂ remained trapped inside the long core, resulting in high sequestration volume.

From the range of injections and temperatures tested, the percentage CO2 stored increases as the rate of injection increases from 0.4 to 1.2 ml/ min, as seen in Table 3. For the 30 °C experimental runs, higher storage volumes were recorded at higher injection rates. At high injections, the ratio of total CO2 injected to that of N2 saturation was low compared to that at lower injections. This allowed most of the CO2 within the core plug to migrate downward and be stored as the CO₂ flow stream traversed longitudinally in the core sample. The N₂ primarily acts as a retardant when in contact with CO2, as reported in our previous works (Moha ned et al., 2019, 2021). Furthermore, the highest CO₂ storages were obtained at injection rates of 1.0 and 1.2 ml/min, resulting in 89.2-89.6% and 71.89-79.17% for 30 and 40 °C, respectively. It can be hypothesised that CO2 storage will be more appealing at lower temperatures as seen in the percentage storability or storage efficiency. Additionally, the plots of the differential pressure in Figs. (8d) and (e) showcase a similar trend or pattern for both temperatures, which was why both tests demonstrated a proximal range of value parameters.

On the other hand, the injection at 0.4 ml/min could not overcome the capillary forces within the narrower pore spaces of the pore matrix. This can be attributed to its density and flow progression with a characteristic differential pressure (Δp) and high permeability (k) recorded during the core flooding experiment. Thus, more of the flow paths become available for steady flow without limitation or curtailment, as seen in Eq. (10), at higher injections. Thus, the flow profile was uninterrupted, explaining the reason behind its lower longitudinal dispersion coefficient and high CO₂ storage with low mixing as expected. This
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Fig. 8. a-e. Differential pressure comparison for 0.4-1.2 ml/min injection at 30 and 40 °C.

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agreed with the works reported by (Abba et al., 2018; Honari et al., 2016; Liu et al., 2018; Mohammed et al., 2020).

$$k = \frac{q\mu L}{A_{c}(\Delta P)}$$
(10)

5. Conclusions

This paper investigated CO2 and N2 behaviour using a core flooding experiment with Bentheimer as the core plug. N2 was used as the continuous phase during the core flooding process, while CO_2 was the dispersed phase. This study is primarily designed to establish why CO2 experiences an extended breakthrough with N2 as the displaced gas during the displacement process. In general, the turbulence effect is undoubtedly responsible for high diffusion and dispersion along the core length due to increased flow velocities. The dispersion and diffusion coefficient increase due to temperature rise. It can be drawn that high temperature encouraged the mixing of gases under motion within the pore channel under reservoir conditions. Dispersivities for 30 and 40 °C of temperature runs were obtained as $\alpha = 0.00222$, and 0.002265 m, respectively. These values are consistent with those reported for sandstones by several researchers. Thus, higher temperatures have a more substantial effect on dispersion and diffusion coefficient, which will eventually lead to higher mixing between CO2 and N2. The CO2 breakthrough tail off with reservoir temperature rise, signifying the diffusion and dispersion coefficient dependence on temperature.

The experiment at 30 °C recorded an extendable breakthrough time over that at 40 °C. The maximum breakthrough of 0.52 PV was recorded at 30 °C at the lowest injection velocity. The concentration profile plots highlighted the trend between the displacing and displaced gas during the core flooding experiment. At the 1.2 ml/min injection rate, the N₂ and CO₂ curves overlapped, and such a plot was in synergy with the breakthrough plot. Thus, it can be deduced that as the interstitial velocity increases during the EGR process, both N₂ and CO₂ experienced similar flow behaviour under reservoir conditions. From the range of

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injections and temperatures tested, the percentage of CO_2 stored increases as the rate of injection increases from 0.4 to 1.2 ml/min. The total CO_2 stored was more promising at higher rates, corresponding with high differential pressure, due to the flow resistance within the flow channels. Future work will aim to elucidate the effect of temperature on storage efficiency during CO_2 geological sequestration in depleted natural eas reservoirs.

Credit author statement

I Nuhu Mohammed was responsible for conducting the experiments, graph plotting using OriginPro software, data analysis, and preparing most part of the manuscript. Abubakar J. Abbas and Godpower C. Enyi contributed to the experimental design methodology, and research supervision. Muhammad Kabir Abba, Onukak Imeh Etim, Salihu M. Suleiman, Hassan Kabiru Yar'adua and Bello Saidu provided the project guidance and edited the manuscript. All the co-authors provided support and motivation for this work, from the experimental design, data analysis, and review of the results. All the authors (Nuhu Mohammed, Abubakar J. Abbas, Godpower C. Enyi, Muhammad Kabir Abba, Onukak Imeh Etim, Salihu M. Suleiman, Hassan Kabiru Yar'adua and Bello Saidu) have approved the version of the manuscript to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

In normal	conditions, vapor is the combination of gas and liquid phases Gas exists in a single thermodynamic state under normal conditions
С	Effluent composition of CO ₂
Vb	Bulk volume
SiCO ₂	Supercritical carbon dioxide
HCPV	Hydrocarbon pore volume
PV	Pore volume
EGR	Enhanced gas recovery
$(\sum V_{N_2})$	Diffusion volume of N ₂
$(\sum V_{00})$	Diffusion volume of CO2
D	Diffusion coefficient, m ² /s
k	Permeability, mD
1AD	One-differential advection dispersion
Q	Flowrate, mil/min
tD	Dimensionless time
xD	Dimensionless distance
KL	Longitudinal dispersion, m ² /s
k	Permeability, md
A	Cross section area, cm ²
L	Length of characteristic scale
ΔP	Differential pressure across the plug, atm
μ	Viscosity, cP
P	Pressure, bar
т	Temperature, ⁰ C
u	Interstitial velocity, m/s
φ	Core porosity, %
α	Dispersivity, m
τ	Tortuosity

Ρ. Peclet number

Medium Peclet number Pem

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The role of N2 as booster gas during enhanced gas recovery by CO2 flooding in porous medium

Nuhu Mohammed^{*}, Abubakar J. Abbas, Godpower C. Enyi

Department of Petroleum and Gas Engineering, University of Salford Manchester, M4 SWT, United Kingdom

ARTICLE INFO ABSTRACT Most research on CO₂ flooding is focusing on CO₂ storage than CH₄ recovery and mostly simulation-based. To our Keywords: Dispension coefficient knowledge, there have been limited reported experimental on OO_2 injections capable of unlocking a high amount of the residual methane due to their miscibility effect. The empirical study has highlighted the impact of N₂ as a CO₂ storage CO2-Breakthrough booster gas during the Enhanced Gas Recovery (EOR) process by CO_2 flooding. The N_2 acts as a buster by representing the reservoir pressure before the CO_2 breakthrough, enabling more CH4 recovery. It also acts as a ter Methane displacement rdant by creating a thin barrier at the CO2-CH4 interface, making it difficult for the CO2 to disperse into the CH4. This result in an extendable breakthrough, influencing the injected $\rm CO_2$ to migrate downward due to gravity for storage within the pore spaces. This study, a core flooding experiment at 1500 paig and 40 °C of pressure and temperature, respectively, was carried out to study the effect of N2 as booster gas during natural displacement in a porous medium (sandstone rock). The recoveries with N2 booster were better off than those without N2 buster (conventional CO2 flooding). Overall, an improved CH4 recovery and dispersion coefficient with substantial storage was noticed, with the optimum at 0.13 fraction of pore volume booster gas. Compared to the 0.4 ml/min optimum conventional CO_2 injection, the results show a 10.64 and 24.84% increase in CH_4 recovery and CO_2 storage, respectively. 0.71 × 10-8 m²/s reduction in dispersion coefficient was recorded than the convention method. The additional CH4 recovery can provide extra revenue to offsets other operational expenses. This research signifies the potential of N_2 as a buster medium on GH_4 recovery, which can be applicable for pilot application within the oil and gas industry.

1. Introduction

The method of injecting CO2 to recover residual natural gas is gaining recognition within the oil and gas industry. A substantial injected volume of CO2 stored provides an additional advantage over the conventional Carbon Capture and Storage (CCS) process. The natural gas recovered can provide extra revenue to offset other operational costs. This mechanism involving a tertiary recovery method is called Enhanced Gas Recovery (EGR) process. Since both CO2 and CH4 are gases, their properties were potentially agreeable for reservoir application due to unique behaviour, and phase change demonstrates by CO2 at supercritical conditions (Oldenburg and Benson, 2002). The density ratio of CO2 to CH4 is in the range of 2-6 at reservoir states (Al-Hasami et al., 2005), which make CO₂ to be classified as high viscous gas (Al-Hasami et al., 2005). Thus, CO_2 can be migrated downwards for storage during the EGR process (Oldenburg, 2001). More so, CO_2 is more soluble in formation water than CH_4 due to its high solubility factor in aqueous solvents. The EGR process is a promising technique for co-current CH4 gas recovery and CO2 storage during natural displacement in a porous medium. However, CO2 and CH4 are completely miscible due to the similarities in their physical properties. This result in an early CO_2 breakthrough during the natural gas displacement process, which has been the major drawback of the technology (Li et al., 2019; Oldenburg and Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; S. Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This problem has affected its applicability within the oil and gas industry because of product contamination because of the high amount of CO2 recorded at the outlet stream (Oldenburg and Benson, 2002; S. S. K. Sim et al., 2009).

Abba et al. (2018) investigated the impact of connate water salinity on the dispersion coefficient in consolidated rocks during the EGR process by CO₂ flooding. The experiment was carried out at 50 °C and

* Corresponding author. E-mail address: n.mohammed5@edu.salford.ac.uk (N. Mohammed).

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Fig. 1. Schematics of conventional CO₂ injection to displace CH₄ without N_2 booster gas (Wang et al., 2018).

1300 psig of temperature and pressure, respectively. The optimum CO_2 injection occurred at 0.3 ml/min, and their result from the core flooding process indicated that the dispersion coefficient decreases with increasing salinity. Hence, the higher the density of the connate water, the lower the dispersion of CO_2 into CH_4 . They use varying salinity concentration, and they were able to report 20 min extendable CO_2 breakthrough at a maximum concentration of 10 % wt. Sodium chloride (NaCl). Unfortunately, a decline in CH_4 recovery was recorded as the salt concentration increases from 5 to 10 %wt., due to the reduction in core sample pore volume causes by the high-density connate water molecule occupying more of the free bubble holes within the core matrix (Abba et al., 2019).

To our knowledge, there are limited experimental findings on $\rm CO_2$ injections capable of unlocking the residual natural gas with a substantial volume of injected CO₂ stored due to their miscibility effect (Abba et al., 2018). This necessitated the need for an in-depth study of using N_2 as a booster before CO_2 introduction. In so doing, the nascent mixing between the two gases (CO2 and CH4) is minimized since injecting a specific volume of N2 prior to the CO2 injection exhibits a re-pressurization effect that yields more CH4 recovery and a minimum fraction of CO2 in the effluent stream of the core holder before and after the CO2 breakthrough. It was evident from the gas chromatography (GC) print out, which results in delaying the CO2 gaining access to the CH4 boundary, making the process more efficient since less product contamination was recorded than the conventional CO2 flooding. More so, determining the best CO2 injection rate before the N2 booster gas inclusion its prerequisite for optimum booster gas volume needed to provide maximum CH4 recovery and minimum CH4-CO2 miscibility (dispersion coefficient).

This paper's objective highlighted the role of N₂ as a booster for CH₄ recovery during the EGR process by CO₂ flooding. The N₂ gas acts as a buster, enabling more CH₄ recovery without cross-contamination, making it difficult for the CO₂ to disperse into CH₄, resulting in a longer CO₂-breakthrough due to the N₂ blanketing effect. This makes the CO₂ descend downward for storage within the pore spaces due to gravity. In this paper, the impact of N₂ as booster gas for natural gas recovery enhancement and miscibility reduction during the CO₂ flooding displacement process was investigated. The experimental runs with N₂ as booster show a promising recovery and CO₂ storage with less contamination than those without a buster gas (conventional CO₂ flooding).

2. Overview concepts and theories

The conventional or traditional approach for CH4 recovery by CO2



Fig. 2. Schematics of conventional CO_2 injection to displace CH_4 with N_2 booster gas (Wang et al., 2018).



Fig. 3. Conventional CO₂ injection concentration profile for systematic optimisation purpose at 0.4 ml/min, 1500 psig, and 40 °C (Mohammed et al., 2020).

injection is depletion development, but such recovery (approximately 35%) is deemed low to offset the CO2 storage cost (Wang t al., 2018). Due to the nascent mixing between the injected CO2 and displaced CH4, an invariable amount to premature CO2 breakthrough in the production well. The aim was to recover a substantial CH4 free from CO₂, enabling more injected CO2 stored in the process. However, that was difficult using the conventional EGR-CO2 injection technique. High injected CO2 fraction was noticed early before or after breakthrough, as seen in Fig. 1, and the value of X0 at the intersection point (1) in Fig. 3. Therefore, a new EGR approach is required to reduce the mole fraction of CO₂ in the recovered CH4. The N2 gas act as a buster by re-pressurising the reservoir pressure before CO2 breakthrough enable more CH4 recovery without contamination. It also acts as a retardant by creating a thin barrier between the CO_2 -CH₄ phase region presented in Fig. 2. This makes it difficult for the CO_2 to disperse into $\mathrm{CH}_4,$ resulting in a longer CO_2 breakthrough, making most of the injected CO2 descending downward for storage within the pore spaces due to gravity. In this study, N2 was employed as a booster gas to delayed CO2 breakthrough with minimum miscibility. In the process, more \mbox{CH}_4 recovery and \mbox{CO}_2 storage were realised, since the produced CO2 fraction has reduced as shown from

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Fig. 4. Schematics of methane displacement with and without cushion gas.

intersection points (2) and (3), X₁, and X₂ in Fig. 3. To maximise both CH₄ recovery and CO₂ storage; (1) the fraction of the produced CO₂ (X₀, X₁, and X₂) needs to be minimized (X₂ < X₁ < X₀), (2) the change in the produced CO₂ fraction (Δ X) and slope (S₁ and S₂) also have to be maximized (Δ X₂ > Δ X₂ and S₂ > S₁). Fig. 3 is the plot of produced CO₂ fractions against displaced CH₄ at 0.4 ml/min optimum conventional CO₂ injection, 1500 psig of pressure, and 40 °C of temperature. These mole fractions are the effluent stream compositions recorded by the GC machine. The optimum booster gas volume was selected based on the above criteria (see Figs. 1 and 4).

2.1. Dispersion coefficient

In this study, the fundamental model equations used are those developed and reported by (Newberg and Foh, 1988; Perkins and Johnston, 1963; Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012; Mamora and Seo, 2002; Liu et al., 2015; Takahashi and Iwasaki, 1970; Abba et al., 2017, 2018; Abba et al., 2019; Fuller et al., 1966) as presented in Eqns. (1)-(9). Details of these equations can be found in our previous publications (Mohammed et al., 2019; Mohammed et al., 2020).

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

Eqn. (1) describes the displacement of methane by carbon dioxide in consolidated rocks, where (C), (x), (u), and (K_L) are the effluent composition measured by the gas chromatography, distance under time (t), interstitial velocity, and longitudinal dispersion coefficient respectively. Invariably Eqn. (1) can be re-written in a dimensionless form (Mamoraand Seo, 2002), as shown in Eqn. (2).

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial t_D} = \frac{\partial C}{\partial t_D}$$
(2)

where.

Parameter	Symbol	Expression
Peclet number	Ρ.	<u>uL</u>
Dimensionless time	t _D	tu .
Dimensionless distance	xp	x.
Interstitial velocity	u	^L Q

Since the injection of CO_2 is at x = 0, then.

 $\begin{array}{l} \mbox{Initial condition: } C=0 \mbox{ at } t_D=0. \\ \mbox{Boundary conditions: } C=1 \mbox{ at } x_D=0, \mbox{ } C\to 0 \mbox{ as } x_D\to\infty \\ \mbox{Therefore, the solution to Eqn. (2) is presented in Eq. (3). } \end{array}$

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{t_D/P_{an}}} \right) + e^{P_{an}r_D} erfc \left(\frac{x_D + t_D}{2\sqrt{t_D/P_{an}}} \right) \right\}$$
(3)

The effluent core flooding composition was fitted with the analytical solution to the one-differential Advection Dispersion (AD) equation $(Eq_{II.3})$ in terms of the *Péclet* number to evaluate the corresponding dispersion coefficient. The experiment's absolute dispersion coefficient is the value that provides the optimum synergy between the experimental result compared to the numerical solution. The medium peclet number (P_{em}) shown in Eqn. (4) was used to predict the dominant displacement mechanism during the EGR process in a porous medium (Perkins and Johnston, 1963). The characteristic length scale (d) is in meters, while (D) represent the molecular diffusion coefficient in n^2/s .

$$P_{em} = \frac{u_m d}{D}$$
(4)

Generally, at $P_{em} < 0.1$, diffusion dominates the dispersion process, and at $P_{em} > 10$, advective mixing dominates the dispersion process (Perkins and Johnston, 1963). However, the process is under the intermediate zone when the *Péclet* number is greater than 0.1 but less than

Table 1

Specification	and	property	of	the	Bandera	grey	core	sample	at	experimental
conditions.										

Core	Length	Diameter	Porosity	Gas Permeability
sample	(mm)	(mm)	(%)	(mD)
Bandera grey	76.02	25.31	19.68	32

10. The solution of Eqn. (3) was used to fit the concentration profiles which the dispersion coefficient was then evaluated. Coats et al. (2009) correlated the dispersion coefficient with the molecular diffusion coefficient, as shown in Eq. 5

$$\frac{K_l}{D} = \frac{1}{\tau} + \alpha \frac{u_m^4}{D} \tag{5}$$

Here α is the dispersivity of the porous medium (m), and (n) represents an exponent. The tortuosity (τ) ranges from 1 to as high as 13 or more for consolidated rocks, as reported by Honari et al. (2013). The parameter (τ) can be obtained empirically through various methods; however, α and n are mainly determined using a core flooding system (Hughes et al., 2012). The intercept from Eq. (5) was used to calculate the tortuosity.

2.2. Diffusion coefficient

The Takahashi & Iwasaki developed in 1970 has been used successfully for diffusion coefficient determination. However, it's mainly applied to the $\rm CO_2-CH_4$ system only. In this report, due to N₂ inclusion, a different model proposed by Fuller et al. (1966) was employed. This correlation presented in Eqn. (6) is applicable for both $\rm CO_2, N_2$ and $\rm CH_4$ system.

$$D_{N2CH4} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{\left(1/\mu_{N_{1}} + 1/\mu_{CH_{4}}\right)}}{P \sum V_{N_{2}} \sum V_{CH_{4}} \left(\sum V_{CH_{4}}\right) \left(\sum V_{CH_{4}}\right)^{1/3}}$$
(6)

where $(\sum V_{N_2})$ and $(\sum V_{CH_4})$ are the values derived from the summation of atomic diffusion volumes of N₂ and CH₄ molecules, respectively. These values are reported in our previous publications (Mohammed et al., 2019). The equation was further simplified to formed Eqns. (7) and (8) after inserting the values of atomic diffusion volumes and the molecular weight of N₂, CH₄ and CO₂.

$$D_{\rm N2CH4} = \frac{10.2 \times 10^{-11} \, T^{1.73}}{P} \tag{7}$$

$$D_{CD2,CH4} = \frac{8.2 \times 10^{-11} T^{1.75}}{p}$$
(8)

where, T is the temperature in kelvin (K) and P is the pressure in megapascal (MPa).

3. Materials and methods

In this study, the potential of N_2 for CH_4 recovery and CO_2 storage was investigated using the CO_2 flooding technique. This entails saturating the core plug with CH_4 at known irreducible water of saturation (Swi), injecting varying amounts of N_2 as a booster prior to CO_2 injection



Fig. 5. CH4 recovery against HCPV of total CO2 injected at 0.2 ml.



Fig. 6. CH4 recovery against HCPV of total CO2 injected at 0.4 ml.

at an optimum rate of 0.4 ml/min. The property of the core plug employed was presented in Table 1.

The core sample was dried overnight in an oven at 105 °C for moisture removal and other volatile compounds. The dried sample was wrapped with cling film and foil paper before being inserted into a heat shrink. This is vital to avoid leaving viscous fingerprints and penetrating the gases through the sleeve into the ring-shaped core holder. The sample was loaded into the core holder and stapled with clamps from both ends. Hydraulic oil was pumped into the ring-shaped core holder to provide the desired overburden pressure, kept at a minimum of 500 psig above the pore pressures to avoid fracturing the core sleeve. The heat jacket was installed on the core holder, and the temperature step-up (40 °C) was observed before CH₄ saturation. The backpressure was engaged, the core sample was saturated with CH₄ at 10% irreducible water saturation until the GC constantly read methane composition greater than 98%. CO_2 was injected at 0.2 ml/min using ISCO pumps C/ D through cell B as shown in Fig. 4. The experiment ended when the



Fig. 7. CH_4 recovery against HCPV of total CO_2 injected at 0.6 ml.



Fig. 8. CH4 recovery against HCPV of total CO2 injected at 0.8 ml.

methane concentration was insignificant from the GC reading (when the mole fraction of produced CO₂ is >98%). Further runs were carried out at increasing CO₂ injection rates of 0.4, 0.6, 0.8, and 1.0 ml/min. At each GC's injection time, the time was noted, and the effluent composition was recorded. The best injection rate was selected and employed as the next step of the experiment (with N₂ as buster gas). The sample was recleaned, dried, and re-saturated with CH₄. Following this, 0.06 HCPV of N₂ was then injected using ISCO pumps A/B through cell A. Further runs were carried out at increasing N₂ booster gas volumes. The experiment was carried out at relevant reservoir pressure of 1500 psig and 40 °C temperature.

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Fig. 9. CH₄ recovery against HCPV of total GO₂ injected at 1.0 ml.

4. Results

4.1. Effect of CO2 injections on methane recovery

To evaluate the CH4 recovery efficiency of each injection rate based on the gas production recorded, the Original Gas in Place (OGIP) was determined using Eqn. (10). The porosity obtained from the Helium Porosimetry, the gas formation volume factor was evaluated at experimental conditions with the compressibility factor (Z), obtained numerically from models in the works reported by (Shabani and Vilcaez, 2017; Ziabakhsh-Ganji and Kooi, 2012). The CH4 gas production was recorded online using the gas flow meter, and its composition was analysed regularly (at 5 min sequence) via the GC machine. The displacing gas migration and breakthroughs were observed in real-time, and the dispersion coefficient, recovery swept efficiency, and CO₂ storage was evaluated. The experiment stopped when the CO2 produced was far more than its injected amount (the produced gas contained an insignificant amount of CH₄). The experimental results for the CO₂ produced at different injections (0.2-1.0 ml/min) were presented in Fig. 17. The miscible displacement takes place at the front of supercritical CO2 (ScCO2). The CO2 injection up to 0.21 HCPV results in less CO2 concentration at the outlet, insignificance natural gas contamination. In the process, the initial CH4 recovery increased linearly. When 0.22 HCPV were injected, the composition of CO2 in the effluent stream raised to about 5%, invariable the percentage recovery increased by 3% to its peak value of 35%. The point can be deemed as a breakthrough point. For injections after breakthrough, a sharp increase in the CO2 outlet composition was noticed until 0.3 HCPV of CO2 were injected, resulting in a high CH4 recovery decline. Further injections to 0.372 HCPV showed less effect with both fractions of CO2 produced and CH4 recovery efficiency kept almost unchanged. This indicates the displacement has reached an endpoint. The same graph pattern was observed at $0.2\,$ ml/min injection. However, the CO_2 presence in the exit stream occurred earlier than that for 0.4 ml/min (Fig. 6), while its maximum CH4 recovery was recorded when a total of 0.3 HCPV of CO2 was injected into the system. This can be seen in Figs. 5 and 17, respectively. A similar trend was noticed in other injection rates, but the decline in methane recovery was huge at higher injection rates (0.6-1.0 ml/min)

13.44 16.80

Table 2

0.8

1.0

2.64 3.49

6.06

7.63

10.99

CH4 Recovery (96) 59.63 39.97

26.61

24.59

27.74

Dispersion Coefficient (10⁻⁸ m²/s)

Results sun	teaults summary for all the experimental runs at diffusion coefficient of 18.48 10^{-8} m ² /s.							
Q (ml/ min)	Interstitial Velocity (10 ⁻⁵ m/s)	Total CO ₂ Injected (HCPV)	CO ₂ Breakthrough (HCPV)	CO ₂ Injected Store (%)				
0.2	3.36	0.36	0.20	35.62				
0.4	6.72	0.37	0.22	58.03				
0.6	10.08	0.56	0.33	56.82				

0.54

0.53

66.10 68.51

0.81

0.90



Fig. 10. Plot of dispersion to diffusion coefficient ratio against intersti-tial velocity.



Fig. 11. Plot of longitudinal dispersion coefficient ratio against injection rates.

with an average of 20% decline, as seen in Fig. 17. More so, the breakthrough graphs at higher injection rates (0.6-1.0 ml/min) in Figs. 7-9 showcase high slope due to the curves' stiffness after the CO2 breakthrough. This signifies the possibility of high miscibility between



Fig. 12. Concentration profile at 0.4 ml/min optimum conve CO2 injection.

the CO2 and CH4 during the displacement process. Overall, there was a substantial methane recovery at lower injection rates (0.2-0.4 ml/min) than those at high injections (0.6-1.0 ml/min). At these rates, poor recovery and sweep efficiency were observed due to higher interstitial velocity. Abba et al. (2018) reported a high interstitial velocity tends to increase the turbulence and eddy current of the flow profile and agitate the gas species' molecules, facilitating the interaction collision between the displacing and displaced gases. This results in a high dispersion coefficient, as seen in Table 2.

$$OGIP = \frac{V_b \varphi(1 - s_{wi})}{B_g}$$
(10)

4.2. Dispersion coefficient and dispersivity

The different injection rates were employed to determine the optimum injection rate from the range of interest. The compositions of CO2 produced were used to evaluate the miscibility rate of CO2-CH4 interaction by adopting the longitudinal dispersion coefficient KL as the fitting parameter. The values of the dispersion coefficients for different injection rates are shown in Table 2. The characteristics length scale of mixing (L) was adjusted in the OriginPro software regression tool to provide a better fit as advised by (Hughes et al., 2012; Liu et al., 2015; Abba et al., 2018), given that the interstitial velocity was kept



Fig. 13. Effects of booster gas on CO2 breakthroughs.

unchanged for each run as assumed in the 1D advection-dispersion equation in Eqn. (2). As expected, the higher injection rates showed an early breakthrough in the CO₂; this agrees with the works reported by (Liu et al., 2015; Abba et al., 2018). Looking at Eqn. (5), It was evident that precise and reliable simulation of dispersion during enhanced recovery process requires a detailed understanding of molecular dispersion (D), tortuosity ($\tau),$ and dispersivity ($\alpha)$ at the condition relevant to natural gas displacement in porous media. The latest two parameters are properties of the porous medium (core sample) of which α can be determined from a set of experimental data in which the flow velocity through the medium is increasing at reasonable intervals like those described in this study. Although the pressure and temperature dependence of longitudinal dispersion coefficient (KL) are acquired predominantly by that of D. Thus, accurate values of the molecular diffusion coefficient are prerequisites to a reliable dispersion correlation. Fuller, Schetter, and Gittings (1966) developed a numerical model through computer-aided correlation of 340 experimental points, expressed in Eqn. (7) was used to evaluate the molecular diffusion coefficient of CO2-CH4 at conditions relevant to enhanced gas recovery. The molecular diffusion coefficients, D, at experimental conditions of 1500 psig pressure and 40 °C temperature were evaluated. Using the measured grain diameter of 57.15 µm reported by Abba et al. (2018) as the characteristic length scale of mixing, the medium Peclet numbers were evaluated using Eqn. (4), taking (u) as the average interstitial velocity of the runs as an input variable. The P_{em} recorded were 0.02, 0.03, 0.03, 0.04, and 0.05. All values were <0.1, which indicated the flow



Fig. 14. Concentration profile comparison at 6% buster gas.



Fig. 15. Concentration profile comparison at 29% buster gas.

Table S

Case Study	Q (ml/min)	Interstitial Velocity (10 ⁻⁵ m/ s)	CO ₂ Injected (HCPV)	CO ₂ Injected Stored (%)	CH4 Recovery (%)	Dispersion Coefficient (10 ⁻⁰ m ² / s)
Without N ₂	0.2	3.36	0.36	35.62	59.63	2.64
booster	0.4	6.72	0.37	58.03	39.97	3.49
	0.6	10.08	0.56	56.82	26.61	6.06
	0.8	13.44	0.81	66.10	24.59	7.63
	1.0	16.80	0.90	68.51	27.74	10.99
With N ₂ booster	(HCPV)					
10100-003-000000000	0.06	6.72	0.492	57.91	89.17	3.59
	0.13	6.72	0.496	68.67	64.81	2.78
	0.19	6.72	0.504	49.06	75.95	3.27
	0.29	6.72	0.348	63.47	44.39	2.59



Fig. 16. A plot of differential pressure drops against experimental time with and without booster gas.

mechanism is dominated by diffusion within the entire experimental tests. Furthermore, the dispersivity (α) can be constructively determined by fixing Eqn. (5) to the plots of K_L/D against u/D, which is a straight line shown in Fig. 10. Considering the reports of (Coats, K.H & Whitso 2004; Keith H. Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012), they dispensed that the values of the dispersivity (α) in consolidated porous media are mostly smaller than 0.01 ft (0.003 m). Hughes et al. (2012) recorded dispersivity in a range of 0.0001–0.0011 m using Donnybrook core. Abba et al. (2018) reported 0.0006 m of dispersivity and tortuosity of 29 in Bandera grey core plug with properties similar to those one used in this work. Generally, the longitudinal dispersion coefficient increases with an increase in flow velocity due to turbulence or eddy current development. The highest and least dispersion were recorded at maximum and minimum injection rates, as evident in Fig. 11 when the dispersion coefficients were plot against tests injection rates, invariably a linear relationship.

Injection at a low rate mainly results in more extended breakthrough (resident) time for gases in contact and increases the mixing of the gases yet again (Abba et al., 2018). This nascent mixing makes it challenging to use conventional CO₂ injection without an external factor to achieve higher CH₄ recovery and CO₂ storage at the same time. To curtail this problem, the inclusion of N₂ as a booster during CH₄ displacement by CO₂ injection was discussed in the next section. On this occasion, a 0.4 ml/min injection rate was employed for further CO₂ injection due to its significant combined CH₄ recovery and a substantial amount of injected CO₂ (HCPV) stored.

4.3. Effect of N2 as a booster gas during CO2 flooding

The breakthrough indicates the first contact in which the injected gas species (CO_2 or N_2) came in contact with the displaced CH_4 gas along the core sample's length scale during the experiment. For conventional CO_2 flooding, the longer the breakthrough, the lower the sweep recovery efficiency due to the nascent mixing between the CO_2 and CH_4 , as evident with higher dispersion coefficients. This results in natural gas

production with low calorific value and high purification cost, rendering the process uneconomical. In contrast, a delay in breakthrough was observed when N2 was employed as a buster gas. Four sets of experiments were carried out at 1500 psig, 40 °C, and at varying booster gas volume of 0.06–0.29 HCPV. The variation in effluent compositions with total gas injection (HCPV) was monitored, as seen in Fig. 12. At the same time. Fig. 13 presented the effect of N₂ booster gas on CO₂ breakthrough compared to the conventional CO2 injection at 0.4 ml/min. The CO2 residence time was delayed for all the booster gas volumes employed. The injected amount of N2 prior to the CO2 injection exhibits a repressurization effect to produce maximum levels of CH4 and a minimum fraction of CO2 in the effluent stream of the core holder before CO2 breakthrough due to its high conductivity. This affirmed the potential of N2 for reservoir maintenance applications. The increase in booster gas volume was directly proportional to delayed CO2 breakthrough, with the maximum at 30% (0.3) fraction of pore volume. The booster composition was monitored throughout the experiments from the GC machine. The higher the booster gas in the system, the more N₂ gas was recorded at the product stream, as seen in Fig. 15. This was a similar trend observed during the CO2 flooding at higher injection rates. However, lower product contamination was recorded at lower booster gas volume with improved CH4 recovery and CO2 storage compared to that at 0.4 ml/min optimum CO2 flooding. This implies that injecting a small amount of N2 before CO2 injection in the reservoir promotes good CH4 recovery and enables substantial volumes of CO₂ storage within the core plug's pore spaces. The introduction of N2 displaces a larger amount of the CH4 until it reached its breakthrough; this allows most of the CO2 later injected to be trapped within the rock space without mixing with the nascent CH4. More so, when the CO2 reaches its breakthrough, a substantial clean volume of CH4 has been recovered. The CO2 find it difficult to disperse itself into the CH4 in the presence of N2, which acted as a barricade wall between the CO2 and CH4 interphase.

To optimize both CH₄ recovery and CO₂ storage, the fraction of the produced CO₂ and N₂ (X) at the exit stream must be minimized, while the change in the produced CO₂ fraction (Δ X) must be maximized. In so doing, the concentration profile curve can be flatting, invariably higher CH₄ recovery and CO₂ storage, as seen in Fig. 3. Natural gas products based on N₂ contaminants are more friendly than CO₂ based contaminants because most natural gas exploration fields accommodate higher nitrogen contamination than CO₂ based impurities. The sweetening process of CH₄-N₂ contamination is less expensive than CH₄-CO₂ due to the high compression energy cost and depressurizing process employed.

More so, substantial CO2 storage at the maximum booster amount was observed when a total fraction of 0.348 HCPV of CO2 was injected. This was within the range of total CO_2 injected during 0.2 and 0.4 ml/min conventional CO₂ flooding. However, the later recorded high CO₂ storage than the latest 0.2 and 0.4 ml/min injections. The excess amount of N₂ injected acted as a retardant, creating a thin barrier between the $\rm CO_2-CH_4$ interface, promoting the CO2 to descend for storage due to gravity. The produced CH4 was grossly contaminated with the N2 than CO2, as seen from the N2 and CO2 intersecting the CH4 curve in Fig. 15. Thus, the least recovery was recorded due to the excess amount of booster gas used. The reduction in the nascent CO2-CH4 mixing was achieved from the low dispersion coefficient value recorded. Furthermore, the experimental run at 0.06, 0.13, and 0.19 fraction of HCPV has a similar amount of total CO2 injected with the 0.6 ml/min conventional CO2 flooding. The test at 0.13 HCPV of N2 buster gave the highest CO2 storage presented in Table 3. This value was characterised by the large differential pressure drop (dp) shown in Fig. 16. The highest recovery occurred when the least booster gas was

used. This value was characterised by the least N₂ product contaminant and differential pressure (dp). However, it recorded the highest mole fraction of CO₂ produced, as presented in Fig. 14. Therefore, the presence of N₂ as a booster or impurity causes large changes in supercritical CO₂ behaviour as reported by (Xidong et al., 2019; Hughes et al., 2012; Janssen et al., 2013; Abba et al., 2018). To reduce gas separation cost, various authors proposed a longer residence (breakthrough) time should be considered for gas injection (Xiangchen et al., 2018) provided the excessive CO₂-CH₄ miscibility can be minimized. This will allow a large storage volume of CO₂ and, at the same time, recovered most of the residual natural gas. It worth noting that higher displacement efficiency is obtained at lower cushion volume.

5. Conclusions

A core flooding experiment was carried out to investigate the production of CH4 during enhanced gas recovery displacement scenarios in N₂ as booster gas, to register the effects of its existence. CH₄ recovery was influenced by the inclusion of N2 as booster gas before the CO2 injection into the reservoir. The displacement efficiency of the current research exhibits improved results than the conventional CO2 flooding. Overall, an improved CH₄ recovery, substantial CO₂ storage and less miscibility effect were noticed than conventional CO2 flooding. The best-improved results occurred at the lower booster gas volumes with the optimum at 0.13 fraction of HCPV. This signifies the potential role of N_2 as a buster medium on CH4 recovery and CO2 storage. During the displacement process, the N_2 acts as a barrier wall, creating a thin film layer between CO₂ and CH4, making it difficult for the CO2 to penetrate and disperse into the CH4 phase due to the blanketing effect of N2 gas. This why a minimum length scale of mixing between displacing and displaced gases was achieved at 0.13 and 0.29 HCPV of buster gas. The critical temperature and pressure

Nomenclature

- Mole fraction of injecting specie x Change in mole fraction of injecting specie ΔX s Slope С Concentration Vb Bulk volume Swi Water of saturation SiCO2 Supercritical carbon dioxide HCPV Hydrocarbon pore volume D Diffusion coefficient, m²/s Flowrate, mil/min 0 Dimensionless time tD Dimensionless distance xD Longitudinal dispersion, m²/s Kı Permeability, md k A Cross section area, cm² L Length of characteristic scale dp Differential pressure across the plug, atm Lexp Experimental length, m Viscosity, cP μ Pressure, psig P т Temperature, K Interstitial velocity, m/s u φ Core porosity, % α Dispersivity, m Tortuosity τ Peclet number Pe Pem Medium Peclet number
- r Radius of core sample, m

points of CO₂, N₂ and CH₄ are 31.05 and 1070, -146.9 and 492, -82.55 °C and 667 psig, respectively. Both nitrogen (N₂) and CO₂ can increase CH₄ recovery from oil and gas reservoirs. However, CO₂ drawbacks are mainly excessive mixing and high compression ratio, thus hindering the overall process non-economically viable.

In contrast, N₂ can be recovered virtually from the atmospheric air through air separation units. It requires less compression ratio than CO_{2} , so a lower amount of it is needed to create high pressure in the CH_4 reservoir. Further work will entail an examination of the effect of connate water salinity on this novel approach.

Credit author statement

I Nuhu Mohammed was responsible for conducting the experiments, graph plotting using OriginPro software, data analysis, and preparing most part of the manuscript. Abubakar J. Abbas and Godpower C. Enyi contributed to the experimental design methodology, and research supervision. All the co-authors provided support and motivation for this work, from the experimental design, data analysis, and review of the results.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A

Fig. 17. CO2 produced against HCPV of CO2 injected at different injection rates of 0.2-1.0 ml/min



Fig. 18. Concentration profile comparison at 13 and 19% booster gas

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Enhanced gas recovery by nitrogen injection: The effects of injection velocity during natural gas displacement in consolidated rocks

Nuhu Mohammed^{*}, Abubakar J. Abbas, Godpower C. Enyi, Donatus E. Edem, Salihu M. Suleiman

Department of Petroleum and Gas Engineering, University of Salford Manchester, M4 5WT, United Kingdom

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Keywords: Dispersion coefficient Enhanced gas recovery Breakthrough Concentration profile Methane displacement	The choice of the flow velocity in EGR thus becomes important since higher injection rates could lead to pre- mature mixing of the fluids and lower injection rates generally provide longer resident times for the fluids in contact and indirectly increases the mixing of the gases. Additionally, the medium peclet numbers mostly indicate the best injection rates that translate to a smoother displacement with a lower dispersion coefficient during the EGR process. Therefore, N2 Injection into natural gas reservoirs offers the potential to higher recovery efficiency with less mixing compared to conventional CO ₂ injection. The atmospheric air contained 79% of N ₂ , making it readily available than CO ₂ with 400 ppm air composition. More so, N ₂ requires less compression ratio, which is why a lower amount of it was required to initiate much pressure in the CH ₄ reservoir during displacement. These made the use of N ₂ more economically feasible and friendly for the EGR process. A labo- ratory core flooding experiment was carried out to simulate the effect of injection rates. The results showed that a medium peclet number could be used to predict the best injection rate that translates to a smoother displacement with a lower dispersion coefficient during the EGR process. CH ₄ recovery and efficiency were highest at lower injection velocities experienced in both core samples. This could be attributed to insignificance nascent mixing observed as seen on their recorded low longitudinal dispersion coefficient rescovery and efficiency due to their high interstitial velocities as the N ₂ plumes transverses into the core sample during CH ₄ displacement. Overall, the least methane production and efficiency were ourcome, the day particle as a result of the heterogeneity effect due to the presence of higher clay contents in Bandera core sample were overcome, the cay particle occupied those pores thereby sealing some of the flow paths within the pore matrix. This reduces the flow channels, significantly, through which the				

1. Introduction

Primary oil and gas recovery methods unlock only about 10% of the oil and gas initially in place, while secondary recovery efforts obtain an additional 20-40%. Therefore, a substantial quantity of oil and gas remains in the formation until more advanced recovery methods are employed. These methods are known as enhanced oil or gas recovery techniques (Anonymous, 2020). Enhanced gas recovery (EGR) and storage by CO_2 injection are gaining recognition within the research environment as its combined natural gas (CH₄) recovery and CO₂ storage benefits. Even though, both nitrogen $\left(N_{2}\right)$ and CO_{2} can be used to

increase hydrocarbons (HCs) yield from oil and gas reservoirs. However, CO2 drawbacks are mainly excessive mixing and high compression ratio, thus hindering the overall process less economical. In contrast, N₂ could be easily obtained through cryogenic air separation. It requires less compression ratio than CO₂, which is why a lower amount of it was required to initiate much pressure in the CH₄ reservoir. Also, the sweetening process cost of natural gas contaminated with N2 is less than that with CO_2 . This was why the fraction of produced N_2 tolerance is higher than the CO₂ limit during the natural gas exploration.

The promotion of EGR is still at its infant stage due, to the excessive mixing between the injected (displacing fluid) CO_2 and the nascent

* Corresponding author. E-mail address: n.mohammed5@edu.salford.ac.uk (N. Mohammed).

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displaced fluid (natural gas) during the flooding process (Oldenburg and Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This adulterates the recovered natural gas and thus, reduces its heating and market value, which results in the high cost of the sweetening process to maintain its purity standard for consumption (Oldenburg and Benson, 2002; Sim et al., 2009). Such an overall problem has not only limited the EGR project to a few pilot trials (Pooladi- Darvish et al., 2008) but also made the process apparently uneconomical because of unprecedented mixing with the displaced gas. This makes the whole phenomenon to be poorly understood (Patel et al., 2016). Thus, finding an alternative gas with good displacement properties and minimal miscibility could be a nice development for the oil and gas industry.

Several authors (Gu et al., 2019; Hughes et al., 2012; Jans 2018; Abba et al., 2018) have carried out an extensive study on how to delay CO_2 breakthrough time during EGR process. Among them, Abba et al. (2018) and Gu et al. (2019) were able to achieve reasonable improvement. Abba et al. (2018) use varying connate water concentration and was able to delay CO_2 breakthrough by 20 min at a concentration of 10% wt. sodium chloride (NaCl). On the other hand, Gu et al. (2019) use different mole ratios of CO2/N2 mixture gases in coalbed core samples. They reveal that injection of No-rich mixtures contributes to preventing the nascent early breakthrough of injected CO2 and safely stored large volumes of CO2 into the shale sediment over the long term (Gu et al., 2019). The injection of CO_2 into the reservoir generally results in premature breakthrough due to nascent mixing with methane, eventually limiting it application for efficient natural gas recovery. This was the reason why many researches on carbon dioxide injections were tailored toward storage rather than recovery. Furthermore, most of the works on the effect of CO2 injection on gas production are simulation-based. Till date, no established efficient alternative gas and injection rate capable of unlocking the residual gas beneath the ground has been highlighted. This necessitated the need for an in-depth study to use N₂ as an alternative to minimize such complex phenomenon of gas-gas miscibility since both CO2 and CH4 are miscible in all outcomes (Abba et al., 2018; Honari et al., 2016). The choice of the flow velocity in EGR thus becomes important since higher injection rates could lead to premature mixing of the fluids while lower injection rates generally provide longer resident times for the fluids in contact and indirectly increases the mixing of the gases yet again. In this research, the experimental study of the effect of N₂ injection rates during the EGR process using consolidated rocks was conducted. Determining the best and optimum injection rate is vital for better recovery and less miscibility. This could provide reservoir engineers, geologist, and production engineers with the desired tools to successfully characterize the transport of injected N2 as it plumes transverse within the porous media during the displacement process. The mechanism behind the concept of the enhanced gas recovery process is well demonstrated using a dispersion theory as will be explained in the next two sections.

1.1. Dispersion theory and equation

Newberg and Foh (1988) used a single parameter diffusion-like model based on the 1D Advection-Dispersion equation (Perkins and Johnston, 1963; Coats et al., 2009). The model is mostly used to describe the flow of gas transport through a porous medium along the x-direction as shown in Eq. (2.1):

$$K_{L}\frac{\partial^{2}C}{\partial x^{2}} - u \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
(2.1)

The effluent composition (C) from the GC at distance (x) under time (t), longitudinal dispersion coefficient (K_1), and interstitial velocity (u) are key parameters in the above equation. The displacement of methane by N_2 in consolidated rocks is governed by Eq. (2.1). This model is

widely accepted to simulate fluids movement in porous medium. However, simulation studies have proved that using the equation in its current form resulted in some abnormal behaviour named upstream migration. It occurs especially when the concentration gradient (dC/dX) along the length scale becomes positive, which is invariable like the case of supercritical N₂ flowing through a contaminant after breakthrough in the porous medium generating a large magnitude of both dC/dX and dispersion coefficient. Invariably Eq. (2.1) can be re-written in a dimensionless form (Mamora and Seo, 2002) as follows;

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2.2)

Where;

Parameter	Symbol	Expression
Peclet number	Pe	uL
		$\overline{K_L}$
Dimensionless time	t _D	tu
		L
Dimensionless distance	x_D	<u>x</u>
		L
Interstitial velocity	u	Q
		$\pi r^2 \varphi$

Since the injection of N_2 is at x = 0, then Initial condition: C = 0 at $t_D = 0$,

Boundary conditions: C = 1 at $x_D = 0$, $C \to 0$ as $x_D \to \infty$ Therefore, the solution to Eq. (2.2) maybe presented as follows:

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{t_D/P_e}} \right) + e^{P_e x_D} erfc \left(\frac{x_D + t_D}{2\sqrt{t_D/P_e}} \right) \right\}$$
(2.3)

The effluent core flooding composition could be fitted into the analytical solution of the 1D differential Advection Dispersion (AD) equation (Eq. (2.3)) in terms of the *Péclet* number to evaluate the corresponding dispersion coefficient. The real dispersion coefficient for the experiment is the value which provides the optimum synergy between the experimental result compared to the numerical solution.

In (1963) Perkins & Johnston proposed a widely accepted model that can predict the dominant displacement mechanism during the EGR process in a porous medium. This model equation can be present as:

$$\mathbf{P}_{\rm em} = \frac{u_m d}{D} \tag{2.4}$$

Where;

 P_{exp} is the experimental medium Péclet number, which can be evaluated using the average interstitial velocity (u) in m/s, D is the molecular diffusion coefficient in m²/s, and d is the characteristic length scale in meters. The characteristic length scale is defined as the average medium-grain diameter of the core sample or sand pack. Generally, at $P_{\rm cm} < 0.1$, diffusion dominates the dispersion process, and at $P_{\rm cm} > 10$ advective mixing dominates the dispersion process. The analytical solution to Eq. (2.3) is used to fit the concentration profiles obtained from the experimental data to evaluate the dispersion coefficient.

Coats et al. (2009) correlated the dispersion coefficient with the molecular diffusion coefficient as shown in Eq. (2.5).

$$\frac{\kappa_l}{D} = \frac{1}{\tau} + \alpha \frac{u_m^\prime}{D} \tag{2.5}$$

Here, α is in meter (m) and is called the dispersivity of the porous medium, and n represent an exponent. The tortuosity (τ) can range from 1 to as high as 13 or more for consolidated rocks as reported by Honari et al. (2013). The tortuosity τ , can be obtained empirically through various methods, whereas n is mostly determined using a core flooding system (Hughes et al., 2012).

1.2. Diffusion theory and equation

The diffusion coefficient (D) signifies the extent or magnitude at which a substance or fluid disperses through a unit area (m²) per unit time (s) at a given unit of a concentration gradient. The proposed empirical model which relates the molecular diffusion, temperature, and pressure for empirical diffusion coefficient determination as indicated by (Hughes et al., 2012; Liu et al., 2015) was developed by Takahashi and Iwasaki in (1970). Similarly, empircal equation has been tested by various researches in determining the real and accurate diffusivity using Eq. (2.6) at conditions applicable to EGR by CO₂ injection. The diffusion coefficient of CO₂ in CH₄ was dignified at 298–348 K and pressures of 5–15 MPa in a porous bronze plug (Takahashi and Iwasaki, 1970). The results were well within the range of conditions applicable to the EGR process (Abba et al., 2017).

$$D_{\text{CO2,CH4}} = \frac{\left(-4.3844 \times 10^{-13} \, P + 8.5440 \times 10^{-11} \,\right) T^{1.75}}{P} \tag{2.6}$$

where $D_{\rm CO2},_{\rm CH4}$ is the molecular diffusion coefficient of CO₂ in pure CH₄ calculated in m² s⁻¹ with P in MPa and T in K. The absolute average deviation (AAD) of this correlation from the experimental data was 1.5% over the range of 298–348 K and 5–15 MPa (Abba et al., 2017, 2018). In this study, a different model was used to cater for the inclusion of Nitrogen (N₂) gas during the natural gas displacement. This model equation was presented in Eq. (2.7). It is a correlation formula obtained by Fuller et al. (1966) by means of computer-aided correlation of 340 experimental points, expressed as:

$$D_{\text{N2,CH4}} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{\left(1/\mu_{N_2} + 1/\mu_{CH_4}\right)}}{P \sum V_{N_2} \sum V_{CH_4} \left(\sum V_{CH_4}\right) \left(\sum V_{CH_4}\right)^{1/3}}$$
(2.7)

Where $(\sum V_{N_2})$ and $(\sum V_{CH_4})$ are the values derived from the summation of atomic diffusion volumes of N₂ and CH₄ molecules respectively. These values and other simple molecules are presented in Table 1.

The equation was further simplified after inserting the values of atomic diffusion volumes and the molecular weight of nitrogen and

 Table 1

 Atomic diffusion contributions for various gas element and molecules

S/N	Molecule	Diffusion volume
1	Не	2.67
2	Ne	5.98
3	Ar	16.2
4	Kr	24.5
5	Xe	32.7
6	H ₂	6.12
7	D_2	6.84
8	N ₂	18.5
9	O2	16.3
10	Air	19.7
11	CO	18.0
12	CO ₂	26.9
13	N ₂ O	35.9
14	NH ₃	20.7
15	H ₂ O	13.1
16	SF ₆	71.3
17	Cl ₂	38.4
18	Br ₂	69.0
19	SO ₂	41.8
20	C	15.9
21	Н	2.31
22	0	6.11
23	N	1.51
24	F	14.7
25	Cl	21.0
26	Br	21.9
27	I	29.8
28	S	22.9

(Source: Fuller et al., 1966)

methane. The same was applied for carbon dioxide and methane displacement mechanism. These simplified equations were presented in equations 2.8, and 2.9 respectively.

$$D_{\rm N2,CH4} = \frac{10.2 \times 10^{-11} T^{1.75}}{P}$$
(2.8)

$$D_{\text{CO2,CH4}} = \frac{8.2 \times 10^{-11} T^{1.75}}{P}$$
(2.9)

where T and P are temperatures and pressure in kelvin (K) and megapascal (MPa) respectively. For example, at the same temperature and pressure, Eq. (2.9) was validated using the experimental work of Abba et al. (2018). The molecular diffusion coefficient ($D_{CO2,CH4}$) was found to be 22.52×10^{-8} m²/s, which was 0.18% absolute average deviation (AAD) when compared with Abba et al. (2018) results.

2. Materials and method

In this research, an experimental study using a core flooding system to investigate the effect of injecting velocity during EGR process. The experiment was conducted by saturating the core plug with CH_4 and injecting of N_2 at different injection rates. The core plugs used were *Berea* and *Bandera* Gray sandstones whose properties as presented in Table 2.

2.1. Materials used

For decades, sandstones core samples have been widely recognised as the best rock for testing the efficiency of chemical surfactants. Berea sandstone is a sedimentary rock whose grains are predominantly sandsized and are composed of quartz held together by silica. The relatively high porosity and permeability of Berea sandstone make it a good reservoir rock. There are 3 major variations of sandstone namely Slit rock, Liver rock, and Dundee. The one used for this experiment was the Slit rock type with visible laminations and classified as homogenous. It has a permeability rating between 100 and 300mD. On the other hand, Bandera gray is non-homogenous due to the presence of higher clay contents sealing off the narrower paths within the pore matrix. Thus, making it low permeable and less porous. Both core samples originated from Cleveland quarries in Texas, USA. Core plug of dimension 1.0-inch diameter by 3.0-inch length was used as present in Table 2. The mineralogy of the core samples is presented in Table 3. For consistency, the porosity and permeability of the sandstone core samples were determined and compared with the ones provided by the supplier (Kocurek Industries INC, Hard Rock Division, 8535 State Highway 36 S Caldwell, TX 77836, Texas USA). Research-grade CO2, N2, and CH4 with a purity greater than 99.99% were sourced from BOC UK.

2.2. Apparatus and procedure

2.2.1. Apparatus

The experimental set-up consists of mainly two units; Core Lab UFS-200 core flooding system with inbuild Smart Flood software and packed column design Agilent 7890 A model Gas Chromatography (GC) machine model. The online concentration measurement of core flooding

Table 2

Dimensions	Dimensions and petrophysical properties of the core plugs.							
Core sample	Length (mm)	Diameter (mm)	Bulk Vol. (cm ³)	Porosity (%)	Gas Permeability (md)			
Bandera gray	76.02	25.31	38.27	19.68	32			
Berea	76.07	25.49	38.85	20.53	214			

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Table 3

The mineral contents of Bandera and Berea gray core samples.

Mineral Class	Minerals	Chemical Formula	Mineral Rocks (%)	
			Berea gray	Bandera gray
Phyllosilicates (Clays)	Muscovite	KAl ₂ (AlSi ₃) O ₁₀ (OH) ₂	-	-
	Biotite	K(MgFe ²⁺) (AlSi ₃) O ₁₀ (OH) ₂	_	_
	Illite	K _{0.75} (Al _{1.75} [MgFe] _{0.25}) (Al _{0.5} Si _{3.5}) O ₁₀ (OH) ₂	1.0	10
	Chlorites	(Mg, Fe) ₃ (Si, Al) ₄ O ₁₀ (OH) ₅ (Mg, Fe) ₃ (OH) ₆	2.0	1.0
	Kaolinites	Al ₂ SiO ₅ (OH) ₄	5.0	3.0
	Montmorillonite	$M_{0,3}Al_2(Al_{0,3}Si_{3,7}) O_{10}(OH)_2 M^+ = Ca^{2+}, Mg^{2+}, K^+, etc.$	-	-
Tectosilicates	Quartz	SiO ₂	87	59
	Albite	(K, Na) AlSi ₃ O ₈	2.0	12
Carbonates	Calcite	CaCO ₃	2.0	-
	Dolomite	Ca, Mg (CO ₃) ₂	1.0	15
Oxides	Ilmenite	Fe ²⁺ TiO ₃	-	-

effluents was achieved using the GC machine. These values were used in plotting the injection fluids concentration profile and methane recovery efficiency evaluation as the experiment progress with time. Schematic of the equipment set-up is presented in Fig. 1.

The UFS-200 core flooding system is rated to 5000 and 3750 psig overburden and pore pressure respectively. The injection system of the equipment is made up of a pair of dual ISCO two-barrel metering pump system (A/B and C/D) for constant flow, pulseless transition and to maintain an accurate flow rate range of 0–200 ml/min with a maximum pressure rating of 3750 psig. The pumps are attached to a pair of two stainless-steel floating piston accumulators which are also rated for 5000 psig working pressure and temperature of 177 °C. They are designed for injection of the fluids of interest and can withstand up to 7500 psig test pressure. Hydraulic pump with a maximum output of 10,000 psig was used to set the overburden confining pressure. The Smart Flood 1.0 software forms an essential unit of the system which interfaces the UFS system and the computer data-acquisition-control (DAC) system hardware. It generates on-screen automatic logging of

test data for all measured values like pressures, temperatures, volumes, etc., to a computer data file. A Rosemount Static DP transmitter with an accuracy of 0.0055% was responsible for measuring the differential pressures across the entire Hassler-type core holder, which was used to house the core sample. The core sample is clutch inside the core holder by a Viton rubber sleeve. A core holder heat jacket (containing 1 m tubing coil) to simulate the required temperature was also employed with an accuracy of 0.1%. Dome type back pressure regulator integrated into the flooding system ensured the confinement of the desired pressures within the core holder. Such desired pressure regulator pass through the mass flow controllers, that measure the volume of the actual effluents produced before been analysed by the GC system in place.

2.2.2. Procedure

The core sample was dried overnight in an oven at 105 $^\circ \rm C$ for moisture removal and other volatile compounds. The dried sample was wrapped with cling film and then foil paper before inserted into a heat



Fig. 1. Schematics of experimentational set-up for N_2 gas injection during methane displacement. $\label{eq:rescaled} 4$

shrink. This is vital to avoid viscous fingering and the penetration of the gases into the ring-shaped core holder through the sleeve. It was then loaded into the core holder and staple with clamps from both ends. Hydraulic oil was then pumped into the ring-shaped core holder to provide the desired overburden pressure, which was kept at a minimum of 500 psig above the pore pressures to avoid fracturing of the core sleeve. The heat jacket was then installed on the core holder and the temperature step-up (40 °C) was observed prior to methane saturation. Backpressure was engaged, CH4 was slowly injected into the core sample from the $\rm CH_4$ cylinder through ISCO pumps A/B and accumulator or cell A to saturate the core plug until the GC constantly read methane >98%. Pumps A/B was stopped and N2 was injected at 0.2 ml/min using ISCO pumps C/D through accumulator or cell B. The experiment elapsed when the methane concentration was insignificant from the GC reading or the CO2 concentration was >98%. Further runs were carried out at increasing $N_{\rm 2}$ injection rates of 0.4, 0.6, 0.8, and 1.0 ml/min. These flowrates were selected based on the medium peclet number $\left(P_{em}\right)$ presented in Table 4. At each injection time of the GC, the time was noted and the effluent composition which was later used to evaluate CH4 recovery efficiency and dispersion coefficient was recorded. The investigation was carried out at 1500 psig pressure and 40 °C temperature. This condition was chosen based on a normal gas pressure reservoir with a gradient of 0.451 psi/ft, an average reservoir depth of 1 km, and a geothermal temperature of 35-40 °C/km.

3. Results and discussion

3.1. Original gas in place (OGIP) determination

In order to evaluate the CH_4 recovery efficiency of each injection rate, the Original Gas in Place (OGIP) must be determined.

$$OGIP = \frac{V_b \varphi(1 - s_w)}{B_e}$$
(2.10)

 V_b is the bulk volume of the reservoir ft^3 , φ is reservoir porosity, S_w is formation water saturation, and Bg is gas formation volume factor, ft^3/scf .

$$B_g = \frac{P_{sc}}{T_{sr}} \times z \frac{T}{P}$$
(2.11)

Where z is gas compressibility factor, P_{sc} and T_{sc} are pressure and temperature at standard conditions; P and T are pressure and temperatures at desired conditions. Taking P_{sc} and T_{sc} to be 14.696 psia and 18 °C (291.15 K), Eq. (2.11) becomes;

$$B_g = z \frac{1}{20P}$$
(2.12)

To determine the z factor from chart, a pseudo-reduced properties/ conditions of CH_4 at the experimental conditions must be deduced. The correlation for the pseudo pressure is presented as follows:

$$P_r = \frac{P}{P_c}$$

And for the temperature;

Table 4

Petrophysical	properties and	OGIP for	the core plug	s under i	investigation.

Core sample	Length (mm)	Diameter (mm)	Porosity (%)	Bulk Volume (cm ³)	Gas in Place (cm ³)	Gas in Place (PV)
Bandera gray	76.02	25.31	19.68	38.27	868.7	115
Berea gray	76.07	25.23	20.53	38.85	919.94	115

PV means pore volume.

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 $T_r = \frac{T}{T_c}$

Where P_r is pseudoreduced pressure, P and T are the experimental pressure (1500 psig) and temperature (313.15 K), respectively, P_c is the critical pressure (46 bar or 676 psig), T_r is the pseudoreduced temperature, T_c is the critical temperature of the gas in K. These parameters input variables to evaluate the z factor using the Standing and Katz (1941) chart.

$$P_r = \frac{1500}{676} = 2.22$$
$$T_r = \frac{313.15}{190.6} = 1.6.4$$

Using these values, gas compressibility factor, z, was obtained from the Standing and Katz chart as 0.86.

The obtained z factor was then inputted in Eq. (2.12) and \boldsymbol{B}_g was computed as:

$$B_g = 0.87 x \frac{313.15}{20x1500} = 0.00867 \text{ cm}^3 / \text{scm}^3$$

The porosities and bulk volumes from Table 2 were used to calculate the OGIP of the core plugs. Since the experiment was carried out under dried condition, $S_{\rm w}=0$

$$OGIP = \frac{38.27x0.1968(1-0)}{0.00867} = 868.7 \ cm^3$$

These results summarily is presented in Table 4.

The OGIP mainly depends on the rock porosity and bulk volume as evidence with the Berea gray core sample recording approximately 920 cm³ of natural gas within its pore spaces. Thus, the more the number of void spaces within the reservoir rock the larger the quantity of gas required to fill those empty spaces under normal conditions.

3.2. Repeatability and reproducibility of the experimental rig and method

The iterability of an experiment is vital as it is an indication that the method employed, and the experimental set-up has guarantee reproducibility of result outputs. Prior to the main experiment, test runs were performed to confirm the iterability of the test runs. Two test runs were carried out using N₂ as displacing gas at an arbitrary injection rate of 0.6 ml/min, temperature and pressure of 40 °C, and 1500 psig respectively. The concentration profile was generated from the effluent stream



Fig. 2. Concentration profile for repeatability and reproducibility runs at test conditions.

concentration recorded by the GC as shown in Fig. 2. The dispersion coefficients were determined for runs 1 and 2 as 7.0×10^{-8} and 6.4×10^{-8} m²/s respectively. Considering these values, along with Fig. 2 plot, its evidenced that the method and experimental set-up employed have guarantee reproducibility of results. Therefore, the same methodological procedure would be adopted for subsequent experimental runs.

The choice of the flow velocity in EGR is important because higher injection rates could lead to premature mixing of the fluids and lower injection rates generally provide longer resident times for the fluids in contact and indirectly increases the mixing of the gases again (Abba et al., 2018). The medium peclet number mostly indicate the best injection rate that translate to a smoother displacement with a lower dispersion coefficient during the EGR process, which gives an overview of the injection scenarios employed in this study. Knowing that the displacement mechanism is dominated by diffusion like pattern, the choice of lower injection rates will provide unwrinkled concentration profiles for proper investigation as averse to higher injection rates. The earlier may likely generate higher mixing, and the later, with high values of medium peclet number, will as well increases the mixing of the fluids resulting in poor sweep efficiency. Thus, selecting moderate or optimum gas injection rate is paramount in order to achieve a sustainable, economical, and efficient EGR process. In this research methane recovery efficiency, dispersion coefficient and other selection criteria were useful in selecting the best or optimum injection rate. For this work the core holder orientation was fixed at horizontal orientation for all the core plugs since the effect of gravity for vertical orientation is insignificant as reported by (Hughes et al., 2012; Liu et al., 2015; Abba et al., 2018).

3.3. Effect of injection rates on recovery by N_2 injection

The best N₂ injection rate was selected based on high CH₄ recovery and low dispersion (mixing). Considering Table 5, at lower velocities, flow transport in porous media is mostly diffusion like and, on the other hand, it always dispersion dominant at higher flow velocities (Huysmans and Dassargues, 2005; Yu et al., 1999). Identifying the displacement phenomenon in fluid transport in porous media is quite important especially when investigating solute transport in sandstone rocks. For numerical and empirical simulation, selecting precise and accurate input variables is a precondition to procuring accurate results, reasonable enough to provide the framework for pilot and field displacement process applicable to the EGR process. Therefore, underrating or overrating the injection rate could lead to wrong prediction which could jeopardise the integrity of the concept aim and render the entire technique uneconomical and inefficient.

From Table 5, all the medium Peclet number value, P_{env} within the proposed range of injection rate selected (0.2–1.0 ml/min) fall below 0.1 using the grain diameters (94.66 and 57.15 µm) as length scale of mixing reported by Abba et al. (2018) for *Berea* and *Bandera* gay. This implies diffusion is dominant within the range of injection rates for the experiment. However, for Berea gray, the peclet number (P_{exv}) evaluated from the assumed dispersion coefficient (K_a) at maximum injection (1.0 ml/min) initially gave an indication of diffusion dominant flow but later showed high values of P_{exp} at higher injection (0.8–1.0 ml/min). Thus, making it fell within a transition region between molecular diffusion and mechanical dispersion displacement mechanisms. In both situations where the displacement was dominated by diffusion, the injection rate plays a key role due to its influence on factors that affect mixing between the displacing and displaced fluids. Furthermore, at lower values of P_{exp} where diffusion is the dominant displacement mechanism, flow is driven by the concentration gradient, and the transport is influence by mobility ratio via the flow velocity (Abba et al., 2018).

Tables 11 and 12, in the appendix present the core flooding effluent composition for each of the runs recorded from the gas chromatography for each plug. The Tables presents the percentages by volume of N_2 at each injection point at approximately 5 min intervals to create a concentration profile in Figs. 3 and 4. This was used to evaluate the longitudinal dispersion coefficient using Eq. (2.3). The effect of varying injection rates on breakthrough, methane recovery, and dispersion coefficient were presented in Tables 6 and 7, while the plot of methane recovery efficiency against experimental time is shown in Figs. 5 and 6.

The selection of the fluid flow velocity during EGR thus becomes important and necessary as higher injection rates usually resulted to premature mixing of the fluids, while lower injection rates mostly lead to a longer resident times (breakthrough) for the fluids in contact during CH₄ displacement process. Consequently, it indirectly increases the mixing of these gases. The P_{exp} values give an indication of the optimum injection rates as presented in Table 5, which then transcribe into a greater displacement process.



Fig. 3. Concentration profile for Berea gray at varying injection rate (0.2–1.0 ml/min).

Га	ble	5

Peclet number comparison as injection rate selection criteria.

Core Samples	Q (ml/min)	Interstitial Velocity (10 ⁻⁵ m/s)	Diffusion Coefficient (10 ⁻⁸ m ² /s)	Dispersion Coefficient (10 ⁻⁸ m ² /s)	$P_{em} = \frac{u_m d_p}{D}$	$P_{exp} = \frac{u_m d}{K_{Lmax}}$
Berea gray	0.2	3.18	22.99	9.12	0.013	0.033
	0.4	6.36	22.99	9.12	0.026	0.066
	0.6	9.54	22.99	9.12	0.039	0.099
	0.8	12.72	22.99	9.12	0.052	0.132
	1.0	15.90	22.99	9.12	0.066	0.165
Bandera gray	0.2	3.36	22.99	13.13	0.008	0.015
	0.4	6.72	22.99	13.13	0.017	0.029
	0.6	10.08	22.99	13.13	0.025	0.044
	0.8	13.44	22.99	13.13	0.033	0.059
	1.0	16.80	22.99	13.13	0.042	0.073

K_{Lmax} is the maximum dispersion coefficient for each of the core samples.



Fig. 4. Concentration profile for Bandera gray at varying injection rate (0.2–1.0 ml/min).

Table 6

Effect of injection rates on CH4 recovery and breakthrough.

Core Samples	Q (ml∕ min)	Breakthrough (min)	CH ₄ Produced (cm ³)	$\frac{RF}{OGIP} = \frac{CH_4Preduced}{OGIP} \times 100$
Berea gray	0.2	93.33	640.59	69.63
	0.4	73.32	819.09	89.04
	0.6	42.15	559.45	60.81
	0.8	40.15	476.28	51.77
	1.0	39.99	478.06	51.97
Bandera	0.2	76.32	550.53	63.37
gray	0.4	82.49	652.20	75.08
	0.6	35.65	495.76	57.07
	0.8	26.82	402.13	46.29
	1.0	35.32	313.69	36.11

Table 7

Dispersion coefficient determine	nation for different	N ₂ injection rates.	
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Core Samples	Q (ml/ min)	Interstitial Velocity (10 ^{–5} m/s)	Dispersion Coefficient (10 ⁻⁸ m²/s)	Diffusion Coefficient (10 ⁻⁸ m ² /s)
Berea	0.2	3.18	1.47	22.99
gray	0.4	6.36	4.21	22.99
	0.6	9.54	5.32	22.99
	0.8	12.72	7.84	22.99
	1.0	15.90	9.12	22.99
Bandera	0.2	3.36	5.36	22.99
gray	0.4	6.72	7.80	22.99
	0.6	10.08	10.10	22.99
	0.8	13.44	10.35	22.99
	1.0	16.80	13.13	22.99

 $\rm CH_4$ realised was determined based on the total volume or amount of effluents produced at the end of the core flooding experiment. These volumes were fractions of the original gas in place in the core samples. The results recorded are presented in Tables 8, 13 and 14.

Figs. 5 and 6 are representation of the results of the CH₄ recovery efficiency obtained from the core flooding experiments using different injection rates at the same reservoir conditions. These figures are parabolic in shape. The vertical axis represents the cumulative CH₄ produced in pore volumes (PV) from time t = 0 to time $t = t_{xx}$, where x is the time at which the CH₄ recovery is insignificant as noticed from the online GC machine. At time t_{xx} , the experiment comes to an end because





Fig. 5. Graphical representation of CH_4 volumes produced from all the experiments on Berea gray.



Fig. 6. Graphical representation of ${\rm CH}_4$ volumes produced from all the experiments on Bandera gray.

most of the $\ensuremath{\mathsf{CH}}_4$ initially in place has been recovered. The set target is to recover 100% of the 115 PV of the gas initially in place with minimum contamination. Prior to N_2 injection, the system was fully saturated with CH4. N2 was then slowly injected at a known rate using the ISCO pump C/D through cell B. As more pore volume of N2 is injected into the system, free contaminate CH_4 is produced until breakthrough due to phase change and gravity effect as a result of the rise in pressure. The lower the fraction of $N_{\rm 2}$ produced the more CH_4 recovery is recorded. The recovery efficiency is defined as the ratio of CH₄ produced to the original gas in place. After the breakthrough, the fraction of N2 in the exit stream begins to rise while CH4 recovery starts declining until it reaches nearly zero at $t \; = \; t_x$ due to product contamination. The maximum CH_4 recovery efficiency was recorded at breakthrough. The breakthrough is set at a 15% maximum product contamination. In other words, the time at which the mole fraction of N2 produced reached a maximum of 0.15 as shown in Tables 11 and 12. Considering the experimental run at 0.2 ml/min, the recovery was considerable though the combined breakthrough time was longer and hence a stream of CH₄ contaminated by the N2 was recovered as seen in Table 6. In that, there

Table 8

Effect of injectio	on rates on	CH4 recovery	and	breakthroug

Core Samples	Q (ml/min)	Breakthrough (min)	CH ₄ Produced (cm ³)	$\mathbf{RF} = \frac{\mathbf{CH}_{4}\mathbf{Produced}}{\mathbf{OGIP}} \times 100$	Dispersion Coefficient $(10^{-8} \text{ m}^2/\text{s})$
Berea gray	0.2	93.33	646.55	70.28	1.47
0.5	0.4	73.32	819.09	89.04	4.21
	0.6	42.15	559.45	60.81	5.32
	0.8	40.15	476.28	51.77	7.84
	1.0	39.99	478.06	51.97	9.12
Bandera gray	0.2	76.32	550.53	63.37	5.36
	0.4	77.16	652.20	75.08	7.80
	0.6	35.65	495.76	57.07	10.10
	0.8	26.82	402.13	46.29	10.35
	1.0	35.32	313.69	36.11	13.13

was a risk of substantial length scale of mixing between N₂ and CH₄ given the nature of their similarities in property and miscibility despite their low dispersion coefficient values (1.47×10^{-8} and 5.36×10^{-8} m²/s) in Table 7. Similar trend was observed with CO₂ injection at varying injection rates as reported by Abba et al. (2018). This is not an economical imitative being the fact that more CH₄ will be manufactured which will be highly contaminated by the injected N₂ thereby undermining the recovery concept and rendering the EGR process uneconomical.

Consequently, the experimental run at 0.4 ml/min presents a different scenario with the highest methane recovery and efficiency. There was substantial CH₄ recovery and less longitudinal dispersion coefficient in compared to the runs with 0.6-1.0 ml/min injections that showcases a deficient recovery efficiency, breakthrough time and dispersion coefficient trends due to higher interstitial velocity (9.54–16.80 \times 10 $^{-5}$ m/s) as the N_2 plumes transverses through the core sample during the core flooding experiment. More so, high mean interstitial velocities (um) grossly increases the molecular kinetic energy, by creating turbulence or eddy current which later influences molecular agitation of the gas, and thus, alleviate the interaction between the displacing and displaced gases. Finally, the summary result shown in Table 8, provides evidence that the best (optimum) injection rate for N2 injection for both Bandera and Berea gray occurs at 0.4 ml/min considering its recovery efficiency, longitudinal dispersion coefficient, and breakthrough time values compared to other injection rates (0.2, 0.6, 0.8, and 1.0 ml/min).

3.4. Effect of injection rates on dispersivity

Looking at Eq. (2.5), It evident that precise and reliable simulation of dispersion in an enhanced recovery process requires a detailed understanding of molecular dispersion (D), tortuosity (τ), and dispersivity (α) at the condition relevant to natural gas displacement in porous media. The latter two parameters are properties of the porous medium (core sample) of which α can be determined from a set of experimental data in which the flow velocity through the medium is increasing at reasonable intervals like those described in this study. Although, the pressure and temperature dependence of longitudinal dispersion coefficient (KL) are acquired predominantly by D, accurate values of the molecular diffusion coefficient are prerequisites to a reliable dispersion correlation. A numerical model developed by Fuller et al. (1966) by means of computer-aided correlation of 340 experimental points, expressed in Eq. (2.7) was used to evaluate the molecular diffusion coefficient of N₂-CH₄ at conditions relevant to EGR and the miscible displacements. The equation was further simplified by inserting the values of atomic diffusion volumes and the molecular weight of N2 and CH4 as shown in Eq. (2.8). Therefore, using Eq. (2.8), the molecular diffusion coefficients, D, at experimental conditions of 1500 psig and 40 °C of pressure and temperature were evaluated and present in Table 15. Furthermore, the dispersivity (α) can be constructively determined by fixing Eq. (2.5) to the plots of KL/D against u/D which is a straight line as shown in Figs. 7 and 8.



Fig. 7. Plot of dispersion to diffusion coefficient ratio against interstitial velocity for Berea gray.



Fig. 8. Plot of dispersion to diffusion coefficient ratio against interstitial velocity for Bandera gray.

Also, the effect of injection rates on the longitudinal dispersion coefficient was presented in Figs. 9 and 10 for *Berea* and *Bandera* gray respectively.

Reports of (Coats, K.H & Whitson, 2004; Keith H. Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012; Abba et al., 2018) dispensed that the values of the dispersivity (α) in consolidated porous media are mostly smaller than 0.01 ft (0.003 m). Hughes et al. (2012) further recorded dispersivity in a range of 0.0001 m to 0.0011 m using



Fig. 9. Relationship of coefficient of longitudinal dispersion with flow injections for Berea gray.

Donnybrook core sample with petrophysical properties like the ones considered in this work. More so, accurate determination of dispersivity is quite important being an experimental property of a porous medium that examines the characteristic dispersion of the medium by correlating the components of pore velocity to the dispersion coefficient. This parameter is highly sensitive to invigorate fluid flow in the model of the reservoir rock. Considering Figs. 7 and 8, the dispersivity as measured of the slopes was found to be 0.0005 m for both Berea and Bandera core samples. This lies within the range of values obtained in the literature. The similarities could be attributed to proximity in their porosities values as indicated in Table 2. To explain further, the measured dispersivity (0.0005 m) was employed as the characteristic length scale of mixing in Eq. (2.4) to re-evaluate the medium peclet ($P_{\rm em}$) and experimental peclet ($P_{\rm exp}$) number at varying injection rates. These values were presented in Table 9.

Both samples recorded approximately the same average medium peclet number of 0.219 and 0.208 for Bandera and Berea gray respectively. The key factor responsible for this is the interstitial velocity since both α and D are the same for the core plugs. However, considering the interstitial velocity equation, $u = \frac{Q}{m_{eq}^2}$, it can be observed that porosity



Fig. 10. Relationship of coefficient of longitudinal dispersion with flow injections for Bandera gray.

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Peclet numbers determination using α as characteristic length scale of mixing.

Core Samples	Q (ml/ min)	<i>u_m</i> (10 ⁻⁵ m/s)	D (10 ⁻⁸ m ² /s)	K _L (10 ⁻⁸ m ² /s)	$\frac{P_{cm}}{\frac{u_m\alpha}{D}} =$	$\frac{P_{exp}}{u_m \alpha} = \frac{u_m \alpha}{K_L}$
Berea	0.2	3.18	22.99	1.47	0.069	1.081
gray	0.4	6.36	22.99	4.21	0.138	0.755
	0.6	9.54	22.99	5.32	0.207	0.896
	0.8	12.72	22.99	7.84	0.278	0.811
	1.0	15.90	22.99	9.12	0.346	0.872
Bandera	0.2	3.36	22.99	5.36	0.074	0.313
gray	0.4	6.72	22.99	7.80	0.146	0.431
	0.6	10.08	22.99	10.10	0.219	0.499
	0.8	13.44	22.99	10.35	0.292	0.649
	1.0	16.80	22.99	13.13	0.365	0.640

 $K_{\rm L}$ is the respective dispersion coefficient for each injection rate across the core samples.

 (φ) remain the only dependant variable. Meaning that the lower the porosity, the higher the injection flow velocity (Inversely proportion) since the same rate of injections (Q) was employed for both plugs. Therefore, it is paramount that both would have approximately the same medium peclet number due to their nearness porosity values. This shows that the displacement mechanism lies in the transition zone between molecular diffusion and mechanical dispersion in both core plugs, driven by both concentration and velocity.

In contrast, using measured grain diameter of 94.66 and 57.15 μm for Berea and Bandera gray, reported by Abba et al. (2018) as the characteristic length scale of mixing, medium peclet number was evaluated using Eq. (2.4), taking (u) as the average interstitial velocity of the runs as an input variable. The P_{cm} recorded were 0.03 and 0.04 which indicate that the flow mechanism is dominated by diffusion within the entire experimental tests for both core plugs since both values are <0.1 as earlier stated. With this, the selection of gas injection rates based on dispersivity value was quite misleading, and this could result in over or underestimation of transport parameters in porous media. The summary of the effect of injection rates on longitudinal dispersion coefficients of Berea and Bandera gray is presented in Table 10.

Generally, the longitudinal dispersion coefficient increases with an increase in flow velocity due to turbulence or eddy current development as evident in Table 10. Therefore, Bandera gray with the slightest permeability (32 mD) displayed a remarkably higher dispersion coefficient compared to Berea gray (214 mD). Furthermore, since interstitial velocity is a function of porosity as earlier stated, the core plug with the highest porosity will record the lowest interstitial velocity with the least dispersion coefficients at lower injection rates as seen above. However, the dispersion coefficient rises remarkably at higher injection rates in both the core samples, with the highest value of 13.13×10^{-8} m²/s

Table 10

Table 9

Summary of the effect of interstitial velocity on longitudinal dispersion coefficient.

Q (ml/ min)	Pressure (psig)	Temperature (⁰ C)	Interstitial Velocity (10 ⁻⁵ m/s)	Dispersion Coefficient (10 ⁻⁸ m²/s)
Berea gray	1500	40		
0.2			3.18	1.47
0.4			6.36	4.21
0.6			9.54	5.32
0.8			12.72	7.84
1.0			15.90	9.12
Bandera	gray			
0.2			3.36	5.36
0.4			6.72	7.80
0.6			10.08	10.10
0.8			13.44	10.35
1.0			16.80	13.13

recorded for Bandera gray compared to Berea gray with $9.12 \times 10^{-8} \text{ m}^2/\text{s}$ at maximum injection rate (1.0 ml/min). That is about 44% raise. In general, producing reservoirs are quantified based on pore volume (PV). For easier and error-free evaluation the original gas in place and residual methane recovery or residual methane volume recorded are quantified using a dimensionless parameter called Pore Volume (PV). This is defined as the ratio of the original gas in place or residual CH₄ recovered to that of the grain volume recorded using Helium Porosimeter. The pore volume was determined to be 7.53 and 7.97 cm⁴ for Bandera and Berea gray core plugs respectively. The best CH₄ recovery occurred at 0.4 ml/min injection. This yielded 819 and 652 cm³ CH₄ recoveries for Bandera and Berea gray. Thus, in turn, the PV values (103 and 87) were obtained as the ratio of 819 to 7.97 and 652 to 7.53.

4. Conclusion

Identifying displacement phenomenon in fluid transport in porous media is quite important especially when investigating solute transport in sandstone rocks. The choice of the flow velocity in EGR thus becomes important since higher injection rates could lead to premature mixing of the fluids and lower injection rates generally provide longer resident times for the fluids in contact and indirectly increases the mixing of the gases again. The medium peclet numbers mostly indicate the best injection rates that translate to a smoother displacement with a lower dispersion coefficient during the EGR process, which gives an overview of the injection scenarios. In this study, Berea and Bandera gray sandstone core plugs were used as the standard porous medium to carry out a core flooding experiment to investigate the effect of injection velocity on $\rm CH_4$ recovery by nitrogen injection. The maximum $\rm CH_4$ recovery efficiency was recorded at breakthrough. The breakthrough is set at 10-15% of product contamination and the CH4 recovery efficiency was good at a lower injection rate for both core samples. This was due to less mixing observed as seen on their low longitudinal dispersion coefficient results. Consequently, the experimental runs at high injection rates (0.6–1.0 ml/min) present a different scenario with a poor recovery efficiency as a result of higher interstitial velocities as the N2 plumes transverses into the core sample during CH4 displacement. More so, high

Nomenclature

yCO_2	CO_2 mole fraction
yN_2	N_2 mole fraction
D	Diffusion coefficient, m ² /s
Q	Flowrate, mil/min
tD	Dimensionless time
x_D	Dimensionless distance
d	Characteristic length scale, m
KL	Longitudinal dispersion, m ² /s
L	Core sample length, mm
L_{exp}	Experimental length, m
μ	Viscosity, cP
Р	Pressure, psig
Т	Temperature, K
u	Interstitial velocity, m/s
φ	Core porosity, %
α	Dispersivity, m
τ	Tortuosity
$P_{\rm exp}$	Experimental Peclet number
Pem	Medium Peclet number

PemMedium Peclet numberrRadius of core sample, m

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mean interstitial velocities (um) grossly increases the molecular kinetic energy, by creating turbulence or eddy current which later influences the molecular agitation of gas species. Hence, it alleviates the interaction between the displacing and displaced gases. Maximum CH_4 recovery was obtained at 0.4 ml/min for both core samples and thus, Berea recorded 18% more in recovery than Bandera gray at the said injection. The recoveries were 103 and 87 pore volumes (PV) for Bandera and Berea gray core plugs respectively. Thus, with the results from the CH₄ recovery efficiency and dispersion coefficient determination, it is apparent that the optimum injection was 0.4 ml/min for both core samples. The selection of gas injection rates based on dispersivity is quite misleading, and this could result in over or underestimation of transport parameters in porous media. The dispersion coefficient rises remarkably at higher injection rates for both the core plugs, with the highest value recorded on Bandera compared to Berea gray (about 44% higher) at the maximum injection rate. The effect of heterogeneity was more pronounced in Bandera than Berea gray. This could be due to the presence of high contents of clay minerals (Illite, chlorites, and kaolinites), which account for the large volumes of CH4 recovered compared to that of the Bandera core sample. The total clay contents were higher in Bandera than the Berea core sample with 75%. Further work will entail an examination of the effect of heterogeneity on dispersion coefficient and CH4 recovery efficiency.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix

Table 11 Berea gray effluent mole fraction of N_2 produced recorded from the GC for the experimental runs.

Injection at 0.2	ml	Injection at 0.4	ml	Injection at 0.6	ml	Injection at 0.8	ml	Injection at 1.0	ml
Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N2 (yN2)
0.16	0.001	0.15	0.001	0.15	0.001	0.15	0.001	0.16	0.001
6.33	0.001	6.32	0.001	6.32	0.001	5.98	0.001	6.83	0.001
11.99	0.001	12.15	0.001	12.15	0.001	11.32	0.001	12.49	0.001
17.49	0.001	18.48	0.001	18.15	0.001	18.65	0.011	18.16	0.001
23.32	0.001	24.15	0.001	24.48	0.031	24.15	0.018	21.82	0.001
28.82	0.001	32.98	0.001	30.32	0.051	29.48	0.040	29.17	0.002
34.49	0.001	38.65	0.001	35.98	0.083	34.82	0.081	34.49	0.020
40.82	0.011	44.32	0.001	42.15	0.132	40.15	0.146	39.99	0.115
46.66	0.015	50.32	0.001	47.82	0.200	46.98	0.232	45.32	0.343
52.99	0.02	55.82	0.016	53.32	0.286	53.48	0.332	50.66	0.618
58.66	0.026	61.98	0.020	58.82	0.391	58.98	0.436	55.99	0.826
64.32	0.034	67.65	0.021	64.48	0.523	64.32	0.541	61.49	0.925
70.32	0.043	73.32	0.122	69.98	0.653	69.98	0.651	66.83	0.958
76.16	0.053	78.82	0.153	75.65	0.767	75.32	0.745	72.33	0.980
81.99	0.065	84.48	0.186	81.65	0.855	81.15	0.804	77.83	0.986
87.66	0.079	90.32	0.222	87.48	0.912	86.82	0.858	83.32	0.987
93.33	0.144	95.98	0.262	93.15	0.943	92.32	0.894		
99.16	0.245	101.66	0.305	98.65	0.965	98.65	0.918		
104.82	0.353	108.32	0.349	104.32	0.974	103.99	0.934		
110.66	0.462	113.98	0.395	110.32	0.981	110.48	0.945		
116.5	0.559	119.65	0.442	116.65	0.983	115.82	0.958		
122.49	0.648	125.32	0.489			121.48	0.959		
127.99	0.763	130.98	0.556			126.98	0.962		
133.99	0.776	136.65	0.604			133.32	0.968		
139.99	0.873	142.32	0.650			139.15	0.973		
145.82	0.932	148.15	0.696			144.49	0.978		
151.49	0.954	153.65	0.742			149.82	0.979		
157.67	0.964	161.15	0.783			155.15	0.981		
163.32	0.969	167.15	0.820			160.65	0.985		
168.83	0.973	173.15	0.853			165.98	0.988		
174.82	0.975	178.66	0.881						
180.49	0.978	184.32	0.903						
186.82	0.98	190.15	0.921						
192.50	0.982	196.32	0.937						
199.00	0.984	201.82	0.950						
205.32	0.985	207.48	0.961						
210.99	0.985	212.99	0.970						
216.49	0.986	218.82	0.976						
222.16	0.986	230.66	0.979						
228.49	0.987	237.15	0.983						
236.82	0.988								
242.32	0.990								
248.16	0.994								

Table 12

Bandera gray effluent mole fraction of N2 produced recorded from the GC for the experimental runs.

Injection at 0.2	ml	Injection at 0.4	ml	Injection at 0.6	ml	Injection at 0.8	ml	Injection at 1.0	ml
Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N2 (yN2)
0.16	0.001	0.16	0.001	0.15	0.001	0.17	0.001	0.15	0.001
3.99	0.001	5.49	0.001	3.48	0.001	5.83	0.001	2.48	0.001
9.32	0.001	11.99	0.001	8.82	0.001	11.33	0.001	7.98	0.001
14.66	0.001	18.16	0.001	14.16	0.001	15.49	0.001	13.82	0.001
19.99	0.001	23.49	0.001	19.48	0.001	21.29	0.013	19.32	0.001
25.65	0.001	28.82	0.001	24.82	0.001	26.82	0.153	24.65	0.015
32.48	0.001	34.16	0.001	30.48	0.001	31.99	0.383	29.98	0.029
38.48	0.001	39.66	0.001	35.65	0.054	37.99	0.609	35.32	0.100
43.82	0.001	44.99	0.001	41.16	0.169	43.5	0.79	40.82	0.227
49.16	0.001	50.32	0.001	46.48	0.322	48.82	0.884	46.32	0.378
54.48	0.001	55.82	0.001	51.82	0.491	54.15	0.934	51.66	0.524
59.82	0.001	61.16	0.001	57.15	0.649	59.49	0.96	57.16	0.656
65.15	0.001	66.49	0.001	62.99	0.777	65	0.971	63.98	0.753
70.82	0.001	71.82	0.001	68.32	0.857	70.32	0.977	69.32	0.839
76.32	0.032	77.16	0.018	73.82	0.907	75.66	0.98	74.83	0.884
82.15	0.708	82.49	0.057	79.15	0.937	81.15	0.982	80.15	0.914
87.65	0.957	87.82	0.512	84.65	0.957	86.65	0.984	85.83	0.935
95.15	0.98	93.16	0.845	90.32	0.97	92.5	0.984	91.15	0.95
100.98	0.982	98.66	0.937	95.82	0.976	98	0.985	96.48	0.959
								(continued	on next page)

Table 12 (continued)

Injection at 0.2 ml		Injection at 0.4	ml	Injection at 0.6	ml	Injection at 0.8	ml	Injection at 1.0	ml
Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N ₂ (yN ₂)	Time (min)	N2 (yN2)
106.32	0.983	103.99	0.963	101.15	0.981	104	0.985	101.82	0.965
112.98	0.983	109.32	0.969	106.65	0.982	109.3	0.986	107.32	0.97
118.82	0.984	114.66	0.97	111.99	0.984			112.65	0.973
								117.98	0.976

Та	ble	13	

Berea gray CH_4 production in pore volumes for all the experimental runs.

0.2 ml Injecti	on	0.4 ml Injecti	on	0.6 ml Injecti	on	0.8 ml Injecti	on	1.0 ml Injecti	on
Time (min)	CIL ₁ Prod (PV)	Time (min)	CH4 Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH4 Prod (PV)	Time (min)	CIL ₄ Prod (PV)
0.16	4.17	0.15	4.48	0.15	7.81	0.15	4.65	0.16	6.61
6.33	5.58	6.32	6.14	6.32	12.10	5.98	9.36	6.83	12.31
11.99	9.82	12.15	10.72	12.15	18.08	11.32	14.13	12.49	19.20
17.49	14.06	18.48	15.40	18.15	22.31	18.65	18.80	18.16	26.37
23.32	18.34	24.15	20.11	24.48	26.02	24.15	23.24	21.82	33.71
28.82	22.65	32.98	22.00	30.32	29.85	29.48	27.54	29.17	40.51
34.49	27.00	38.65	26.86	35.98	36.89	34.82	31.06	34.49	45.99
40.82	31.06	44.32	31.79	42.15	39.28	40.15	33.29	39.99	47.97
46.66	35.25	50.32	36.75	47.82	40.49	46.98	34.00	45.32	39.49
52.99	39.43	55.82	41.15	53.32	40.15	53.48	33.18	50.66	24.94
58.66	40.80	61.98	45.95	58.82	37.72	58.98	31.11	55.99	11.63
64.32	44.65	67.65	47.01	64.48	34.39	64.32	27.87	61.49	5.45
70.32	48.56	73.32	50.19	69.98	28.65	69.98	23.17	66.83	3.15
76.16	52.32	78.82	52.84	75.65	21.76	75.32	18.40	72.33	1.55
81.99	56.00	84.48	55.05	81.65	15.17	81.15	15.30	77.83	1.12
87.66	59.41	90.32	56.73	87.48	10.02	86.82	11.94	83.32	1.08
93.33	56.82	95.98	57.75	93.15	7.00	92.32	9.56		
99.16	53.64	101.66	58.22	98.65	4.66	98.65	7.91		
104.82	48.54	108.32	58.09	104.32	3.73	103.99	6.80		
110.66	42.91	113.98	57.31	110.32	2.91	110.48	6.02		
116.50	37.09	119.65	55.96	116.65	2.79	115.82	4.87		
122.49	27.98	125.32	54.12			121.48	5.03		
127.99	22.09	130.98	49.55			126.98	4.89		
133.99	21.93	136.65	46.47			133.32	4.29		
139.99	12.82	142.32	43.14			139.15	3.76		
145.82	7.20	148.15	39.26			144.49	3.19		
151.49	5.09	153.65	34.86			149.82	3.17		
157.67	4.08	161.15	30.63			155.15	2.97		
163.32	3.67	167.15	25.53			160.65	2.42		
168.83	3.25	173.15	21.23			165.98	2.00		
174.82	3.06	178.66	17.49						
180.49	2.74	184.32	14.53						
186.82	2.60	190.15	12.04						
192.50	2.42	196.32	9.77						
199.00	2.19	201.82	7.90						
205.32	2.09	207.48	6.28						
210.99	2.12	212.99	4.93						
216.49	2.01	218.82	4.01						
		230.66	3.57						
		237.15	2.95						

Table 14

Bandera gray CH ₄ productio	n in pore volumes fo	or all the experimental ru	uns.
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0.2 ml Injectio	on	0.4 ml Injecti	on	0.6 ml Injecti	on	0.8 ml Injecti	on	1.0 ml Injecti	on
Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)
0.16	0.02	0.16	0.02	0.15	0.02	0.17	0.02	0.15	0.02
3.99	0.53	5.49	0.73	3.48	0.46	5.83	0.77	2.48	0.33
9.32	1.24	11.99	1.59	8.82	1.17	11.33	1.51	7.98	1.06
14.66	1.95	18.16	2.41	14.16	1.88	15.49	2.06	13.82	1.84
19.99	2.66	23.49	3.12	19.48	2.59	21.29	2.83	19.32	2.57
25.65	3.41	28.82	3.83	24.82	3.30	26.82	3.56	24.65	3.27
32.48	4.31	34.16	4.54	30.48	4.05	31.99	4.25	29.98	3.98
38.48	5.11	39.66	5.27	35.65	4.73	37.99	5.05	35.32	4.69
43.82	5.82	44.99	5.98	41.16	5.47	43.5	5.78	40.82	5.42
49.16	6.53	50.32	6.68	46.48	6.17	48.82	6.48	46.32	6.15
54.48	7.24	55.82	7.41	51.82	6.88	54.15	7.19	51.66	6.86
59.82	7.94	61.16	8.12	57.15	7.59	59.49	7.90	57.16	7.59
65.15	8.65	66.49	8.83	62.99	8.37	65.00	8.63	63.98	8.50
70.82	9.41	71.82	9.54	68.32	9.07	70.32	9.34	69.32	9.21
								(conti	nued on next page)

Table 14 (continued)

0.2 ml Injection 0.4 m		0.4 ml Injecti	on	0.6 ml Injecti	on	0.8 ml Injecti	on	1.0 ml Injecti	on
Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH4 Prod (PV)	Time (min)	CH ₄ Prod (PV)	Time (min)	CH ₄ Prod (PV)
76.32	10.14	77.16	10.25	73.82	9.80	75.66	10.05	74.83	9.94
82.15	10.91	82.49	10.95	79.15	10.51	81.15	10.78	80.15	10.64
87.65	11.64	87.82	11.66	84.65	11.24	86.65	11.51	85.83	11.40
95.15	12.64	93.16	12.37	90.32	11.99	92.50	12.28	91.15	12.10
100.98	13.41	98.66	13.10	95.82	12.73	98.00	13.01	96.48	12.81
106.32	14.12	103.99	13.81	101.15	13.43	104.00	13.81	101.82	13.52
112.98	15.00	109.32	14.52	106.65	14.16	109.30	14.52	107.32	14.25
118.82	15.78	114.66	15.23	111.99	14.87			112.65	14.96
								117.98	15.67

 $\begin{array}{l} \textbf{Table 15} \\ \text{Dispersion coefficients of N_2-CH_4$ as functions of concentration profiles.} \end{array}$

Core Samples	Q (ml/min)	u (10 ⁻⁵ m/s)	$K_L (10^{-8} \text{ m}^2/\text{s})$	$D (10^{-8} \text{ m}^2/\text{s})$	u/D (m ⁻¹)	K _L /D
Berea gray	0.2	3.18	1.47	22.99	138.28	0.100
	0.4	6.36	4.21	22.99	276.56	0.183
	0.6	9.54	5.32	22.99	414.83	0.231
	0.8	12.72	7.84	22.99	553.28	0.341
	1.0	15.90	9.12	22.99	691.61	0.397
Bandera gray	0.2	3.38	5.36	22.99	146.15	0.233
	0.4	6.72	7.80	22.99	292.30	0.339
	0.6	10.08	10.10	22.99	438.45	0.439
	0.8	13.44	10.35	22.99	584.60	0.450
	1.0	16.80	13.13	22.99	730.75	0.571



Fig. 11. Effluent N_2 and CH_4 composition recorded from the GC as a function of displacement time for Bandera gray.



Fig. 12. Effluent N_2 and CH_4 composition recorded from the GC as a function of displacement time for Berea gray.



Fig. 13. Effluent concentration as a function of pore volumes injected observed during a core flooding experiment with N2 and CI14 as displacing and displaced gases at the rate of 0.6 ml/min.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jngse.2020.103513.

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ORIGINAL PAPER-- PRODUCTION ENGINEERING



Alternating N₂ gas injection as a potential technique for enhanced gas recovery and CO₂ storage in consolidated rocks: an experimental study

Nuhu Mohammed¹⁽¹⁰⁾ • Abubakar Jibrin Abbas¹ • Godpower C. Enyi¹ • Salihu M. Suleiman¹ • Donatus E. Edem¹ • Muhammad Kabir Abba¹

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Abstract

The promotion of enhanced gas recovery (EGR) and CO₂ storage is still shrouded in contention and is not well accepted, due to the excessive in situ CO₂ mixing with the nascent natural gas. This adulterates the recovered CH₄ and thus results in a high sweetening process cost thereby making the technique impractical. This has not only limited the field application of EGR in actual projects to a few trails but renders it uneconomical. This study aims to present, experimentally, alternating N₂ injection as a potential technique for EGR and CO₂ storage in sandstone rock cores. A laboratory core flooding experiment was carried out to simulate a detailed process of unsteady-state methane (CH₄) displacement using Bandera grey core plug. This was carried out at 40 °C, 1500 psig, and 0.4 ml/min injection rate by alternative injection of N₂ and CO₂ in succession designed to suit the application based on optimum operating conditions. The results show that both CO₂ storage capacity and CH₄ recovery improved significantly when gas alternating gas (GAG) injection was considered. The best results were observed at lower N₂ cushion volumes (1 and 2 PV). Therefore, the GAG injection method with N₂ as cushion gas can potentially increase both CO₂ storage and CH₄ recovery of the gas reservoir. This technique if employed will assert the current position and provide vital information for further researches aimed at promoting environmental sustainability and economic viability of the EGR and CO₂ sequestration processes.

Keywords Dispersion coefficient · Enhanced gas recovery · Cushion gas · Breakthrough · Concentration profile

List of symbols

- yCO₂ CO₂ mole fraction
- yN₂ N₂ mole fraction
- D Diffusion coefficient, m²/s
- *Q* Flow rate mil/min
- t_D Dimensionless time
- *x_D* Dimensionless distance
- d Characteristic length scale, m
- $K_{\rm L}$ Longitudinal dispersion, m²/s
- *L* Core sample length, mm
- L_{exp} Experimental length, m
- μ Viscosity, cP
- P Pressure, psig

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🖂 Nuhu Mohammed

n.mohammed5@edu.salford.ac.uk

1 University of Salford, Manchester, UK

- T Temperature, K
- *u* Interstitial velocity, m/s
- ϕ Core porosity, %
- α Dispersivity, m
- τ Tortuosity
- Pe Péclet number
- Pe_m Medium Péclet number
- PV Pore volume
- r Radius of core sample, m
- λ_{90} Lambda function at 90% of effluent concentration
- λ_{10} Lambda function at 10% of effluent concentration

Introduction

 CO_2 emissions are generalized as a significant factor responsible for inhibiting climate change that later results to increase in environmental temperature (global warming). It was predicted that there will be a rise in world temperature and sea level from 1.9 to 3.5 °C and 18–30 cm, respectively, by the year 2100. These would be accompanied by

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many foreseen distresses (Meehl et al. 2005). The effective simultaneous enhanced gas recovery and sequestration using CO_2 injection are losing recognition due to high natural gas contamination, premature breakthrough, and high compression ratio, since it requires about six (6) molar volume of it to displaced one (1) molar volume of natural gas, thereby hindering its market and calorific which eventually render the process non-economically viable. In contrast, N₂ can be recovered mostly from the air separation unit (ASU) or as byproducts of oxygen plants. It requires less compression ratio, which is why a lower amount of it is needed to create high pressure in the CH₄ reservoir.

The increase in carbon credit, coupled with earlier energy demand due to population growth, has forced the exploitation of alternative sources of energy, using other fewer or zero-emission technologies (Abba et al. 2017). Natural gas is considered one of the abundant, low emission, cleanest, and affordable sources of fossil fuels (Benson et al. 2005; Al-Abri et al. 2012). Carbon dioxide (CO2) underground storage for simultaneous storage and natural gas (CH₄) displacement is gaining attention worldwide (Ganjdanesh and Hosseini 2017: Raza et al. 2017). This underground storage can be in the form of oil and gas conventional reservoirs or deep saline aquifers (Abba et al. 2018). Conventional natural gas reservoirs have the potential to safely store anthropogenic CO₂, due to its proven integrity of gas storing capability (Kalra and Wu 2014). Thus, in turn, issues of CO₂ leakages and contamination of adjacent freshwater aquifers are minimal. This arises the need for the development of other injection techniques capable of enhancing both natural gas recovery and CO2 storage (Abba et al. 2018).

Tertiary enhanced gas recovery (EGR) and storage by CO_2 injection are gaining recognition within the research environment due to its greenhouse gases (GHGs) reduction potential. Therefore, both nitrogen (N₂) and CO₂ can be used to increase nascent HCs yield from oil and gas reservoirs. However, CO_2 drawbacks are mainly excessive mixing and high compression ratio, thus hindering the overall process uneconomically viable. In contrast, N₂ can be recovered virtually from the atmospheric air, through air separation units. It requires less compression ratio than CO_2 , which is why a lower amount of it was needed to create high pressure in the CH_4 reservoir.

The promotion of EGR is still at its infant stage due, to the excessive mixing between the injected (displacing fluid) CO_2 and the nascent displaced fluid (natural gas) during the flooding process (Oldenburg and Benson 2002; Shtepani 2006; Turta et al. 2007; Sim et al. 2008, 2009; Al-abri et al. 2009; Sidiq et al. 2011; Hughes et al. 2012; Honari et al. 2013, 2015, 2016; Khan et al. 2013; Zhang et al. 2014; Patel et al 2016). This adulterates the recovered natural gas and thus reduces its heating and market value, which results in the high cost of the sweetening process to maintain its

مدينة الملك ميدلغون العلوم والتقنية KACS market value (Oldenburg and Benson 2002; Sim et al. 2009). This has not only limited the EGR project to a few pilot trials (Pooladi-Darvish et al. 2008) but also made the process apparently uneconomical due to unprecedented mixing with the displaced gas, which make the phenomenon to be poorly understood (Patel et al. 2016). Thus, finding a suitable technique for reducing such in situ mixing could be valuable at first by injecting a certain amount of nitrogen gas as cushion gas before the invention of CO_2 , which is the concept behind gas alternating gas injection.

Several authors (Xidong et al. 2019; Hughes et al. 2012; Janssen et al. 2018; Abba et al. 2018) have carried out an extensive study on how to delay CO2 breakthrough time during EGR process. Among them, Abba et al. (2018) and Xidong et al. (2019) were able to achieve reasonable improvement. Abba et al., (2018) use varying connate water concentration and was able to delay CO₂ breakthrough by 20 min at a concentration of 10 wt.% sodium chloride (NaCl). On the other hand, Gu et al. (2019) use different mole ratios of CO2/N2 mixture gases in coalbed core samples. They reveal that injection of N2-rich mixtures contributes to preventing the nascent early breakthrough of injected CO₂ and safely stored large volumes of CO₂ into the shale sediment over the long term. Abba et al. (2019) achieved a high percentage of total CO2 injected stored at 10 wt.% salinity using solubility trapping mechanism, but with least CH₄ recovery resulted from the density of connate water sealing off the narrow pore spaces within the pore matrix.

To our knowledge, no established efficient method capable of improving simultaneous natural gas recovery and CO_2 storage has been highlighted. This necessitated the need for an in-depth study to develop novel approaches and ways to minimizing this complex phenomenon of gas mixing during gas–gas displacements since the two gases (CO_2 and CH_4) are miscible in all outcomes (Abba et al. 2018). This study aims to highlight, experimentally, the potential of using N_2 as cushion gas in a novel gas alternating gas (GAG) technique to reduce or minimize excessive mixing during EGR by CO_2 injection, thereby improving CH_4 recovery while subsequently storing substantial volumes of CO_2 in conventional natural gas reservoirs.

Dispersion theory and equation

The term Péclet number, Pe, is a dimensionless measure of the level of dispersion by a solute which is defined as the ratio of advective to dispersive processes (Rose 1973) as reported by (Ho and Webb 2006). The degree or level of dispersion is inversely proportional to the magnitude of the Péclet number. At low Péclet numbers, the degree of dispersion is large. It is expressed as in Eq. (1). $P_e = \frac{uL}{K_l} \tag{1}$

Péclet number (ratio of convection to dispersion), L is the core sample length.

In 1963, Perkins and Johnston denoted different termed to Péclet number called medium Péclet number (Pe_m). Its value generally determined and describes the dominant displacement fluid region as the dispersion process progresses shown in Eq. (2):

$$Pe_{m} = \frac{ud}{D}$$
(2)

where Pe_m is medium Péclet number, u = is the mean interstitial velocity (m/s), D is the diffusion coefficient (m²/s), and d is the porous medium characteristic length scale, termed as the medium-grain diameter of the sand pack, but it is poorly defined in consolidated medium (Hughes et al. 2012).

Ideally when $Pe_m < 0.1$ diffusion becomes dominants, while advective mixing dominates the dispersion process at higher medium Péclet number i.e. at $Pe_m > 10$.

Delgado, in 2001, uses the Lambda function, by plotting a graph of Lambda at different experimental times against the percent of displacing fluid in an arithmetic probability paper. The dispersion coefficient was then evaluated using Eq. (3).

$$K_L = u \times L \left(\frac{\lambda_{90} - \lambda_{10}}{3.625}\right)^2 \tag{3}$$

where $K_L = \text{longitudinal dispersion coefficient } (m^2/\text{s})$, $u = \frac{Q}{\pi r^2 \phi}$ is the average interstitial velocity (m/s), and ϕ is the porosity, L = length of porous media (m), λ_{90} and $\lambda_{10} = \text{are}$ values of Lambda function at 10 and 90% effluent concentration. In this research, the lambda function techniques were used, as the fundamental equation was derived by considering inert gas (N₂) as one of the displacing fluids.

Diffusion theory and equation

The diffusion coefficient (D) signifies the extent or magnitude at which a substance or fluid disperses through a unit area (m²) per unit time (s) at a given or defined unit concentration gradient. The proposed empirical model which relates the molecular diffusion, temperature, and pressure for empirical diffusion coefficient determination as revealed by (Hughes et al. 2012; Liu et al. 2015) was developed by Takahashi and Iwasaki in 1970. Also, this empirical equation has been tested by various researchers in determining the real and accurate diffusivity using Eq. (4) at conditions applicable to EGR by CO₂ injection. The diffusion coefficient of CO₂ in CH₄ was dignified at 298–348 K and pressures of 5–15 MPa in a porous bronze plug (Takahashi and Iwasaki 1970). The results were well within the range of conditions applicable to EGR (Abba et al. 2017).

$$D_{\rm CO_2,CH_4} = \frac{\left(-4.3844 \times 10^{-13}P + 8.5440 \times 10^{-11}\right)T^{1.75}}{P}$$
(4)

where $D_{\rm CO_3, CH_4}$ is the molecular diffusion coefficient of CO₂ in pure CH₄ calculated in m² s⁻¹ with P in MPa and T in K. The absolute average deviation (AAD) of this correlation from the experimental data was 1.5% over the range of 298–348 K and 5–15 MPa (Abba et al. 2017, 2018). In this study, a different model was used to cater for the inclusion of nitrogen (N₂) gas during the natural gas displacement and CO₂ sequestration. This model equation is presented in Eq. 5. A correlation formula obtained by Fuller et al. (1966) by means of computer-aided correlation of 340 experimental points is expressed as:

$$D_{\rm N_2,CH_4} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{\left(1/\mu_{\rm N_2} + 1/\mu_{\rm CH_4}\right)}}{P\left[\left(\sum V_{\rm N_2}\right)^{1/3} + \left(\sum V_{\rm CH_4}\right)^{1/3}\right]^2} \tag{5}$$

where $(\sum V_{N_2})$ and $(\sum V_{CH_4})$ are the values derived from the summation of atomic diffusion volumes of N₂ and CH₄ molecules, respectively. These values and other simple molecules are presented in Table 1.

The equation was further simplified after inserting the values of atomic diffusion volumes and the molecular weight of nitrogen and methane. The same was applied for carbon dioxide and methane displacement mechanism. These simplified equations are presented in Eqs. (6) and (7)

$$D_{\rm N_2, CH_4} = \frac{10.2 \times 10^{-11} T^{1.75}}{P} \tag{6}$$

$$D_{\rm CO_2,CH_4} = \frac{8.2 \times 10^{-11} T^{1.75}}{P}$$
(7)

where T and P are temperatures and pressure in Kelvin (K) and megapascal (MPa), respectively. For example, at the same temperature and pressure, Eq. (7) was validated using the experimental work of Abba et al, 2018. The molecular diffusion coefficient (D_{CO_2,CH_2}) was found to be 22.52×10^{-8} m²/s. This value is 0.18% in absolute average deviation (AAD) when compared with Abba et al. (2018) findings.

Materials description

In this research, an experimental study approach using the core flooding system was investigated. This entitles saturating the core plug with CH_4 and the injection of CO_2 at different N_2 gas cushion volumes. The core plug use was Bandera grey sandstone as presented in Table 2.

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 Table 1
 Atomic diffusion

 contributions for various gas
 element and molecules

S/N	Molecule	Diffusion volume
1	He	2.67
2	Ne	5.98
3	Ar	16.2
4	Kr	24.5
5	Xe	32.7
6	H_2	6.12
7	D_2	6.84
8	N_2	18.5
9	O_2	16.3
10	Air	19.7
11	CO	18.0
12	CO_2	26.9
13	N_2O	35.9
14	NH ₃	20.7
15	H_2O	13.1
16	SF ₆	71.3
17	Cl ₂	38.4
18	Br ₂	69.0
19	SO_2	41.8
20	С	15.9
21	Н	2.31
22	0	6.11
23	Ν	4.54
24	F	14.7
25	Cl	21.0
26	Br	21.9
27	I	29.8
28	S	22.9

Source: Fuller et al. (1966)

Table 2 Dimensions and petrophysical properties of Bandera grey core sample

Core sample	Length (mm)	Diameter (mm)	Porosity (%)	Gas Per- meability (md)	Gas in Place (PV)
Bandera grey	76.02	25.31	19.68	32	115

Materials

The core plug of dimension 1.0 inch diameter and 3.0 inch length was used as present in Table 2. This sandstone is considered a classic sedimentary rock primarily comprised of quartz, silica, and sand-sized minerals. For consistency, the porosity and permeability of the sandstone core samples were determined and compared with the ones provided by the supplier (Kocurek Industries INC, Hard Rock Division, 8535 State Highway 36 S Caldwell, TX 77836, Texas USA).



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The research-grade CO_2 , N_2 , and CH_4 with a purity greater than 99.99% were sourced from BOC UK.

Experimental method

A sequence of experimental tests was carried out to investigate the potential of N2 as cushion gas for enhanced CH4 recovery and CO2 storage during core flooding experiment with Bandera grey core plug as the porous medium. Prior to the experiment, the core plug petrophysical properties were evaluated to endured are in synergy with the ones from the vendor. The flow behaviour of supercritical N₂, CO₂, and N2-CO2-CH4 interplay was studied using FLUIDATR thermodynamic software. This was vital, in understanding the flow behaviour of supercritical CO₂ as it plumes transverses the pore spaces within the porous medium while displacing the nascent CH₄, especially with the N₂ as cushion gas. Followed to that, a laboratory core flooding experiment was conducted on the Bandera grey core plug to determine the dispersion coefficient, CH4 recovery, and percent of the CO2 injected stored of the system at different CO2 injections and N2 cushion volumes. Further to that, several runs were carried out at four different N2 cushion volumes at varying CO2 injection rates. The effluent stream rates from the core plug were recorded by the two (low and high) gas flow meters. After this, the produced gas compositions are analysed using the Agilent technologies 7890 A model gas chromatography (GC) system at an interval of 5 min elusion time through the sampling valve. The combined data are used to evaluate: one, dispersion coefficient; two, CH4 recovery; and three; percent of total CO2 injected stored at the test reservoir conditions of 1500 psig pressure and 40 °C temperature.

Apparatus and procedure

Apparatus

The experimental set-up consists of mainly two individual units; a core lab UFS-200 core flooding system with inbuilt Smart Flood software and packed column design Agilent 7890A gas chromatography (GC) machine model. The core flooding system, designed for 2-phase liquid/gas steady or unsteady state condition displacements, was reconfigured to accommodate additional N₂ as used in the gas alternating gas injection for this study. The integrated online concentration measurement of core flooding effluents was achieved using the GC machine. These values were used in plotting the injection fluids concentration profile as the experiment progress with time. A schematic of the equipment set-up is presented in Fig. 1.

The UFS-200 core flooding system is rated to 5000 and 3750 psig overburden and pore pressure, respectively. The



Fig. 1 Schematics of experimentational set-up for gas alternating gas injection

injection system of the equipment is made up of a pair of dual ISCO two-barrel metering pump system (A/B and C/D) for constant flow for pulseless transition and to maintain an accurate flow rate range of 0 to 200 ml/min with a maximum pressure rating of 3750 psig. The pumps are attached to a pair of two stainless-steel floating piston accumulators which are also rated for 5000 psig working pressure and temperature of 177 °C. They are designed for injection of the fluids of interest and can withstand up to 7500 psig test pressure. The hydraulic pump with a maximum of 10,000 psig pressure output was used to set the overburden confining pressure. The Smart Flood 1.0 software forms an essential unit of the system which interfaces the UFS system and the computer data-acquisition-control (DAC) system hardware and generates on-screen automatic logging of test data for all measured values like pressures, temperatures, volumes, etc., to a computer data file. A Rosemount Static DP transmitter with an accuracy of 0.0055% was responsible for measuring the differential pressures across the entire Hassler-type core holder, which was used to house the core sample. The core sample is clutch inside the core holder by a Viton rubber sleeve. A core holder heat jacket to simulate the required temperature was also employed with an accuracy of 0.1%. Dome type back pressure regulator integrated into the flooding system ensured the confinement of the desired pressures within the core holder. Such desired pressure was set using the N2 cylinder bottle. The effluents from the back-pressure regulator pass through the mass flow controllers that

measure the volume of the actual effluents produced before been analysed by the GC system in place.

Procedure

The core sample was dried overnight in an oven at 105 °C for moisture removal and other volatile compounds. The dried sample was wrapped with cling film and in foil paper before inserted into a heat shrink. This is vital to avoid viscous fingering and the penetration of the gases through the sleeve into the ring-shaped core holder. It was then loaded into the core holder and staple with clamps from both ends. Hydraulic oil was then pumped into the ring-shaped core holder to provide the desired overburden pressure, which was kept 500 psig above the pore pressures to in other to avoid fracturing of the core sleeve. The heat jacket was then installed on the core holder and the temperature step-up was observed. The backpressure was engaged and CH4 was slowly injected into the core sample from the CH₄ cylinder to saturate the core plug until the GC constantly read methane > 99%. N₂ is then injected as cushion gas for about 20 min (1 PV) before the invention of CO2 at 0.4 ml/min injection rate. Further runs were carried out at increasing N2 cushion volumes. The experiment elapsed when the methane concentration was insignificant from the GC reading or the CO2 concentration was > 99%. At each injection time of the GC, the time was noted and the effluent composition which is then used to evaluate the dispersion coefficient, CH₄ recovery,

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and percent of total CO₂ injected stored was recorded. The investigation was carried out at 1500 psig pressure and 40 °C temperature. This condition was chosen based on a normal gas pressure reservoir with a gradient of 0.451 psi/ft, an average reservoir depth of 1 km, and a geothermal temperature of 35–40 °C/km. The core sample was dried overnight in an oven at 105 °C for moisture removal and other volatile compounds. The dried sample was wrapped with cling film and in foil paper before inserted into a heat shrink.

Results and discussion

Flow behaviour of supercritical $\rm N_2, \, CO_2, \, and \, N_2-CO_2-CH_4$ during simulated EGR

The actual flow behaviour of supercritical CO₂ as it plumes traverses the pore spaces within the core sample to displace the in situ methane is quite complex, especially with the inclusion of inert nitrogen gas. Investigating these complexities of displacing fluids (CO2 and N2) with regard to the nascent CH4 is vital in understanding the trends and expected outcomes of the displacement process knowing that these gases in their supercritical state have unique behaviour by exhibiting the density of a liquid but retain the viscosity of a gas (Abba et al. 2018). CO2 is 2-6 times denser than methane at all relevant reservoir conditions. Besides, CO2 had a lower mobility ratio compared to methane: thus, it was considered as a high viscosity component (Al-Hasami et al. 2005). Due to the favourability of these properties, CO₂ would be migrated downwards, and this relatively would stabilize the displacement process between the injected

CO2 and methane initially in place (Oldenburg and Benson 2002). The supercritical conditions of CO2, N2, and CH4 are (31.05 °C and 73.80 bar), (-146.9 °C and 33.90 bar), and (-82.55 °C and 46 bar), respectively. The experimental conditions employed in this study are well above that of the supercritical temperature and pressure of each single species. The fluids exhibit excellent behaviour due to the response on their transport properties to change from ambient standard conditions to that of EGR condition. A simulation of their respective properties at elevated operational conditions was carried out using FLUIDAT^R software to check the effects of temperature and pressure on the individual gas densities and viscosities at the stated conditions as presented in Fig. 2, 3, and 4. There are pronounced differences in their properties, with CO₂ being much higher and more extreme than those of N2 and CH4. The density was said to increase as the gas pressure increases. This was more significant with CO2 especially at 500-1400 psig range, after which become constant as shown in Fig. 2. This makes CO2 approximately six (6) times denser than N₂ or CH₄, which signifies the possibility of storing more of it at a supercritical state. However, N₂ and CH₄ exhibited similar behavioural trends as the pore pressure raises, justifying why the recovered CH_4 onsite mostly contain higher traces of N2 than CO2 during exploration (Xidong et al. 2019). The kinetic energy of a gas is proportional to its temperature due to the increased rate of collision with the container wall. The reverse was the case to that of liquid fluids due to high inter-molecular forces keeping them close to each other. In general, gas viscosity increases with pressure raise. However, at higher pressures (1300-2000) psig CO₂ maintained high viscosity with a density like that of liquid as observed in Figs. 2 and 3. Also, at





a lower temperature (18–50) °C CO₂ experienced viscosity reduction similar to liquid as evidence of an about 66% reduction in viscosity at 50 °C, shown in Fig. 4. Thus, in turn, based on the proceeding statement, CO₂ demonstrated strange properties behaviour compared to those of N₂ and CH₄ at conditions of temperature and pressure (40 °C and

1500 psig) applicable to EGR. This justifies the selection of the experimental conditions as also, reported by Abba et al. 2018. Thus, it makes the application of supercritical CO_2 for the EGR process to be well accepted globally. Such unique esteem property will grossly affect the flow behaviour of the gases as will be presented in the successive sections.

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The viscosity is said to be increasing at the beginning of the displacement process until the mobility of the displacing phase is less than that of the displaced phase; this makes the mobility ratio to be less than one (unity). Such a state does maximize gas recovery and sweeps efficiency, due to negligible premature mixing, by providing a sharp viscosity gradient at the displacement front without experiencing viscous fingering effect. A condition in which a combination of two fluids escape some part of the reservoir as it progresses along, forming irregular, or fingered profile. Fingering is relatively a routine problem in reservoirs with gas-injection wells (Al-Abri et al. 2012). Fingering effects result mostly in an unproductive sweeping action, which bypasses many recoverable gas volumes, with a premature breakthrough of displacing fluids. In Fig. 5, both the N2 injection (CH4-N2) and CO2 injection (CH4-CO2) display a lower mobility ratio at their respective critical conditions. The mobility ratio of CH4-N2 displacement was low compared to CH4-CO2 at pressure (100-800 psig) below CO2 critical points (33.9 °C and 1070 psig). This means the effect of viscous fingering was minimal as the N2 plume transverse through the core spaces as against that of CO2. The effect of pressure on the CH₄-CO₂ mobility ratio was insignificance above its supercritical state and remains almost constant thereafter. Overall, the supercritical state of gases plays an important role in investigating their flow behaviour with maximum recovery efficiency, creating an even flood front with minimum risk to viscous fingering effect.

On the other hand, the mobility of CH_4-CO_2 displacement was ascending as the temperature increase due to an increase in density with temperature and pressure down the reservoir. However, a reverse scenario was observed for that of the CH_4-N_2 process as the temperature increases to 100 °C as observed in Fig. 6. This is so because as the temperature increases CH_4-N_2 system experienced a high rise in diffusion coefficient compared to those of CH_4-CO_2 and CO_2-N_2 as shown later in Fig. 7. Thus, in turn, CH_4-CO_2 system mobility is more sensitive to change in temperature and pressure compared to that of CH_4-N_2 during EGR and storage.

The developed Eqs. (6), (7) derived from the fundamental (first principle) correlation [Eq. (5)] as reported by Fuller et al. (1966) were used to simulate the effect of pressure and temperature for N2-CH4, CO2-CH4, and CO2-N2 interaction behaviours. This simulation was carried out at constant temperatures of 30, 40, and 50 °C, respectively, at a varying pressure of 100-2000 psig for the stated interactions. In Fig. 7, the molecular diffusion coefficient increases with a roughly constant value of 1.5 m²/s at constant temperatures of 30, 40, and 50 °C over the pressure ranges. These values were more pronounced for CH_4 -N₂ interaction than that of CH₄-CO₂ due to the high density and molecular weight of carbon dioxide compared to that of nitrogen at reservoir condition. Meanwhile, above 1500 psig of pressure, the diffusion coefficient trend was the same for all the temperatures and the decline rate was less notable.



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Temperature plays a significant role in determining the extent of diffusion when two fluids are in contact with each other especially of the same phase. The higher the temperature, the more the kinetic energy due to high collision velocity, which invariably results in the high molecular diffusion coefficient. Such evidence can be seen in Eqs. (6), (7) with the temperature component (in Kelvin) being the rise to the order of 1.75. Viscosities and atomic diffusion coefficient of binary mixtures. Further to that, atoms or molecules with higher viscosities and diffusion volumes do result in lower

molecular diffusion coefficient value compared to those with lower viscosities and diffusion volumes, respectively. Figure 8 presents a plot of diffusion coefficient against temperature. The CH_4 – N_2 binary mixture shows a high periodic increase as the temperature rise to 120 °C (393.15 K). However, a lower rise was experienced for the case of the CH_4 – CO_2 mixture. This was due to high density, viscosity, and diffusion volume of CO_2 at the supercritical condition as against that of N_2 . Also, a similar trend was observed for that of the CO_2 – N_2 binary mixture.

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Fig.8 Effect of temperature on diffusion coefficients for CH_4-N_2 , CH_4-CO_2 , and CO_2-N_2 interaction at constant pressure of 1500 psig



Core flooding experiment

The recovery efficiency and percent of total CO_2 injected stored were analysed by a laboratory displacement system of an experiment to evaluate the concentration profiles of the interacting gases. This involved the injection of N_2 and CO_2 into the Bandera grey core plug at a condition reasonable for the EGR process.

The concept of N₂ as a cushion gas during enhanced gas recovery

The principle behind the whole concept of the core flooding experiment for CH4 displacement in a porous medium is well understood using the concept of dispersion theory and its governing equations. For example, establishing the dominant mechanism of displacement as the displacing gases (N2 and CO₂) transverses the core samples are prerequisites to avoid excessive mixing during the EGR process. If the medium Péclet number in Eq. (2) is less than 0.1, diffusion dominates and the flow is driven by the concentration gradient, and the transport is influenced by the mobility ratio, as evident in most of the experimental EGR process. However, when the Péclet number is above 10 advective mixing dominates due to the turbulence and eddy current effects and the flow is driven by velocity gradient as seen in most displacement at higher injection velocity. In this experiment, the Péclet number was 0.02, meaning the dominant displacement is by diffusion. The rate of gas miscibility during the natural gas displacement process mostly depends on the injection rate of the displacing species. The higher the rate the more mixing will be recorded, and invariably more contaminated CH4 will be recorded. This was why most researches on CO2 injections were tailored toward storage rather than CH4 recovery.



The injected amount of N2 prior to the CO2 injection acts as a barrier by creating a thin film layer between CO2 and CH₄, making it difficult for the carbon dioxide to penetrate and disperse into the methane due to the blanketing nature of nitrogen. This affirmed the use of N2 for reservoir pressure maintenance for decades. The introduction of N2 displaces a larger amount of the CH4 until it reached its breakthrough; this allows most of the CO2 later injected to be trapped within the rock space without mixing with the nascent CH₄. More so, at the time the CO2 reaches its breakthrough a substantial volume of CH4 has been recovered already since the CO₂ will find it difficult to disperse itself into the methane due to the presence of nitrogen gas which acted like a barricaded wall between the CO2 and CH4. A decline in the dispersion coefficient was observed as the cushion gas volume increases; thus, less gas miscibility was noticed with higher CO₂ storage compared to the conventional CO₂ flooding. This signifies the feasibility and potential N2 as a cushioning medium on CH₄ swept recovery efficiency and CO₂ storage for both social and economic benefits.

The variation of effluents against the total injected gases in pore volumes

The breakthrough indicates the first contact point at which the injected gas species $(CO_2 \text{ and } N_2)$ trespass the length scale of the core sample during the laboratory experimental runs. The later the breakthrough the more the sweep efficiency and invariably the volumes of CO_2 stored. On the other hand, the shorter the breakthrough, the larger the dispersion coefficient; an indication for excessive mixing and product contamination. This results in natural gas production with low calorific value and high purification cost, rendering the process uneconomical. The breakthrough points were determined from the plots of the concentration profiles against total gas injection as presented in Fig. 9. The effluents mole fraction was measured online using the integrated GC machine as seen from the experimental setup. Five sets of breakthrough points were measured at 1, 2, 3, and 5 PV of injected gas species. It was observed that there was a delay in the CO₂ breakthrough as the cushion gas volume increases from 1 to 5 PV. This was so because injecting N₂ into the gas-bearing formation can cause a large volume of nascent methane displacement from the reservoir by lowering the partial pressure of CH₄ due to its high conductivity and invariably increase its recovery (Jessen et al. 2008). This accounted for approximately 150% delayed in breakthrough compared to conventional CO₂ injection as evidence in Fig. 9.

The changes in effluent concentration with displacement were ascertained by conventional and gas alternating gas (GAG) displacement simulation (Figs. 10, 11). The N₂ breakthrough occurred when about 6 PV of it been injected into the core sample. This value was roughly 2 times that of the conventional CO₂ injection. The injected pore volume of the CO₂ was earlier detected by the gas chromatography at the same injection temperature and pressure, due to its high diffusion volume. The diffusion volumes of CO₂ and N₂ are 26.9 and 18.5 cm³, respectively (Fuller et al. 1966). In comparison with conventional N₂ displacement, the breakthrough time of N₂ increases when the cushion gas was employed. The increase was highest at 2 PV cushion gas volume. As expected, more product contamination of N2 was recorded as the volume of N2 injected into the system increases. The least contamination was noticed at lower cushion volume with 19% nitrogen contaminants compared to 75% contamination at 5 PV of injected cushion gas. Due to the high cost of natural gas purification, designing an experiment with high product purity is paramount for the economic viability of such a process. Thus, the level of product contamination will be considered in selecting the best and optimum cushion gas volume. Similarly, a prolonged CO2 breakthrough time was recorded at the highest cushion gas volume (5 PV), this was 5.8 PV more than conventional CO₂ flooding. This also resulted in a higher volume of total injected CO2 stored due to lower penetration and dispersion coefficient as later present in Table 4. The combined effect for all the runs is presented in Fig. 12. Thus, in turn, the breakthrough of CO2 can be delayed by increasing N2 cushion gas volume. Overall, a minimum of 3.2 PV delayed longer than the traditional CO2 injection was recorded across all the cushion gas volume tested. It evidence that the presence of impurity (N₂) causes large changes in supercritical CO2 behaviour as reported by several authors (Xidong et al. 2019; Hughes et al. 2012; Janssen et al. 2018; Abba et al. 2018). To reduce the high cost of gas separation, a longer breakthrough with minimum miscibility is preparable for experimental gas injection (Xiangchen et al. 2018). It is worth noting that higher displacement efficiency is obtained at lower cushion volume. The optimization of breakthrough time and displacement efficiency should be expected for the success of the GAG injection process.



Fig. 9 CO_2 breakthrough time of all the experimental runs



Fig. 10 Conventional N₂ and CO₂ injection effluent concentration profiles

Dispersion coefficient and dispersivity

Dispersion can be defined as an irreversible mixing that exists during miscible displacements reported by Adepoju et al. (2013). This phenomenon occurs mainly due to molecular diffusion and mechanical dispersion as the experiment progress, while the displacing fluids CO2 and N2 tend to mix with the displaced CH₄ as shown in the concentration profile plots. The displacement efficiency in miscible flooding is grossly affected by in situ mixing taking place inside the core spaces of the core plug. Also, a transition or mixing zone called 'displacement front' develops when the concentration of methane decreases from > 99% to < 1% as aforementioned in Sect. 4. The dispersion observed reported in Table 5 was used to quantify the nascent mixing as the CO2 plumes transverses through the porous media. These values were evaluated using empirical evaluation [Eq. (3)] and laboratory experiments by analysing the concentration of CO₂ relative to that of CH₄ in the produced effluent stream with the aid of the GC machine. Several repeated experimental displacement tests were carried out to check for uncertainty and repeatability of the research method and set-up. However, such results were demonstrated in our previous publication. The medium Péclet number (Pem) was determined using Eq. (2), in that the characteristic length scale of mixing, d (µm), was obtained from the work of Abba et al. (2019). This value was found to be 57.15 µm for Bandera grey, such value was used in Eq. (2) to determine the dominant phenomenon of displacement mechanism. The $Pe_{\rm m}$ value was calculated to be 0.02, meaning diffusion is the dominant mechanism since its value is < 0.1 as stated in

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Methane recovery

The methane produced was determined based on the total volume and composition of core flooding system effluents recorded by the gas flow meters and gas chromatography. The core flooding experiment was terminated when an insignificance composition (< 0.5%) of CH₄ or (> 99.5%) of CO₂ was noticed from the GC as shown in Fig. 13 with only CO2 peak noticeable. These volumes are a fraction of the original gas in place (OGIP) in the Bandera grey core plug. The result is presented in Fig. 14. As can be observed, the worst CH4 recovery was realized when pure CO2 was injected; this was due to high diffusion volume and low minimum miscibility pressure (MMP) effect as it plumes transverses through the core plug during the displacement process. Considering the GAG injection, the run with 5 PV of cushion gas produced 44.39% CH4 recovery. This poor sweep efficiency was a result of early N2 detection by the GC due to the high volume of it injected and demonstrate similar property behaviour with CH₄ as discussed in Sect. 4.1.

Prior to the core flooding experiment, the OGIP of the Bandera grey core plug was evaluated using the well-known



Fig. 11 Effluents concentration profiles with 1, 2, 3, and 5 PV cushion gas

gas reservoir equation [Eq. (8)] as reported by (Abba et al. 2017, 2018).

$$OGIP = \frac{P_v (1 - s_w)}{B_g}$$
(8)

where G is the original gas in place in scm³, P_v is the pore volume in cm³, s_w is the initial water of saturation fraction $(s_w=0 \text{ for a dry run})$, and B_g is gas formation volume factor in cm³/scm³ for this research. This was then used to determine the percentage of CH₄ recovery as shown in Fig. 14 and Table 3.

Furthermore, the CH_4 recovery was highest for conventional N_2 and 1 PV cushion gas experimental runs. However,

not only the 1 PV cushion gas gives high recovery, but also the CH₄ recovered happens to experience the least impurity with 19% N₂ contamination. This signifies the potential application of N₂ gas during the enhanced gas recovery process.

Carbon dioxide injection and storage

In this study, the amount of CO_2 stored during the gas alternating gas injections was evaluated and recorded using Eq. (9) as reported by Xidong et al. (2019).



Fig. 12 Concentration profiles of all the runs with cushion gas

$$V_{\text{storage}-\text{CO}_2} = V_{t,\text{injected}-\text{CO}_2} - F_{\text{outlet}} \int_{0}^{t} C_{t,\text{CO}_2} dt$$
(9)

where $V_{t,\text{injected}-\text{CO}_2}$ is the volume of injected CO₂ recorded by the high-pressure syringe pump at time t and C_{t,CO_2} is the CO₂ mole percent in the effluent at time t recorded by the gas chromatography (GC) analyser.





Fig. 13 CO_2 and CH_4 composition recorded by the GC at the termination stage of the core flooding experiment

Fig. 14 Graphical representation of percent CH₄ volume produced from all the experi-

mental runs



 Table 3 CH₄ recovery factor evaluation for all the injection runs

S/N	Case study	CH ₄ In (PV)	CH ₄ Produced (PV)	CH ₄ Recovery (%)
1	N ₂ Injection	115	104.18	90.30
2	CO ₂ Injection	115	51.10	44.40
3	1 PV cushion gas	115	102.87	89.17
4	2 PV cushion gas	115	74.77	64.81
5	3 PV cushion gas	115	87.62	75.95
6	5 PV cushion gas	115	51.20	44.39

CH4 in the core sample was measured to be 115 PV, and is presented in Table 2. The total CO2 injected stored is presented in Table 4. From Table 4, it is adequate to know that the most significant amount of total CO2 injected stored of 59.76% was recorded at 2 PV of cushion gas. This was characterized by the large pressure drop (dP) as shown in Fig. 15. The least storage was seen when conventional CO2 injection was applied. This could be due to the high dispersion coefficient $(5.02 \times 10^{-8} \text{ m}^2/\text{s})$ obtained during the pure CO2 injection scenario since this parameter is a key for the economy of the enhanced CH4 recovery projects (Du et al., 2019). Meanwhile, lower dispersion coefficient weakens the instantaneous mixing effect of CO2 and CH4 that inhibits the rapid breakthrough of the injected CO2. As such, the injection of N2 as cushion gas can effectively delay or prolonged the breakthrough point, and invariably and sequester more CO₂ over the long run (Xidong et al. 2019).

 $\mbox{Table 4}\ \mbox{CO}_2$ produced and stored during EGR for all the injection scenarios

S/N	Case study	CO ₂ in (PV)	CO ₂ out (PV)	CO ₂ stored (PV)	CO ₂ stored (%)
1	N ₂ injection	0	0	0	0
2	CO2 injection	6.20	35.63	1.46	23.55
3	1 PV cushion gas	8.80	37.76	3.81	43.30
4	2 PV cushion gas	8.40	25.19	5.02	59.76
5	3 PV cushion gas	8.40	31.93	4.13	49.17
6	5 PV cushion gas	6.40	20.84	3.61	56.41

In consequence, to examine the displacement efficiency in terms of CH₄ recovery and CO₂ sequestration, Tables 3 and 4 were combined to generate Table 5. Looking at the later Table, there was an improvement in both recovery and storage when gas alternating gas injection technique was employed as against that of conventional CO₂ injection. This was so because, as the displacement process proceeds, N₂ does act as a barrier by creating a thin film layer between CO₂ and CH₄, making it difficult for carbon dioxide to penetrate and disperse into the methane due to the blanketing nature of nitrogen. This can be seen, where the least dispersion coefficient of 2.59×10^{-8} m²/s was recorded at the highest cushion gas volume of 5 PV.

Based on the literature consulted, it is quite difficult to achieve simultaneous CH_4 recovery and CO_2 storage using

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Table 5	Efficiency of core
flooding	process in terms
of CH4	recovery and CO2
sequest	ration for all runs

S/N	Case study	Total CO ₂ injected stored (%)	CH ₄ recovery (%)	Dispersion Coefficient (10 ⁻⁸ m ² /s)
1	Conventional N2 Injection	N/A	90.30	4.40
2	Conventional CO2 Injection	23.55	44.40	5.02
3	1 PV cushion gas	43.30	89.17	3.59
4	2 PV cushion gas	59.76	64.81	2.78
5	3 PV cushion gas	49.17	75.95	3.27
6	5 PV cushion gas	56.41	44.39	2.59

Fig. 15 Differential pressure (dP) changes during the experimental runs with cushion gas compared to conventional injections



conventional injection. For example, Abba et al., (2019) in their work reported high CO2 storage of 63.13% at 10 wt.% connate water. The same run yielded the poorest CH4 recovery factor of 16.44% (combined of 79.57%). 'Their reason was due to the restrictive flow when CO2 traverses the core sample as a result of higher salinity of the connate water sealing off the narrower pore spaces within the pore matrix due to its density'. This means one must be compromised at the expense of the other. However, in this study both were improved compared to conventional single injection. A combination of 124.57% (59.76% $\rm CO_2$ storage and 64.81% $\rm CH_4$ recovery) was recorded at 2 PV of cushion gas. The same run gives the second least dispersion coefficient with a prolonged breakthrough point. With the results from the CH₄ recovery efficiency, CO2 storage, and dispersion coefficient, it is apparent that the best and optimum cushion gas volumes for this study occur at 2 PV.

Conclusion

In this study, the Bandera grey sandstone core plug was used as the standard porous media. An empirical and experimental core flooding runs were carried out to investigate the production of methane and carbon dioxide during EGR displacement scenarios in the presence of N2 as cushion gas, to register the effects of its existence. A significant recovery and storage of CH₄ and CO₂ were recorded and analysed where the cushion gas volume was 2 PV; this was attributed to the inhibitory flow of the injected CO2 to disperse itself into the CH4 and was characterized by low dispersion coefficient. The worst result was obtained at the conventional CO₂ injection scenario. This was due to high CO₂ diffusion volume and low conductivity of CO2 as it plumes transverses through the core plug during the displacement runs. Methane recovery and carbon dioxide storage can both be influenced by the addition of N2 as cushion gas prior to CO2 injection into the reservoir. Thus, in turn, the displacement efficiency of the current research exhibits better results than that of conventional CO2 injection. However, the presence



of N_2 tends to increase CH_4 recovery by reducing the partial pressure of methane, and at the same time act as a barrier between CO_2 and CH_4 creating a thin barrier making it difficult for early CO_2 breakthroughs as a result of its blanketing effect. This work shows that N_2 as cushion gas influences both CH_4 recovery and CO_2 sequestration. Further work will entail an examination of the effect of connate water salinity on this novel method. Also, the phase behaviour of mixed gases post breakthrough would be investigated.

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Appendix

ble 6 Effluent concentrations	PVI	CO ₂ Conc. (%)	yCO ₂	N2 Conc. (%)	yN_2	CH ₄ Conc. (%)	yCH_4
'able 6 Effluent concentrations tt 1 PV of cushion gas volume	0.01	0.421	0.0042	0.037	0.0004	99.539	0.9954
	0.32	0.449	0.0045	0.04	0.0004	99.514	0.9951
	0.61	0.465	0.0047	0.042	0.0004	99.493	0.9949
	0.92	0.482	0.0048	0.042	0.0004	99.476	0.9948
	1.20	0.485	0.0049	0.044	0.0004	99.471	0.9947
	1.50	0.501	0.005	0.044	0.0004	99.455	0.9946
	1.81	0.501	0.005	0.044	0.0004	99.455	0.9946
	2.11	0.510	0.005	0.045	0.0005	99.445	0.9945
	2.40	0.560	0.0056	0.045	0.0005	99.395	0.9940
	2.68	0.587	0.0059	0.046	0.0005	99.367	0.9937
	2.97	0.614	0.0061	0.046	0.0005	99.340	0.9934
	3.27	0.615	0.0062	0.046	0.0005	99.339	0.9934
	3.57	0.674	0.0067	0.046	0.0005	99.280	0.9928
	3.87	0.71	0.0071	0.046	0.0005	99.244	0.9924
	4.16	0.739	0.0074	0.046	0.0005	99.215	0.9922
	4.46	0.764	0.0076	0.047	0.0005	99.189	0.9919
	4.76	0.79	0.0079	0.047	0.0005	99.163	0.9916
	5.08	0.819	0.0082	0.047	0.0005	99.134	0.9913
	5.37	0.841	0.0084	0.050	0.0005	99.109	0.9911
	5.67	0.856	0.0086	0.050	0.0005	99.094	0.9909
	5.96	0.856	0.0086	0.051	0.0005	99.093	0.9909
	6.26	0.857	0.0086	0.249	0.0025	98.894	0.9889
	6.55	0.876	0.0088	1.908	0.0191	97.216	0.9722
	6.85	1.166	0.0117	7.961	0.0796	90.873	0.9087
	7.14	7.107	0.0711	16.814	0.1681	76.079	0.7608
	7.44	27.371	0.2737	19.025	0.1903	53.604	0.536
	7.75	56.115	0.5612	13.234	0.1323	30.651	0.3065
	8.04	75.681	0.7568	7.141	0.0714	17.178	0.1718
	8.34	87.422	0.8742	3.143	0.0314	9.435	0.0944
	8.64	94.339	0.9434	0.950	0.0095	4.711	0.0471
	8.94	96.827	0.9683	0.408	0.0041	2.765	0.0277
	9.24	98.946	0.9895	0.105	0.0011	0.949	0.0095
	9.58	99.226	0.9923	0.069	0.0007	0.484	0.0048
	9.89	99.317	0.9932	0.060	0.0006	0.404	0.0040

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Table 7 Effluent concentrations at 2 PV of cushion gas volume	PVI	CO ₂ Conc. (%)	yCO ₂	N ₂ Conc. (%)	yN ₂	CH ₄ Conc. (%)	yCH ₄
	0.01	0.018	0.0002	0.027	0.0003	99.955	0.9996
	0.32	0.018	0.0002	0.033	0.0003	99.949	0.9995
	0.64	0.025	0.0003	0.039	0.0004	99.936	0.9994
	0.94	0.030	0.0003	0.042	0.0004	99.928	0.9993
	1.22	0.034	0.0003	0.046	0.0005	99.920	0.9992
	1.52	0.038	0.0004	0.049	0.0005	99.913	0.9991
	1.81	0.040	0.0004	0.051	0.0005	99.909	0.9991
	2.11	0.042	0.0004	0.053	0.0005	99.905	0.9991
	2.41	0.044	0.0004	0.054	0.0005	99.902	0.9990
	2.70	0.046	0.0005	0.055	0.0006	99.899	0.9990
	2.98	0.048	0.0005	0.057	0.0006	99.895	0.9990
	3.27	0.049	0.0005	0.056	0.0006	99.895	0.9990
	3.57	0.051	0.0005	0.057	0.0006	99.892	0.9989
	3.85	0.052	0.0005	0.057	0.0006	99.891	0.9989
	4.13	0.053	0.0005	0.058	0.0006	99.889	0.9989
	4.43	0.056	0.0006	0.059	0.0006	99.885	0.9989
	4.71	0.056	0.0006	0.059	0.0006	99.885	0.9989
	5.00	0.057	0.0006	0.060	0.0006	99.883	0.9988
	5.28	0.057	0.0006	0.061	0.0006	99.882	0.9988
	5.58	0.058	0.0006	0.061	0.0006	99.881	0.9988
	5.86	0.059	0.0006	0.062	0.0006	99.879	0.9988
	6.15	0.060	0.0006	0.062	0.0006	99.878	0.9988
	6.46	0.061	0.0006	0.063	0.0006	99.876	0.9988
	6.75	0.063	0.0006	0.065	0.0007	99.872	0.9987
	7.05	0.064	0.0006	0.066	0.0007	99.870	0.9987
	7.33	0.067	0.0007	0.067	0.0007	99.866	0.9987
	7.62	0.067	0.0007	0.080	0.0008	99.925	0.9993
	7.91	0.069	0.0007	0.918	0.0092	99.013	0.9901
	8.21	0.070	0.0007	7.307	0.0731	92.623	0.9262
	8.49	2.1450	0.0215	21.087	0.2109	76.768	0.7677
	8.77	26.814	0.2681	22.894	0.2289	50.292	0.5029
	9.07	72.473	0.7247	9.315	0.0932	18.212	0.1821
	9.35	90.375	0.9038	2.685	0.0269	6.940	0.0694
	9.64	96.228	0.9623	0.814	0.0081	2.958	0.0296
	9.92	98.660	0.9866	0.243	0.0024	1.097	0.0110
	10.20	99.152	0.9915	0.152	0.0015	0.696	0.0070
	10.50	99.335	0.9934	0.121	0.0012	0.479	0.0048

PVI is the total amount of injected gas in pore volumes

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Table 8 Effluent concentrations at 3 PV of cushion gas volume	PVI	CO ₂ Conc. (%)	yCO ₂	N ₂ Conc. (%)	yN ₂	CH4 Conc. (%)	yCH ₄
	0.01	0.118	0.0012	0.041	0.0004	99.841	0.9984
	0.31	0.131	0.0013	0.041	0.0004	99.828	0.9983
	0.60	0.137	0.0014	0.413	0.0041	99.815	0.9982
	0.94	0.142	0.0014	0.043	0.0004	99.799	0.998
	1.23	0.157	0.0016	0.044	0.0004	99.792	0.9979
	1.52	0.162	0.0016	0.046	0.0005	99.792	0.9979
	1.81	0.162	0.0016	0.046	0.0005	99.789	0.9979
	2.09	0.164	0.0016	0.047	0.0005	99.782	0.9978
	2.38	0.169	0.0017	0.049	0.0005	99.782	0.9978
	2.67	0.169	0.0017	0.049	0.0005	99.777	0.9978
	2.97	0.173	0.0017	0.050	0.0005	99.771	0.9977
	3.24	0.179	0.0018	0.050	0.0005	99.765	0.9977
	3.53	0.185	0.0019	0.050	0.0005	99.763	0.9976
	3.82	0.186	0.0019	0.051	0.0005	99.758	0.9976
	4.12	0.191	0.0019	0.051	0.0005	99.754	0.9975
	4.40	0.193	0.0019	0.053	0.0005	99.749	0.9975
	4.71	0.197	0.002	0.054	0.0005	99.748	0.9975
	4.99	0.197	0.002	0.055	0.0006	99.745	0.9975
	5.30	0.199	0.002	0.056	0.0006	99.741	0.9974
	5.59	0.200	0.002	0.059	0.0006	99.741	0.9974
	5.88	0.200	0.002	0.059	0.0006	99.737	0.9974
	6.17	0.204	0.002	0.059	0.0006	99.716	0.9972
	6.45	0.205	0.0021	0.079	0.0008	99.450	0.9945
	6.78	0.205	0.0021	2.694	0.0269	97.101	0.9710
	7.06	0.205	0.0021	10.214	0.1021	89.581	0.8958
	7.35	0.387	0.0039	25.009	0.2501	74.604	0.7460
	7.68	1.141	0.0114	44.953	0.4495	53.906	0.5391
	7.98	3.269	0.0327	59.989	0.5999	36.742	0.3674
	8.26	21.793	0.2179	53.931	0.5393	24.276	0.2428
	8.56	60.864	0.6086	26.340	0.2634	12.796	0.1280
	8.85	82.816	0.8282	10.089	0.1009	7.095	0.0710
	9.14	91.405	0.9141	4.088	0.0409	4.507	0.0451
	9.43	94.774	0.9477	2.017	0.0202	3.209	0.0321
	9.73	96.533	0.9653	1.111	0.0111	2.356	0.0236
	10.00	97.503	0.975	0.727	0.0073	1.770	0.0177
	10.30	97.995	0.98	0.559	0.0056	1.446	0.0145
	10.60	98.154	0.9815	0.509	0.0051	1.337	0.0134
	10.90	98.247	0.9825	0.486	0.0049	1.267	0.0127
	11.20	98.378	0.9838	0.455	0.0046	1.167	0.0117
	11.60	98.533	0.9853	0.413	0.0041	1.054	0.0105

PVI is the total amount of injected gas in pore volumes

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Table 9 Effluent concentrations at 5 PV of cushion gas volume	Time	CO ₂ Conc. (%)	yCO ₂	N ₂ Conc. (%)	yN ₂	CH ₄ Conc. (%)	yCH ₄
	0.01	0.047	0.0005	0.039	0.0004	99.914	0.9991
	0.31	0.055	0.0006	0.039	0.0004	99.906	0.9991
	0.66	0.071	0.0007	0.039	0.0004	99.890	0.9989
	0.96	0.085	0.0009	0.039	0.0004	99.876	0.9988
	1.25	0.099	0.0010	0.040	0.0004	99.861	0.9986
	1.53	0.108	0.0011	0.041	0.0004	99.851	0.9985
	1.83	0.115	0.0012	0.041	0.0004	99.844	0.9984
	2.15	0.122	0.0012	0.042	0.0004	99.836	0.9984
	2.44	0.125	0.0013	0.042	0.0004	99.833	0.9983
	2.73	0.128	0.0013	0.043	0.0004	99.829	0.9983
	3.02	0.134	0.0013	0.044	0.0004	99.822	0.9982
	3.31	0.135	0.0014	0.044	0.0004	99.821	0.9982
	3.59	0.136	0.0014	0.044	0.0004	99.820	0.9982
	3.88	0.138	0.0014	0.044	0.0004	99.818	0.9982
	4.17	0.141	0.0014	0.045	0.0005	99.814	0.9981
	4.46	0.143	0.0014	0.046	0.0005	99.811	0.9981
	4.74	0.143	0.0014	0.053	0.0005	99.804	0.9980
	5.05	0.149	0.0015	0.06	0.0006	99.791	0.9979
	5.35	0.151	0.0015	0.06	0.0006	99.789	0.9979
	5.63	0.156	0.0016	0.068	0.0007	99.776	0.9978
	5.92	0.160	0.0016	0.079	0.0008	99.761	0.9976
	6.21	0.164	0.0016	0.094	0.0009	99.742	0.9974
	6.50	0.167	0.0017	0.164	0.0016	99.669	0.9967
	6.79	0.171	0.0017	0.709	0.0071	99.120	0.9912
	7.07	0.174	0.0017	2.063	0.0206	97.763	0.9776
	7.36	0.177	0.0018	5.162	0.0516	94.661	0.9466
	7.65	0.180	0.0018	10.918	0.1092	88.902	0.889
	7.95	0.181	0.0018	19.534	0.1953	80.285	0.8029
	8.23	0.186	0.0019	30.643	0.3064	69.171	0.6917
	8.53	0.190	0.0019	44.933	0.4493	54.877	0.5488
	8.83	0.192	0.0019	60.055	0.6006	39.753	0.3975
	9.12	0.200	0.0020	70.416	0.7042	29.384	0.2938
	9.41	3.406	0.0341	75.774	0.7577	20.820	0.2082
	9.72	60.648	0.6065	30.691	0.3069	8.661	0.0866
	10.00	88.588	0.8859	7.601	0.076	3.811	0.0381
	10.30	97.136	0.9714	1.593	0.0159	1.271	0.0127
	10.60	98.501	0.985	0.716	0.0072	0.783	0.0078
	10.90	99.045	0.9905	0.413	0.0041	0.501	0.0050
	11.20	99.237	0.9924	0.303	0.0030	0.399	0.0040

PVI is the total amount of injected gas in pore volumes

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The Potential of N_2 as Cushion Gas on Dispersion Coefficient of SuperCritical CO₂ in Sandstone Core Plug During Enhanced Gas Recovery by CO₂ Injection

Nuhu Mohammed, Abbas Jibrin Abubakar, and Godpower Chimagwu Enyi, University of Salford, Manchester

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Abstract

Despite the several kinds of literature on the dispersion behaviour of supercritical CO₂ in CH₄ at conditions relevant to enhanced gas recovery (EGR), studies have so far limited in keeping this parameter as low as possible. This study aims to highlight, experimentally, to determine the effect of N2 as cushion gas on the dispersion coefficient in consolidated sandstones core plug under reservoir conditions applicable to EGR. A laboratory core flooding experiment was carried out to simulate a detailed process of an unsteady state methane displacement in Bandera gray and Bentheimer core plugs at reservoir conditions of 40oC temperature, 1500 psig of pressure, the optimum injection rate of 0.4 ml/min, and at varying N₂ cushion volumes (8-36 cm3). Further experimental runs were carried out to investigate the effect of high CO_2 injection rates (0.6-1.2 ml/min) on the longitudinal coefficient of dispersion as it plumes transverses into the core plugs during the EGR process. The coefficient of longitudinal dispersion declines with raises in cushion gas volume, hence the higher the amount of N2 cushion volume the less the dispersion of CO_2 into CH₄. This is due to the high shielding barrier inhibited by nitrogen, making it difficult for the CO₂ to dispersed itself and mixed with the nascent natural gas resulting in delayed breakthrough as it plumes transverses into the CH₄ during the displacement process. The inclusion of N₂ as cushion gas prior to CO₂ injection recorded the highest decline at 36cm₃ cushion volume, presenting a 48 and 28% reduction in longitudinal dispersion coefficient for Bandera and Bentheimer core samples respectively, compared to that of conventional/traditional CO2 injection (with zero cushion volume). Recording lower nascent CO2-CH4 mixing resulting in less natural gas contamination and more storage volumes. Also, a reverse phenomenon was observed when the CO₂ injection rate was increased from 0.6-1.2 ml/min due to the high diffusion rate of CO₂ at higher interstitial velocities, resulting in a rapid increase in dispersion coefficient and indirectly high widespread contamination of the remaining natural gas.

Introduction

The promotion of EGR is still at its infant stage, due to the excessive mixing between the injected (displacing fluid). CO₂ and the nascent displaced fluid (natural gas) during the flooding process (Oldenburg & Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; S. Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This adulterates the recovered natural gas and thus, reduces its heating and market value, which results in the high cost of the sweetening process to maintain its purity standard for consumption (Oldenburg & Benson 2002; S. S. K. Sim et al., 2009). Such an overall problem has not only limited the EGR project to a few pilot trials (Pooladi- Darvish et al., 2008) but also made the process apparently uneconomical because of unprecedented mixing with the displaced gas. This makes the whole phenomenon to be poorly understood (Patel et al., 2016). Thus, finding an alternative gas with good displacement properties and minimal miscibility could be a nice development for the oil and gas industry.

Several authors (Gu et al., 2019; Hughes et al., 2012; Janssen et al., 2018; Abba et al., 2018) have carried out an extensive study on how to delay CO₂ breakthrough time during EGR process. Among them, Abba et al., (2018) and Gu et al., (2019) were able to achieve reasonable improvement. Abba et al., (2018) use varying connate water concentration and was able to delay CO₂ breakthrough by 20 minutes at a concentration of 10% wt. sodium chloride (NaCl). On the other hand, Gu et al., (2019) use different mole ratios of CO2/N2 mixture gases in coalbed core samples. They reveal that injection of N2-rich mixtures contributes to preventing the nascent early breakthrough of injected CO2 and safely stored large volumes of CO₂ into the shale sediment over the long term (Gu et al., 2019). The injection of CO₂ into the reservoir generally results in premature breakthrough due to nascent mixing with methane, eventually limiting it application for efficient natural gas recovery. This was the reason why many researches on carbon dioxide injections were tailored toward storage rather than recovery. Furthermore, most of the works on the effect of CO₂ injection on gas production are simulation-based. Till date, no established efficient alternative gas and injection rate capable of unlocking the residual gas beneath the ground has been highlighted. This necessitated the need for an in-depth study to use N2 as an alternative to minimize such complex phenomenon of gas-gas miscibility since both CO₂ and CH₄ are miscible in all outcomes (Abba et al., 2018; Honari et al., 2016; Liu et al., 2015).

Solute dispersion is defined as the contiguous proliferating of a solute plume over a period. The spreading is fundamentally a mixing and further dilution of the solute plume with the inhabitant fluid, as presented in Figure 1 (Ho & Webb, 2006). Examination of dispersion is critical to the interpretation of gas-phase transport in porous media. Several transport concepts that were originally evolved to describe behaviour in saturated porous media, and later for unsaturated water flow, can also be applied to the transport of gases in unsaturated systems, including the concepts of dispersion (Costanza-Robinson & Brusseau, 2006). However, any complex examination of gas-phase systems requires careful consideration of the unique rigorous media have air-filled porosities that vary spatially and temporally which later depend on soil-water content and grain particle-size distribution (Costanza-Robinson & Brusseau, 2006). Gas-phase diffusion coefficients are mostly of the orders of 4-6 in magnitude larger than aqueous-phase value. In contrast to water, gases are seriously affected by pressure and temperature changes due to an increase in kinetic energy. Further to that gases also experience slip-flow along pore walls, often termed the Klinkenberg effect, while water does not (Costanza-Robinson & Brusseau, 2006).



Figure 1—Spreading of a solute plume from an instantaneous point source (Costanza-Robinson & Brusseau, 2006)

In Fig. 1 (A) represent a two-dimensional spatial 'snapshots' (concentration versus x-y coordinate) as a function of time (t), while (B) present a temporal breakthrough curves (concentration against time) as function of distance along axis of flow in the x-coordinate.

This experimental study, however limited, has highlighted the impact of N_2 as buster and retardant for minimizing CO_2 -CH₄ disperison during the EGR process by CO_2 core flooding. The N_2 gas acts as a buster or cushion gas by re-pressurising the reservoir pressure prior to CO_2 -breakthrough enable more CH₄ recovery without contamination, and also acted as a retardant by creating a thin barrier in between CO_2 -CH₄ phase region, making it difficult for the CO_2 to disperse into the methane resulting to a lower longitudinal dispersion coefficient thereby, forcing most of the CO_2 to descend downward for storage within the pore spaces due to gravity. In this report, the the potential of N_2 as buster gas on dispersion coefficient of supercritical CO_2 in sandstone rocks during EGR process was investigated.

Dispersion Theory and Equation

Newberg and Foh (1988) used a single parameter diffusion-like model based on the 1D Advection-Dispersion equation (Perkins & Johnston, 1963; Coats et al., 2009). The model is mostly used to describe the flow of gas transport through a porous medium along the x-direction as shown in Eq. 1:

$$K_L \frac{\partial^2 C}{\partial^2 X} - u \frac{\partial C}{\partial X} = \frac{\partial C}{\partial t} \tag{1}$$

The effluent composition (C) from the GC at distance (x) under time (t), longitudinal dispersion coefficient (K_L), and interstitial velocity (u) are key parameters in the above equation. The displacement of methane by N_2 in consolidated rocks is governed by Eq. 1. This model is widely accepted to simulate fluids movement in porous medium. However, simulation studies have proved that using the equation in its current form resulted in some abnormal behaviour named upstream migration. It occurs especially when the concentration gradient (dC/dx) along the length scale becomes positive, which is invariable like the case of supercritical CO₂ flowing through a contaminant after breakthrough in the porous medium generating a large magnitude of both dC/dx and dispersion coefficient. Invariably Eq. 1 can be re-written in a dimensionless form (Mamora and Seo, 2002) as follows;

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2)

Where;

Parameter	Symbol	Expression
Peclet number	Pe	uL K L
Dimensionless time	t_D	tu L
Dimensionless distance	x_D	x L
Interstitial velocity	u	Q π r 2 φ

Since the injection of CO_2 is at x = 0, then

Initial condition: C = 0 at $t_D = 0$,

Boundary conditions: C = 1 at xD = 0, $C \rightarrow 0$ as $xD \rightarrow \infty$

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{t_D/P_e}} \right) + e^{P_e x_D erfc} \left(\frac{x_D + t_D}{2\sqrt{t_D/P_e}} \right) \right\}$$
(3)

The effluent core flooding composition could be fitted into the analytical solution of the 1D differential Advection Dispersion (AD) equation (Eq.3) in terms of the *Péeclet* number to evaluate the corresponding dispersion coefficient. The real dispersion coefficient for the experiment is the value which provides the optimum synergy between the experimental result compared to the numerical solution.

In (1963) Perkins & Johnston proposed a widely accepted model that can predict the dominant displacement mechanism during the EGR process in a porous medium. This model equation can be present as:

$$P_{em} = \frac{u_m d}{D} \tag{4}$$

Where;

 P_{exp} is the experimental medium Péclet number, which can be evaluated using the average interstitial velocity (u) in m/s, D is the molecular diffusion coefficient in m₂/s, and d is the characteristic length scale in meters. The characteristic length scale is defined as the average medium-grain diameter of the core sample or sand pack. Generally, at $P_{em} < 0.1$, diffusion dominates the dispersion process, and at $P_{em} > 10$ advective mixing dominates the dispersion process. The analytical solution to Eq. 3 is used to fit the concentration profiles obtained from the experimental data to evaluate the dispersion coefficient.

Coats et al., (2009) correlated the dispersion coefficient with the molecular diffusion coefficient as shown in Eq. 5.

$$\frac{K_l}{D} = \frac{1}{\tau} + \alpha \frac{u_m^n}{D} \tag{5}$$

Here, α is in meter (m) and is called the dispersivity of the porous medium, and n represent an exponent. The tortuosity (t) can range from 1 to as high as 13 or more for consolidated rocks.as reported by Honari et al., (2013). The tortuosity #, can be obtained empirically through various methods, whereas n is mostly determined using a core flooding system (Hughes et al., 2012).

Diffusion Theory and Equation

The diffusion coefficient (D) signifies the extent or magnitude at which a substance or fluid disperses through a unit area (m_2) per unit time (s) at a given unit of a concentration gradient. The proposed empirical model which relates the molecular diffusion, temperature, and pressure for empirical diffusion coefficient determination as indicated by (Hughes et al., 2012; Liu et al., 2015) was developed by Takahashi and Iwasaki in (1970). Similarly, empirical equation has been tested by various researches in determining the real and

accurate diffusivity using Eq.6 at conditions applicable to EGR by CO_2 injection. The diffusion coefficient of CO_2 in CH_4 was dignified at 298-348K and pressures of 5-15MPa in a porous bronze plug (Takahashi and Iwasaki, 1970). The results were well within the range of conditions applicable to the EGR process (Abba et al., 2017).

$$D_{CO2,CH4} = \frac{(-4.3844 \times 10^{-13} P + 8.5440 \times 10^{-11}) T^{1.75}}{P}$$
(6)

where DCO_2 , CH_4 is the molecular diffusion coefficient of CO_2 in pure CH_4 calculated in $m_2 s^{-1}$ with P in MPa and T in K. The absolute average deviation (AAD) of this correlation from the experimental data was 1.5% over the range of 298-348K and 5–15 MPa (Abba et al., 2017; Abba et al., 2018). In this study, a different model was used to cater for the inclusion of Nitrogen (N₂) gas during the natural gas displacement. This model equation was presented in Eq.7. it is a correlation formula obtained by Fuller, Schetter, and Gittings (1966) by means of computer-aided correlation of 340 experimental points, expressed as:

$$D_{N2,CH4} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{\left(1/\mu_{N_2} + 1/\mu_{CH4}\right)}}{P\left[\left(\Sigma V_{N_2}\right)^{1/3} + \left(\Sigma V_{CH4}\right)^{1/3}\right]^2}$$
(7)

Where ($\sum V_{N2}$ and ($\sum V_{CH4}$ are the values derived from the summation of atomic diffusion volumes of N₂ and CH₄ molecules respectively. These values and other simple molecules are presented in Table 1.

S/N	Molecule	Diffusion volume
1	He	2.67
2	Ne	5.98
3	Ar	16.2
4	Kr	24.5
5	Xe	32.7
6	H ₂	6.12
7	D ₂	6.84
8	N_2	18.5
9	O ₂	16.3
10	Air	19.7
11	CO	18.0
12	CO ₂	26.9
13	N_2O	35.9
14	NH ₃	20.7
15	H_2O	13.1
16	SF_6	71.3
17	Cl ₂	38.4
18	Br ₂	69.0
19	SO ₂	41.8
20	С	15.9
21	Н	2.31
22	0	6.11

Table 1—Atomic diffusion contributions for various gas element and molecules

S/N	Molecule	Diffusion volume	
23	Ν	4.54	
24	F	14.7	
25	Cl	21.0	
26	Br	21.9	
7 I		29.8	
28	S	22.9	

The equation was further simplified after inserting the values of atomic diffusion volumes and the molecular weight of nitrogen and methane. The same was applied for carbon dioxide and methane displacement mechanism. These simplified equations were presented in equation 8, and 9 respectively.

$$D_{N2CH4} = \frac{10.2 \times 10^{-11} T^{1.75}}{P}$$
(8)

$$D_{CO2,CH4} = \frac{8.2 \times 10^{-11} T^{1.75}}{P}$$
(9)

where T and P are temperatures and pressure in kelvin (K) and megapascal (MPa) respectively. For example, at the same temperature and pressure, Eq.9 was validated using the experimental work of Abba et al, (2018). The molecular diffusion coefficient (DCO₂,CH₄) was found to be 22.52 x10⁻⁸ m₂/s, which was 0.18% absolute average deviation (AAD) when compared with Abba et al, (2018) results.

Methodology, Application of Equipment and Process

In this research, an experimental study using a core flooding system to investigate the effect of injecting velocity during EGR process. The experiment was conducted by saturating the core plug with CH_4 , injecting of varying volumes of N_2 s buster or cushion gas prior to the CO_2 injection at different high injection rates. The core plugs used were Bandera gray and Bentheimer sandstones and its properties are presented in Table 2.

Table 2—Dimensions and petrophysical properties of the core plugs

Core sample	Length (mm)	Diameter (mm)	Bulk Vol. (cm ³)	Porosity (%)	Gas Permeability (md)
Bandera gray	76.02	25.31	38.27	19.68	32
Bentheimer	76.23	25.23	38.13	22.80	2100

For decades, sandstones core samples have been widely recognised as the best rock for testing the efficiency of chemical surfactants. Berea sandstone is a sedimentary rock whose grains are predominantly sand-sized and are composed of quartz held together by silica. The relatively high porosity and permeability of Berea sandstone make it a good reservoir rock. There are 3 major variations of sandstone namely Slit rock, Liver rock, and Dundee. The one used for this experiment was the Slit rock type with visible laminations and classified as homogenous. It has a permeability rating between 100-300mD. On the other hand, Bandera gray is non-homogenous due to the presence of higher clay contents sealing off the narrower paths within the pore matrix. Thus, making it low permeable and less porous. Both core samples originated from Cleveland quarries in Texas, USA. Core plug of dimension 1.0-inch diameter by 3.0-inch length was used as present in Table 2. The mineralogy of the core samples is presented in Table 3. For consistency, the porosity and permeability of the sandstone core samples were determined and compared with the ones provided by the supplier (Kocurek Industries INC, Hard Rock Division, 8535 State Highway 36 S Caldwell, TX 77836,

Texas USA). Research-grade CO_2 , N_2 , and CH_4 with a purity greater than 99.99% were sourced from BOC UK.

Mineral Class	Minerals	Chemical Formula	Mineral Rocks (wt.%)	
			Bandera gray	Bentheimer
Phyllosilicates	Muscovite	KAl ₂ (AlSi ₃) O ₁₀ (OH) ₂	-	
(Clays)	Biotite	K(MgFe ²⁺) (AlSi ₃) O ₁₀ (OH) ₂	-	-
	Illite	$K_{0.75}(Al_{1.75}[MgFe]_{0.25})~(Al_{0.5}Si_{3.5})~O_{10}~(OH)_2$	10	-
	Chlorites	$(Mg, Fe)_3 (Si, Al)_4 O_{10} (OH)_8 (Mg, Fe)_3 (OH)_6$	1.0	-
	Kaolinites	Al ₂ SiO ₅ (OH) ₄	3.0	2.50
	Montmorillonite	$M_{0.3}Al_2(Al_{0.3}Si_{3.7}) \ O_{10}(OH)_2 \ M^+=Ca^{2+}, \ Mg^{2+}, \ K^+, \ etc.$	-	0.18
Tectosilicates	Quartz	SiO ₂	59	92
	Albite	(K, Na) AlSi ₃ O ₈	12	4.86
Carbonates	Calcite	CaCO ₃	-	-
	Dolomite	Ca, Mg (CO ₃) ₂	15	0.46
Oxides	Ilmenite	Fe ²⁺ TiO ₃	-	-

Table 3—The mineral contents of Bandera gray and Bentheimer core samples

The experimental set-up consists of mainly two units; Core Lab UFS-200 core flooding system with inbuild Smart Flood software and packed column design Agilent 7890A model Gas Chromatography (GC) machine model. The online concentration measurement of core flooding effluents was achieved using the GC machine. These values were used in plotting the injection fluids concentration profile and methane recovery efficiency evaluation as the experiment progress with time. Schematic of the equipment set-up is presented in Figure 2.



Figure 2—Schematics of experimentational set-up for CO_2 core flooding in the presence of N_2 as cushion gas during CH_4 displacement

The UFS-200 core flooding system is rated to 5,000 and 3,750 psig overburden and pore pressure respectively. The injection system of the equipment is made up of a pair of dual ISCO two-barrel metering pump system (A/B and C/D) for constant flow, pulseless transition and to maintain an accurate flow rate range of 0 to 200 ml/min with a maximum pressure rating of 3,750 psig. The pumps are attached to a pair of two stainless-steel floating piston accumulators which are also rated for 5,000 psig working pressure and temperature of 177°C. They are designed for injection of the fluids of interest and can withstand up to 7,500 psig test pressure. Hydraulic pump with a maximum output of 10,000 psig was used to set the overburden confining pressure. The Smart Flood 1.0 software forms an essential unit of the system which interfaces the UFS system and the computer data-acquisition-control (DAC) system hardware. It generates on-screen automatic logging of test data for all measured values like pressures, temperatures, volumes, etc., to a computer data file. A Rosemount Static DP transmitter with an accuracy of 0.0055% was responsible for measuring the differential pressures across the entire Hassler-type core holder, which was used to house the core sample. The core sample is clutch inside the core holder by a Viton rubber sleeve. A core holder heat jacket (containing 1m tubing coil) to simulate the required temperature was also employed with an accuracy of 0.1%. Dome type back pressure regulator integrated into the flooding system ensured the confinement of the desired pressures within the core holder. Such desired pressure was set using N_2 cylinder bottle. The effluents from the back-pressure regulator pass through the mass flow controllers, that measure the volume of the actual effluents produced before been analysed by the GC system in place.

Procedure

The core sample was dried overnight in an oven at 105 °C for moisture removal and other volatile compounds. The dried sample was wrapped with cling film and then foil paper before inserted into a heat shrink. This is vital to avoid viscous fingering and the penetration of the gases into the ring-shaped core holder through the sleeve. It was then loaded into the core holder and staple with clamps from both ends. Hydraulic oil was then pumped into the ring-shaped core holder to provide the desired overburden pressure, which was kept at a minimum of 500 psig above the pore pressures to avoid fracturing of the core sleeve. The heat jacket was then installed on the core holder and the temperature step-up (40 0C) was observed prior to methane saturation. Backpressure was engaged, CH₄ was slowly injected into the core sample from the CH₄ cylinder to saturate the core plug until the GC constantly read methane >98%. $8cm_3$ of N₂ was injected at 0.4 ml/min using ISCO pumps A/B through accumulator or cell A. Pumps A/B was stopped and CO₂ was injected using ISCO pumps C/D through accumulator or cell B at the same injection rate until the experiment get to completion. The experiment elapsed when the methane concentration was insignificant from the GC reading or the CO_2 concentration was > 98%. Further runs were carried out at increasing N_2 cushion volumes and varying CO₂ injection rates to investigate their effects on the longitudinal dispersion coefficient. At each injection time of the GC, the time was noted and the effluent composition which was later used to evaluate the dispersion coefficient was recorded. The investigation was carried out at 1500 psig pressure and 40 0C temperature. This condition was chosen based on a normal gas pressure reservoir with a gradient of 0.451 psi/ft, an average reservoir depth of 1km, and a geothermal temperature of 35-40 °C/km.

Results and Discussion

The concentration profiles recorded from the gas chromatography were used to evaluate the rate of mixing (K_L) between the injected N₂/CO₂ and the residual CH₄ using Eq.2 with K_L as the fitting parameter. The length scale of mixing (L) was adjusted in the regression analysis using OriginPro software to provide a better curve fitting as advice by (Hughes et al., 2012; Liu et al., 2015) given that the interstitial velocity was held constant as assumed in the 1D advection-dispersion in Eq.1. After the analysis converges the displayed K_L value was recorded. Four sets of experiments were carried out at 1500 psig, 40 0C, and at varying buster

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gas volume of 8-36cm₃. The injected amount of N₂ prior to the CO₂ injection exhibits a re-pressurisation effect due to its high conductivity, minimising gas miscibility with minimum fraction of CO₂ in the effluent stream of the core holder as recorded by the GC. This affirmed the potential of N₂ for reservoir maintenance applications. The increase in buster gas volume was in direct proportion to decline in dispersion effect. The higher the buster gas in the system the more N₂ mole fraction was produced, invariably lowering the CH₄ sweet value, which was a similar trend observed during the CO₂ flooding at higher injection rates. The excess injected N₂ acted as a retardant, creating a thin barrier between the CO₂-CH₄ interface, promoting the CO₂ to descend for storage due to gravity with evidence in the lowest dispersion recorded at 36cm₃ buster volume as presented in Table 4.

Core Samples	Q (ml/min)	¹ Dispersion Coefficient (10 ⁻⁸ m ² /s)	² Dispersion Coefficient (10 ⁻⁸ m ² /s)
N_2	0.4	4.40	5.18
CO_2	0.4	5.02	3.70
Cushion gas	(cm ³)		
volumes	8	3.59	3.70
	16	2.78	3.01
	24	3.27	2.82
	36	2,59	2,65

Table 4—Effect of N₂ as buster/cushion gas on longitudinal dispersion coeffiecient

Where, 1 and 2 represent Bandera and Bentheimer core samples

Looking at Eq.5, It evident that precise and reliable simulation of dispersion in an enhanced recovery process requires a detailed understanding of molecular dispersion (D), tortuosity (τ), and dispersivity (α) at the condition relevant to natural gas displacement in porous media. The latter two parameters are properties of the porous medium (core sample) of which α can be determined from a set of experimental data in which the flow velocity through the medium is increasing at reasonable intervals like those described in this study. Although, the pressure and temperature dependence of longitudinal dispersion coefficient (K_L) are acquired predominantly by D, accurate values of the molecular diffusion coefficient are prerequisites to a reliable dispersion correlation. A numerical model developed by Fuller, Schetter, and Gittings (1966) by means of computer-aided correlation of 340 experimental points, expressed in Eq.6 and 7 were was used to evaluate the molecular diffusion coefficient of N₂-CH₄ and CO₂-CH₄ at conditions relevant to EGR and the miscible displacements. The equation was further simplified by inserting the values of atomic diffusion volumes and the molecular weight of CO₂ and CH₄ as shown in Eq.8 and 9. Therefore, using Eq.9, the molecular diffusion coefficients, D, at experimental conditions of 1500 psig and 40 °C of pressure and temperature were evaluated and present in Table 5. Furthermore, the dispersivity (α) can be constructively determined by fixing Eq.5 to the plots of K_L/D against u/D which is a straight line as shown in Fig.3 and 4.

Core Samples	Q (ml/min)	u (10 ⁻⁵ m/s)	K _L (10 ⁻⁸ m ² /s)	D (10 ⁻⁸ m ² /s)	u/D (m ⁻¹)	K _l /D
Bentheimer	0.4	5,98	3,70	22.99	260.01	0.161
	0.6	8.95	5.86	22.99	389.30	0.255
	0.8	11.93	8.06	22.99	518.92	0.351
	1.0	14.91	9.50	22.99	648.54	0.413
	1.2	17.89	11.40	22.99	778.16	0.496
Bandera gray	0.4	6.87	2.85	22.99	298.83	0.124
	0.6	10.30	4.57	22.99	448.02	0.199
	0.8	13.73	6.30	22.99	597.22	0.274
	1.0	17.16	7.87	22.99	746.41	0.342
	1.2	20.60	10.10	22.99	896.02	0.439

Table 5—Dispersion coefficients of CO2-CH4 as functions of concentration profiles at high injection rate









Reports of (Coats, K.H & Whitson, 2004; Keith H. Coats et al., 2009; Honari et al., 2013; Hughes et al., 2012; Abba et al., 2018) dispensed that the values of the dispersivity (α) in consolidated porous media are mostly smaller than 0.01 ft (0.003 m). Hughes et al., (2012) further recorded dispersivity in a range of 0.0001 m to 0.0011m using Donnybrook core sample with petrophysical properties like the ones considered in this work. More so, accurate determination of dispersivity is quite important being an experimental property of a porous medium that examines the characteristic dispersion of the medium by correlating the components of pore velocity to the dispersion coefficient. This parameter is highly sensitive to invigorate fluid flow in the model of the reservoir rock. Considering Figure 3 and 4, the dispersivity as measured of the slopes was found to be 0.0006 and 0.0005m for Bentheimer and Bandera core samples. This lies within the range of values obtained in the literature. The summary of the effect of injection rates on longitudinal dispersion coefficients of Berea and Bandera gray is presented in Table 6.

Q (ml/min)	Pressure (psig)	Temperature (°C)	Interstitial Velocity (10 ⁻⁵ m/s)	Dispersion Coefficient (10 ⁻⁸ m ² /s)
Bentheimer	1500	40		
0.4			5.96	3.70
0.6			8.95	5.86
0.8			11.93	8.06
1.0			14.91	9.50
1.2			17.89	11.40
Bandera gray				
0.4			6.87	2.85

Table 6-Summary of the effect of interstitial velocity on longitudinal dispersion coefficient

Q (ml/min)	Pressure (psig)	Temperature (°C)	Interstitial Velocity (10 ⁻⁵ m/s)	Dispersion Coefficient (10 ⁻⁸ m ² /s)
0.6			10.30	4.57
0.8			13.73	6.30
1.0			17.16	7.87
1.2			20.60	10.10

Generally, the longitudinal dispersion coefficient increases with an increase in flow velocity due to turbulence or eddy current development as evident in Table 6. Therefore, Bentheimer core sample with high permeability displayed a remarkably higher dispersion coefficient compared to Bandera gray gray as seen in Figure 9 and 10. Furthermore, since high porous materials experience less resitance to flow, the core plug with the highest porosity will record high gas movement invariable high mixing especially at higher injection rates. However, the dispersion coefficient rises slowly at lower injection rates in both the core samples. The highest dispersion was observed at $11.40 \times 10^{-8} \text{ m}_2/\text{s}$ for Bentheimer compared to Bandera gray with $10.10 \times 10^{-8} \text{ m}_2/\text{s}$ at maximum injection rate of 1.2 ml/min, about 11.40% raise.



Figure 5—Relationship of coefficient of longitudinal dispersion with flow injections for Bentheimer



Figure 6-Relationship of coefficient of longitudinal dispersion with flow injections for Bandera gray

Conclusion

The coefficient of longitudinal dispersion declines with raises in cushion gas volume, hence the higher the amount of N₂ cushion volume the less the dispersion of CO₂ into CH₄. This is due to the high shielding barrier inhibited by nitrogen, making it difficult for the CO2 to dispersed itself and mixed with the nascent natural gas resulting in delayed breakthrough as it plumes transverses into the CH4 during the displacement process. The CO2-CH4 dispersion was influenced with the inclusion of N2 as cushion or buster gas prior to the CO2 injection into the reservoir. The longitudinal dispersion coefficient exhibits less miscibility compared to that of conventional carbon dioxide flooding. Overall, a less CO2-CH4 dispersion was noticed for all the runs compared to traditional CO_2 injection with the best result result at 36 cm₃ buster gas volume. This is equivalent to 48 and 28% reduction in longitudinal dispersion coefficient for Bandera and Bentheimer core samples respectively due to N₂ addition, compared to that of conventional/traditional CO₂ injection (with zero cushion volume). Recording lower nascent CO2-CH4 mixing resulting in less natural gas contamination and more storage volumes. This re-affirmed the potential of N_2 as buster gas on dispersion coefficient of supercritical CO2 in sandstone rocks during EGR process. It was also found that the flow mechanism was controlled by advective mixing, meaning the medium peclet number is greater than 10 (P_{cm}>10). However, a reverse phenomenon was observed when the CO2 injection rate was increased from 0.6-1.2 ml/min due to the high diffusion rate of CO₂ at higher interstitial velocities, resulting in a rapid increase in dispersion coefficient and indirectly high widespread contamination of the remaining natural gas. In this study, the dispersivity (α) value was found to be 0.0006 and 0.0005m which is quite within the range reported by (Hughes et al, 2012; Abba et al, 2018) for consolidated rocks.

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Nomenclature

- yCO_2 CO₂ mole fraction
 - yN_2 N₂ mole fraction
 - D Diffusion coefficient, m2/s
 - Q Flowrate, mil/min
 - t_D Dimentionless time
 - x_D Dimentionless distance
 - d Characteristic length scale, m
 - K_L Longitudinal dispersion, m2/s
 - L Core sample length, mm
 - L_{exp} Experimental length, m
 - μ Viscosity, cP
 - P Pressure, psig
 - T Temperature, K
 - u Interstitial velocity, m/s
 - $\phi~$ Core porosity, %
 - α Dispersivity, m
 - τ Tortuosity
 - P_e Peclet number
 - Pem Medium Peclet number
 - r Radius of core sample, m

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Alternating N₂ and CO₂ Injection as Prospective Technique for Delaying CO₂ Breakthrough During During Enhanced Gas Recovery in Consolidated Rocks.

Nuhu Mohammed, Abbas Jibrin Abubakar, and Godpower Chimagwu Enyi, University of Salford, Manchester

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Abstract

The use of carbon dioxide (CO₂) for simultaneous methane recovery and CO₂ storage is gaining recognition globally within the oil and gas industries. On the other hand, most of the residual natural gas recovered during the EGR process is highly contaminated with the injected CO₂ due to their nascent miscibility nature, resulting in premature breakthrough. In this study, N₂ gas was used as a buster to mitigate such early mixing between the CH₄ and CO₂. The experiment was administered at reservoir conditions of 40oC temperature, 1500 psig of pressure, the optimum injection rate of 0.4ml/min, and at varying N₂ cushion volumes (8-36 cm³) using Bandera gray as the porous medium. Further experimental tests were administered to study the effect of this technique on connate water salinity with 5-20% water salinity been considered. The increase in buster gas volume was in direct proportion to delayed CO₂ breakthrough, with the maximum at 36cm³ buster volume. This breakthrough occurred at 177 minutes which is 110min additional delayed than the conventional CO₂ flooding with a breakthrough time of 67 minutes. This was due to the high shielding barrier inhibited by nitrogen, making it difficult for the CO₂ to dispersed itself and mixed with the nascent natural gas resulting in delayed breakthrough as it plumes transverses into the CH₄ during the displacement process. Furthermore, a poor performance was observed with the inclusion of the connate water salinity, especially at 20% wt. This was because the free pore spaces were already occupied by connate water molecules prior to the cushion gas injection which hinders its economic potential application.

Introduction

As time progresses, the reservoir pressure tends to decline, as such, production of natural gas from the reservoirs can be obstructed and the reservoirs are neglected. These reservoirs are termed depleted oil and gas fields (Abba et al., 2017). Such oil and gas fields are uninhibited for a variety of reasons; common amongst which is poor production outputs, other reasons could be because of large water invasion (Kalra & Wu 2014). These depleted reservoirs are not empty of residual HCs in-situ and the need for further production and recovery to account for the rising energy demand. This merit the employment of Enhanced Gas Recovery (EGR) techniques, especially when CH_4 is displaced and CO_2 is stored. The services of these

isolated gas reservoirs may be used for anthropogenic CO_2 geological storage (Abba et al., 2017). The concept of EGR by CO_2 injection exploits the availability of residual methane in the reservoir and at the same time store the injected CO_2 .

Furthermore, the irreversible mixing that occurs during fluids displacement by a miscible process is termed dispersion (Adepoju et al., 2013). This mixing occurs when miscible fluids meet one another, and their molecules interact at conditions that encourage the thermodynamic instability between them (Abba et al., 2018). Molecular diffusion and mechanical dispersion are the two mechanisms that simultaneously play roles in the mixing between two miscible fluids as reported by (Perkins & Johnston, 1963). They defined the mixing that occurs in the porous medium as a diffusion-like process and is a function of the velocity and concentration gradients.

Several researchers have administered different injection methods to delayed CO₂ residence time during the enhanced gas recovery process, but just few were successful since b. Abba et a.l, (2018) was able to achieve additional of 20min delayed compared to conventional CO2 injection at a connate water salinity of 10% wt. of sodium chloride. To date, no established efficient method capable of delaying such CO_2 breakthrough which would indirectly improve simultaneous natural gas recovery and carbon dioxide sequestration since both gases are miscible in all proportions (Abba et al., 2018; Honari et al., 2016; Liu et al., 2015; Mohammed et al., 2020). In 2009 and 2010, Sidiq and Amin carried out an experiment using a laboratory core flooding device to measure the CO₂ breakthrough profile using a mixture of 98%CO₂ + 2%CH₄ injection fluid over a long 194mm sandstone. It was noted that the core sample was fully saturated with 25-90% CH₄ first before the mixed gas injection. Also, the porous core plug was initially saturated with a known salinity which was later lowered to irreducible water content using the gas mixture. The experimental condition was at 160 °C and 40.7 MPa of temperature and pressure respectively. Their measured dispersion coefficient has limited applicability, due to the approximation method employed in determining the respective dispersion coefficient. This makes it difficult to accurately identify the initial point of the concave slope which amounts to high uncertainty in the dispersion coefficient extrapolated due to small disturbances in the breakthrough point (Sidiq & Amin, 2009; Sidiq & Amin, 2010). This initiated the significance and importance of developing a new and efficient injection scenario capable of delaying CO₂ residence time as it plumes transverses through the porous medium, during the EGR displacement experiment using a laboratory core flooding system.

This experimental study, however limited, has highlighted the impact of N_2 as buster and retardant for minimizing delaying CO₂ residence time during the EGR process by CO₂ core flooding. The N_2 gas acts as a buster or cushion gas by re-pressurising the reservoir pressure prior to CO₂-breakthrough enable more CH₄ recovery without contamination, and also acted as a retardant by creating a thin barrier in between CO₂-CH₄ phase region, making it tough for the CO₂ to disperse into the methane resulting to a lower longitudinal dispersion coefficient thereby, forcing most of the CO₂ to descend downward for storage within the pore spaces due to gravity. In this report, the the potential of N_2 as buster gas in delaying CO₂ breakthrough in consolidated rocks during EGR process was investigated.

Dispersion and Diffusion Coefficients

The existing mixing drive mechanism found in CH_4 - CO_2 and CH_4 - N_2 interaction behavior are mostly diffusion-match as a result of velocity and concentration difference within the sandstone rocks (Abba et al., 2017). The extent of miscibility is generally measured by the diffusion coefficient. This means higher and lower dispersion coefficients are a good indication of excess and minimal length scale of mixing whenever two or more miscible fluids encounter during core flooding displacement experiment. Depending on the flux direction, this coefficient is classified into a longitudinal and transverse dispersion coefficient with the earlier occurring in the main convective flux and can be obtained experimentally

(Perkins and Johnston, 1963). Two giant scientists Newbey and Foh (1988) developed a simplified model correlation using generated experimental results (Abba et al., 2017) as presented in Eq. 2. The numerical dispersivity model was used to evaluate the longitudinal dispersion coefficient based on the displacing gas concentrations obtained directly from the gas chromatography analyser during the CO₂ core flooding process as it plumes transverses through the Bandera gray porous medium (Mohammed et al., 2020). Furthermore, Mamora and Seo (2002) reviewed the above Eq. 1 and simplified it further in a dimensionless form as shown in Eq. 2. This was so, to avoid unpredictable upstream migration resulting in viscous fingering particularly when the $\left(\frac{\partial C}{\partial x}\right)$ term of Eq.1 becomes positive as similar to the case of supercritical CO₂ injection passing through a mixed stream after breakthrough, and invariably magnitude of longitudinal dispersion coefficient (Mohammed et al., 2020).

$$K_L \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \tag{1}$$

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2)

Where;

Table 1—Host rock properties

Parameter	Symbol	Expression	
Peclet number	P_{e}	uLKL	
Dimensionless time	t_D	tuL	
Dimensionless distance	x_D	xL	
Interstitial velocity	u	Qπr2φ	

Source: (Mohammed et al., 2020)

The solution to the ordinary differential equation (Eq. 1) based on 1D advection-dispersion equation was sited in Eq. 3, under a known boundary conditions: C = 1 at $x_D = 0$, $C \rightarrow 0$ as $x_D \rightarrow \infty$.

$$C = \frac{1}{2} \left\{ erfc \left(\frac{x_D - t_D}{2\sqrt{tD/Pe}} \right) + e^{Pex_Derfc} \left(\frac{x_D + t_D}{2\sqrt{tD/Pe}} \right) \right\}$$
(3)

Perkins and Johnston (1963) developed the most used-acceptable model equation that was used in determining the dominant mechanism factor during the EGR process, as presented in Eq. 4. This equation demonstrates the relationship between the medium peclet number (P_{cm}) and that of interstitial velocity (u) at a constant value of diffusion coefficient (D) and the characteristic length scale of mixing (d).

$$P_{em} = \frac{u_m d}{D} \tag{4}$$

The proposed model assumption was that a process is said to be diffusion-like if $P_{em} \le 0.1$ and advective-like if $P_{em} \ge 10$.

To evaluate the dispersivity of the porous medium Coats et al., (2009) proposed a model correlating the dispersion and diffusion coefficient shown in Eq. 5. Also, to measure the dispersivity experimentally, the left-hand side of Eq. 5 was plotted against the ratio of interstitial velocity and molecular diffusion coefficient. The intercept on the vertical axis was later used to calculate the tortuosity (τ). This value ranges from 1-13, reported by (Honari et al., 2013; Hughes et al., 2012) for consolidated sandstone rocks.

$$\frac{Kl}{D} = \frac{1}{\tau} + \frac{u_m'}{D} \tag{5}$$

The molecular diffusion coefficient (D) used in this study was developed by (Takahashi and Iwasaki, 1970; Fuller, Schetter, and Gittings, 1966) and reported in our previous publication (Mohammed et al., 2020).

Materials

The core plug used was Bandera gray and its properties are similar with the one reported in our previous authorship (Mohammed et al., 2020) as shown in Tables 2 and 3. Other details of material uses and sources can be found in our published work (Mohammed et al., 2019; Mohammed et al., 2020).

Core sample	Length (mm)	Diameter (mm)	Bulk Vol. (cm ³)	Porosity (%)	Gas Permeability (md)
Bandera gray	76.02	25.31	38.27	19.68	32

Table 2—Bandera gray core plug petrophysical properties

Source: (Mohammed et al., 2020)

Table 3—Bandera gray mineral contents				
Mineral Class	Minerals	Chemical Formula	Mineral Rocks (%)	
Phyllosilicates (Clays)	Muscovite	KAl ₂ (AlSi ₃) O ₁₀ (OH) ₂	-	
	Biotite	K(MgFe ²⁺) (AlSi ₃) O ₁₀ (OH) ₂	-	
	Illite	$K_{0.75}(Al_{1.75}[MgFe]_{0.25})\;(Al_{0.5}Si_{3.5})\;O_{10}\;(OH)_2$	1.0	
	Chlorites	(Mg, Fe)3 (Si, Al)4 O10 (OH)s (Mg, Fe)3 (OH)6	2.0	
	Kaolinites	Al ₂ SiO ₅ (OH) ₄	5.0	
	Montmorillonite	$M_{0.3}Al_2(Al_{0.3}Si_{3.7}) O_{10}(OH)_2 M^+ = Ca^{2+}, Mg^{2+}, K^+, etc.$	-	
Tectosilicates	Quartz	SiO ₂	87	
	Albite	(K, Na) AlSi ₃ O ₈	2.0	
Carbonates	Calcite	CaCO ₃	2.0	
	Dolomite	Ca, Mg (CO ₃) ₂	1.0	
Oxides	Ilmenite	Fe ²⁺ TiO ₃	-	

Source: (Mohammed et al., 2020)

Methodology

Prior to the CO₂ and N₂ injection, the Bandera gray core plug was fully saturated with CH₄ to create the artificial gas reservoir. The investigation was administered at varying volumes (8-36 cm³) of N₂ as buster or cushion gas prior to the CO₂ injection at 0.4ml/min. Further experimental tests were administered to study the effect of the cushion gas in the presence of connate water salinity of 5, 10, and 20% wt. The experimental set-up used is shown in Figure 1. The details of Fig. 1 have been reported by Mohammed et al., (2020).

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cushion gas during EGR displacement process (Mohammed et al., 2020)

Procedure

 8cm^3 of N₂ was injected at 0.4 ml/min before injecting the CO₂ later at the same injection rate. The experiment end when high mole composition of CO₂ was recorded from the gas chromatopgraphy. The experiment was repeated at increasing N₂ cushion volumes for 16, 24, and 36 cm³ in other to determine the best buster volume. Further experimental runs were administered at the optimum buster gas volume in the presence of connate water salinity of 5, 10, and 20% wt. These results were later used to investigate the changes in CO₂ breakthrough at different buster gas volumes and connate water salinities. The operating temperature (40 °C/104 °F) and pressure (1500 psig/103.4 bar) for this study are within the range of a normal gas reservoir. The experimental temperature and pressure were selected based on a normal gas pressure reservoir with a gradient of 0.451 psi/ft, an average reservoir depth of 1km, and a geothermal temperature of 35-40 °C/km (Mohammed et al., 2020).

Results and Discussion

The CO₂ residence time (breakthrough time) showcases the initial interaction period were the CO₂ or N₂ mixed with the residual CH₄ along the scale of the Bandera gray porous medium as the ecperiment proceeds. The more the breakthrough, the lower the mole fraction of CO₂ produced at the effluent stream provided that the dispersion coefficient is minimal, while the shorter the breakthrough, the high the risk of contaminating the recovered residual gas from the reservoir. This amounts to CH₄ production with lower calorific heat, higher purification cost, and rendering the process uneconomical (Mohammed et al., 2020). Four sets of experiments are carried out at 1500 psig, 40 °C, and at varying buster gas volume of 8-36cm³. The variation in effluent compositions with displacement time for the conventional CO₂ and N₂ flooding was monitored as presented in Figure 2. Tables 5 and 6 present the core flooding production data for the conventional N₂ and CO₂ injection at 0.4ml/min optimum injection rate, while the effect of gas buster volumes on CO₂

breakthrough were shown in Tables 7-10. The CO2 residence time was delayed for all the buster gas volumes employed. The injected amount of N₂ prior to the CO₂ injection exhibits a re-pressurisation effect to generate higher level of CH4 with minimum fraction of carbon dioxide in the effluent stream of the core holder prior to CO₂ breakthrough due to its high conductivity. This asserted the potential of N₂ for reservoir conservation applications (Mohammed et al., 2020). The increase in buster gas volume was in direct proportion to delayed CO2 breakthrough, with the maximum at 36cm3 buster volume. This breakthrough occurred at 177 minutes which is 110 min longer the conventional CO₂ flooding with a breakthrough time of 67 minutes. The higher the buster gas in the system the more delayed CO2 breakthrough was recorded, invariably higher storage. The introduction of N₂ displaces a larger amount of the CH₄ until it reached its breakthrough, this allows most of the CO₂ later injected to be trapped within the rock space without mixing with the nascent CH₄. More so, at the time the CO_2 reaches its breakthrough a substantial volume of CH_4 has been recovered already since the CO2 will find it difficult to disperse itself into the methane due to the presence of nitrogen gas which acted like a barricaded wall between the CO2 and CH4 (Mohammed et al., 2020). Natural gas products based on N2 contaminants are more friendly than CO2 based contaminants because most natural gas exploration fields do accommodate higher nitrogen contamination than CO2 based impurities. The sweetening process of CH₄-N₂ contamination is less expensive compared to CH₄-CO₂ due to the high compression energy cost and depressurizing process employed. Furthermore, a poor performance was observed with the inclusion of the connate water salinity, especially at 20% wt. This is because the free pore spaces were already occupied by connate water molecules prior to the cushion gas injection which hinders its economical potential application.



The CO₂ breakthrough increases with an increase in buster gas volume due to the blanketing effect of nitrogen especially at excess cushion gas volume as seen in Figure 2. However, a reverse scanerio was

observed when connate water was employed. The higher the salinity concentration the lower the CO_2 breakthrough since most of the available void spaces were already accommodate by the salt solution prior to the buster gas and CO_2 injection. As noticed in Table 11-13, the CO_2 breakthrough time occurred at 99.65, 88.15, and 66.49 minutes. Invariably, a longer breakthrough was realized during the 5wt.% connate water salinity run, while an earlier residence time was observed at 20wt.% salinity. The later was due to the reduction in core sample pore volume that results in low natural gas recovery as seen in Table 4. This is because of the high connate water density occupying more of the free void spaces within the pore matrix (Abba et al., 2018).

Items	Q (ml/min)	Resisdence Time (min)	Recovery Factor (%)
N ₂	0.4	115.82	90.30
CO_2	0.4	67.32	44.41
Cushion gas volumes	(cm ³)		
	8	134.48	89.17
	16	159.82	64.81
	24	150.15	75.95
	36	177.15	44.38
Connate water salinity	(wt.%)		
	5	99.65	13.65
	10	88.15	17.23
	20	66,49	12.45

Table 4—The effect of buster gas volume and connate water salinity on CO_2 breakthrough

Table 5—Core flooding experimental production data by N ₂ injection	n without cushion gas at 0.4ml/min optimum injection rate
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Time	Volume injected (PV)	N ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
0.15	0.01	0.044	408	31.964	3.68
5.82	0.31	0.045	404	63,608	7.322
11.32	0.6	0.045	403	95.152	10.95
16.82	0.89	0.045	410	127.25	14.65
22.32	1.19	0.045	412	159.51	18.36
27.82	1.48	0.045	413	191.81	22.08
33.32	1.77	0.046	413	224.05	25.79
38.82	2.06	0.046	420	256.8	29.56
44.32	2.35	0.046	422	289.75	33.35
49.82	2.65	0.046	424	322.84	37.16
55.32	2.94	0.046	430	356.45	41.03
60.82	3.23	0.047	396	387.33	44.59
66.32	3.52	0.047	401	418.68	48.2
71.82	3.82	0.047	415	450.88	51.9
77.32	4.11	10.049	422	483.85	55.7
82.82	4.4	0.052	433	517.6	59.58
88.32	4.69	0.058	453	552.96	63.65

Time	Volume injected (PV)	N ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
93.65	4.97	0.065	412	585.13	67.36
99.32	5.28	0.073	439	619.31	71.29
104.65	5.56	0.093	438	653.49	75.23
110.48	5.87	0.378	434	687.27	79.12
115.82	6.15	2.749	426	704.54	81.1
121.32	6.44	12.32	454	666.56	76,73
126.98	6.75	31.91	187	526.48	60.61
132.48	7.04	55.39	351	354.9	40.85
137.98	7.33	74.19	100	204.62	23.56
143.82	7.64	85.98	99	109.63	12.62
149.48	7.94	91.31	288	67.959	7.823
154.82	8.22	93.92	81	46.518	5.355
160.32	8.52	95.50	119	33.69	3.878
165.82	8.81	96.41	130	26.312	3.029
171.32	9.1	97.02	141	22.034	2.536
176.82	9.39	97.31	138	19.346	2.227
182.66	9.7	97.54	113	17.564	2.022
188.15	9.99	97.68	297	16.792	1.933
193,65	10.3	97.78	295	16.368	1.884
199.32	10.6	97.83	296	16.298	1.876
205.15	10.9	97.87	295	16.254	1.871
210.65	11.2	97.89	136	16,256	1.871
216.15	11.5	97.91	123	16.279	1.874
221.48	11.8	97.96	293	16,092	1.852
226.98	12.1	97.96	293	16.45	1.894
232.82	12.4	97.99	288	16.45	1.894
238.65	12.7	98.03	287	16,423	1.891
244.15	13	98.06	293	16.468	1.896

Table 6—Core flooding experimental production data by CO₂ injection without cushion gas at 0.4ml/min optimum injection rate

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH4 produced (cm3)	Recovery factor (%)
0.15	0.01	0,139	394	31.21	3,59
5.15	0.27	0.150	398	62.60	7.21
11.32	0.60	0.125	393	93.57	10.77
16.82	0.89	0.113	140	104.60	12.04
22.32	1.19	0.173	407	136.70	15.73
27.82	1.48	0.191	410	169.00	19.46
33.32	1.77	0.199	415	201.70	23.22
39.48	2.10	0.205	115	210.80	24.26
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Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
44,98	2.39	0,208	434	245.00	28.20
50.65	2.69	0.214	164	257.90	29.69
56.32	2.99	0.216	458	294.00	33.85
61.82	3.28	0.228	169	307,30	35,38
67.32	3.58	4.339	482	332.90	38.32
72.65	3,86	38.95	433	233,10	26.83
78.15	4.15	70.50	164	115.90	13.34
83.65	4.44	81.21	371	78.48	9.03
89.15	4.74	88.61	476	52.19	6.01
94.65	5.03	92.99	588	35.21	4.05
100.15	5.32	96.02	568	21.65	2.49
105.65	5.61	97.57	210	13.34	1.54
111.15	5.90	98.46	252	8.390	0.97
116.48	6.19	98.97	603	5.730	0.66

Table 7—Core flooding experimental production data by CO_2 injection at 8cm³ cushion gas volume

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
0.16	0.01	0.421	352	27.55	3.17
5,98	0.32	0,449	385	57,67	6,64
11.49	0.61	0.465	352	85.21	9.81
17.32	0.92	0.482	376	114.60	13.19
22.65	1.20	0.501	426	147.90	17.03
28.15	1.50	0.485	379	177.50	20.44
33.98	1.81	0,560	388	207.80	23.92
39.65	2.11	0.587	388	238.10	27.41
45.15	2.40	0.614	430	271.70	31.27
50.48	2.68	0,501	368	300.30	34.56
55.98	2.97	0.51	383	330.10	38.00
61.65	3.27	0.615	396	361.00	41.56
67.15	3.57	0.674	358	388.90	44.77
72.82	3.87	0.71	373	417.90	48.11
78,32	4.16	0.739	337	444,10	51.12
83.98	4.46	0.764	401	475.30	54.71
89.65	4.76	0.79	366	503.80	57.99
95.65	5.08	0.819	358	531.60	61.20
101.15	5.37	0.841	391	562.00	64.70
106,65	5.67	0.856	388	592.20	68.18
112.15	5.96	0.856	421	625.00	71.95
117.82	6.26	0.824	407	656.70	75.59

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
123.32	6.55	0.757	462	683.20	78.65
128,98	6.85	1.166	448	670.50	77.19
134.48	7.14	7.107	415	585.90	67.45
140.15	7.44	27.371	103	416.10	47.90
145.82	7.75	56.115	375	245.00	28.21
151.32	8.04	75.681	364	139,90	16,11
156.98	8.34	87.422	394	78.58	9.05
162.65	8.64	94.339	432	39.76	4.58
168.32	8.94	96.827	440	23.77	2.74
173.98	9.24	98.946	529	7.41	0.85
180.32	9.58	99.226	547	5.01	0.58
186.15	9.89	99.317	570	4.36	0.50

Table 8—Core flooding experimental production data by CO₂ injection at 16cm³ cushion gas volume

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
0,15	0.01	0.018	115	1.06	1.06
5.98	0.32	0.018	370	4.46	4.46
11.98	0.64	0.025	372	7.89	7.89
17.65	0.94	0,030	371	11.29	11.29
22.98	1.22	0.034	123	12.42	12.42
28.65	1.52	0.038	114	13.47	13.47
34.15	1.81	0.040	132	14.68	14.68
39.65	2.11	0.042	384	18.21	18.21
45.32	2.41	0.044	113	19.24	19.24
50.82	2.7	0.046	117	20.32	20.32
56.15	2.98	0.048	112	21.34	21.34
61.65	3.27	0.049	126	22.50	22.50
67.15	3.57	0.051	125	23.64	23.64
72.48	3.85	0.052	136	24.89	24.89
77.82	4.13	0.053	378	28.36	28.36
83.32	4.43	0.056	382	31.86	31.86
88.65	4.71	0.056	344	35.02	35.02
94.15	5.00	0.056	349	38.22	38.22
99.48	5.28	0.057	352	41.45	41.45
104.98	5.58	0.057	357	44.72	44.72
110.32	5.86	0.058	104	45.66	45.66
115.82	6.15	0.059	371	49.07	49.07
121.65	6.46	0.060	124	50.2	50.20
126.98	6.75	0.061	152	51.59	51.59

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Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH4 produced (cm3)	Recovery factor (%)
132.65	7.05	0.063	399	55.24	55.24
137.98	7.33	0.064	165	56.74	56.74
143.48	7.62	0.067	184	58.42	58.42
148.98	7.91	0.067	174	59,7	59.70
154.48	8.21	0.069	183	57.42	57.42
159.82	8,49	2,150	191	48,91	48.91
165.15	8.77	26.81	153	32.75	32.75
170.65	9.07	72.47	408	12.55	12.55
175.98	9.35	90.38	411	5.04	5.04
181.48	9.64	96.23	226	2.21	2.21
186.82	9.92	98.66	222	0.79	0.79
192.15	10.2	99.15	550	0.50	0.50
197.48	10.5	99.20	552	0.42	0.42

Table 9—Core flooding experimental production data by CO_2 injection at 24cm³ cushion gas volume

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
0.15	0.01	0.118	407	32.49	3.74
5.82	0.31	0.131	404	64.74	7.45
11,32	0.60	0,137	132	75.28	8,67
17.65	0.94	0.142	143	86.70	9.98
23.15	1.23	0.157	126	96.74	11.14
28.65	1.52	0.162	414	129.79	14.94
33.98	1.81	0.162	413	162.74	18.73
39.32	2.09	0.164	140	173.92	20.02
44.82	2.38	0.169	134	184.60	21.25
50.32	2.67	0.169	141	195.84	22.54
55.82	2.97	0.173	148	207.65	23.90
60.98	3.24	0.179	303	231.83	26.69
66.48	3,53	0.185	409	264.44	30.44
71.98	3.82	0.186	436	299.23	34.45
77.48	4.12	0.191	414	332.26	38.25
82.82	4.40	0,193	416	365,45	42.07
88.62	4.71	0.197	417	398.72	45.90
93.98	4.99	0.197	398	430.46	49.55
99.82	5.30	0.199	418	463.79	53.39
105.32	5.59	0.200	136	474.62	54.64
110.65	5.88	0.200	435	509.33	58,63
116.15	6.17	0.204	459	545.93	62.84
121.48	6.45	0.205	452	580.37	66.81

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
127.65	6.78	0,205	172	592.46	68.20
132.98	7.06	0.205	158	546.80	62.94
138.32	7.35	0.387	142	463.52	53.36
144.65	7.68	1.141	410	352,60	40.59
150.15	7.98	3.269	363	251.00	28.89
155,48	8,26	21.79	339	172.44	19.85
161.15	8.56	60.86	358	94.57	10.89
166.65	8.85	82.82	352	54.42	6.26
172.15	9.14	91.41	353	35.85	4,13
177.48	9.43	94.77	163	25.95	2.99
183.15	9.73	96.53	160	19.35	2.23
188.65	10.00	97.50	178	14.80	1.70
194.32	10.30	98.00	173	12.28	1.41
199.82	10,60	98.15	148	11.51	1,32
205.32	10.90	98.25	376	11.27	1.30
211.15	11.20	98.38	381	10.76	1.24
217.48	11.60	98.53	384	10.05	1.16

Table 10—Core flooding experimental production data by CO_2 injection at 36cm³ cushion gas volume

Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
0.15	0.01	0.047	130	10.38	1.20
5.82	0.31	0.055	128	20.6	2.37
12.48	0.66	0.071	133	31.218	3.59
17.98	0.96	0.085	144	42.714	4.92
23.48	1.25	0.099	147	54.45	6.27
28.82	1.53	0.108	149	66.344	7.64
34,48	1.83	0.115	153	78.558	9.04
40.48	2.15	0.122	138	89.574	10.31
45.98	2.44	0.125	142	100.9	11.62
51.32	2.73	0.128	117	110.24	12.69
56.82	3.02	0.134	122	119.97	13.81
62.32	3,31	0,135	122	129.7	14.93
67.65	3.59	0.136	123	139.52	16.06
72.98	3.88	0.138	131	149.97	17.26
78.48	4.17	0.141	139	161.06	18.54
83.98	4.46	0.143	134	171.75	19.77
89.32	4.74	0.143	422	205,43	23.65
94.98	5.05	0.149	113	214.44	24.68
100.65	5.35	0.151	120	224.01	25.79

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Time	Volume injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ produced (cm ³)	Recovery factor (%)
105.98	5.63	0.156	132	234,54	27.00
111.48	5.92	0.16	156	246.99	28.43
116.82	6.21	0.164	130	257.35	29.63
122.32	6.50	0.167	132	267.75	30.82
127.82	6.79	0.171	129	276.53	31.83
133,15	7.07	0,174	388	303,12	34.89
138.48	7.36	0.177	380	322.33	37.10
143.98	7.65	0.18	132	312.17	35.94
149.65	7.95	0.181	130	290.32	33.42
154.98	8.23	0.186	133	257.62	29.66
160.66	8.53	0.19	136	210.51	24.23
166.15	8.83	0.192	138	157.09	18.08
171.65	9.12	0.200	121	119.18	13.72
177.15	9,41	3,406	342	89.70	10,33
182.98	9.72	60.648	393	40.05	4.61
188.48	10.00	88.588	149	18.07	2.08
193.82	10.30	97.136	519	6.39	0.74
199.32	10.60	98.501	537	4.05	0.47
204.65	10.90	99.045	209	2.88	0.33
209.98	11.20	99.237	235	2.37	0.27

Table 11—Core flooding experimental production data by CO2 injection at optimum cushion gas volume and 5% wt water salinity

Time	Volume Injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ Produced (cm ³)	Recovery Factor (%)
0.15	0.01	0.055	10	0.79	0.09
7.15	0.38	0.057	10	1.58	0.18
12.66	0.67	0.059	16	2.84	0.33
18.15	0.96	0.059	53	6.97	0.80
23.49	1.25	0.061	17	8.29	0.95
28.98	1.54	0.061	23	10.08	1.16
34.48	1.83	0.064	80	16.33	1.88
39.82	2.12	0.064	187	30.72	3.54
45.15	2.40	0.065	88	37.54	4.32
50.66	2.69	0.066	93	44.59	5.13
56.32	2.99	0.066	90	51.45	5.92
61.65	3.27	0.067	41	19.15	2.20
67.15	3.57	0.067	42	22.29	2.57
72.82	3.87	0.068	25	24.13	2.78
78.15	4.15	0.069	101	31.81	3.66
83.48	4.43	0.069	119	59.3	6.83

Time	Volume Injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ Produced (cm ³)	Recovery Factor (%)
88.98	4.73	0.086	283	79.37	9.14
94.32	5.01	0.115	256	88.23	10.20
99.65	5.29	20.99	75	55.89	6.43
105.82	5.62	94.72	164	2.44	0.28
111.32	5.91	97.26	160	1.29	0.15
116,98	6.21	98.09	230	1.09	0.13
122.48	6.51	98.50	204	1.08	0.12
128.15	6.81	98.84	272	0.86	0.10
133.48	7.09	99.05	186	0.72	0.08
138.98	7.38	99.09	444	0.91	0.11
144.98	7.70	99.29	218	0.73	0.08
150.65	8.00	99.35	362	0.72	0.08

Table 12—Core flooding experimental production data by CO₂ injection at optimum cushion gas volume and 10% wt water salinity

Time	Volume Injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ Produced (cm ³)	Recovery Factor (%)
0,15	0.01	0,594	522	41.16	4.74
6.15	0.33	0.606	420	74.13	8.53
11.65	0.62	0.619	444	109.00	12.50
16,98	0,9	0,627	331	127,60	14.70
22.48	1.19	0.676	97	42.87	4.93
27.99	1.49	0.679	122	21.35	2.46
33.48	1.78	0.682	121	21.10	2.43
38.82	2.06	0.701	118	21.37	2.46
44.32	2.35	0.726	276	19.61	2.26
49.65	2.64	0.735	210	16.28	1.87
55.15	2.93	0.741	170	16.40	1.89
60.65	3.22	0,800	108	16.95	1.95
65.98	3.50	0.861	158	15.29	1.76
71.65	3.81	0.917	100	12.84	1.48
77.16	4.10	0.995	298	10.84	1.25
82.65	4.39	1.094	350	11.58	1.33
88,15	4.68	36,15	383	12.14	1.40
93.48	4.97	96.44	116	4.20	0.48
98.98	5.26	97.97	338	2.92	0.34
104.32	5.54	98.29	276	2.81	0.32
110.49	5.87	98.54	308	2.44	0.28

Time	Volume Injected (PV)	CO ₂ Concentration (%)	Gas Production (cm ³)	CH ₄ Produced (cm ³)	Recovery Factor (%)
0.16	0.01	0.171	655	52.11	6.00
6.16	0.33	0.263	446	87.19	10.00
11.66	0.62	0.264	304	32.60	3.75
16.99	0.9	0.284	119	11.82	1.36
22.49	1.19	0.321	127	9.25	1.06
27.82	1.48	0.332	270	10.75	1.24
33,16	1,76	0.337	298	12.36	1.42
38.66	2.05	0.365	307	11.05	1.27
44.00	2.34	0.407	320	10.38	1.19
49.82	2.65	0.472	263	8.66	1.00
55.32	2.94	0.603	250	9.09	1.05
60.99	3.24	0.761	300	9,79	1.13
66.49	3.53	4.839	341	8.92	1.03
71.99	3.82	78.6	370	8.76	1.01
77.66	4.13	93.82	401	7.39	0.85
83.32	4.43	95.96	396	4.47	0.51
88.82	4.72	97.31	444	4.83	0.56
94.49	5.02	97.82	407	4.16	0.48
100.15	5.32	97.93	428	4.03	0.46
105,99	5.63	98.17	397	4.28	0.49
112.66	5.98	98.47	424	4.02	0.46
118.49	6.29	98.65	464	3.72	0.43

Table 13—Core flooding experimental production data by CO2 injection at optimum cushion gas volume and 20wt.% water salinity

Conclusion

The CO₂ breakthrough time increases with raises in cushion gas volume, hence the higher the amount of N₂ cushion volume the longer the breakthrough. This is due to the high shielding barrier inhibited by nitrogen, making it difficult for the CO₂ to dispersed itself and mixed with the nascent natural gas resulting in delayed breakthrough as it plumes transverses into the CH₄ during the core flooding experiment. The CO₂-CH₄ breakthrough was influenced by the inclusion of N₂ as a cushion or buster gas prior to the CO₂ injection into the reservoir. Overall, a delay in CO₂ breakthrough was noticed for those tests with buster gas compared to that of traditional CO₂ injection with the longest delay at 36 cm³ buster gas volume. This is equivalent to 110 min longer compared to that of conventional/traditional CO₂ injection (with zero cushion volume). This re-affirmed the potential of N₂ as buster gas in delaying CO₂ breakthrough during the EGR process. Furthermore, a poor performance was observed with the inclusion of the connate water salinity and a reverse trend was also observed in the existence of connate water especially at 20wt.% salinity. The higher the salinity concentration the lower the CO₂ breakthrough since most of the free bubble void spaces was inhabited with the salt solution prior to the buster gas and CO₂ injection.

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Nomenclature

- C Carbon dioxide effluent composition
- yCO_2 CO₂ mole fraction
 - yN_2 N₂ mole fraction
 - D Diffusion coeffcient, m^{2/s}
 - Q Flowrate, ml/min
 - t_D Dimensionless time
 - x_D Dimentionless distance
 - d Characteristic length scale, m
 - K_L Longitudinal dispersion, m²/s
 - L Core sample length, mm
 - Lexp Experimental length, m
 - μ ; Viscosity, cP
 - P Pressure, psig
 - T Temperature, K
 - um Interstitial velocity, m/s
 - ϕ Core porosity, %
 - α Dispersivity, m
 - τ Tortuosity
 - P_e Peclet number
 - Pem Medium Peclet number
 - r Radius of core sample, m

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Flow Characteristics Through Gas Alternating Gas Injection During Enhanced Gas Recovery

Nuhu Mohammed, Abbas Jibrin Abubakar, Godpower Chimagwu Enyi, and Ghasem Nasr Ghavami, University of Salford, Manchester

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Abstract

Gas and liquid flooding using carbon dioxide (CO₂), nitrogen (N₂), or brine solution have become one of the promising enhanced gas (EGR) and oil recovery (EOR) technologies for residual hydrocarbons (HCs) enhancement in conventional oil and gas reservoir respectively. However, the flow mechanism between the displacing and displaced fluids are not yet clear, especially for the novel gas alternating gas injection method adopted in this study. This experimental study investigates the flow mechanism of N2-CO2-CH4 through gas alternating gas injection techniques in consolidated rocks during EGR. The research presents a better flow behaviour characteristic using a novel N2 alternating CO2 during EGR. These values were used in determining the optimum injection rate with the minimum in situ mixing and high displacement front. An experimental laboratory core flooding, experiment was done to imitate a detailed process of an unsteady state N2-CO2-CH4 displacement in Bandera grey core sample at 35-40°C of temperature, 1500 psig of pressure, and at 0.2, 0.4, 0.6, 0.8 and 1.0 ml/min N2 alternating CO2 injection rates to evaluate the displacement flow characteristics, such as diffusion coefficient, dispersion coefficient, density and viscosity, mobility ratio, and dispersivity. The CO₂ was injected after 4-5 cm³ of N₂ injection throughout the runs at the experimental condition. The findings indicated that gas alternating gas injection technique presents a better flow behaviour characteristic compared to that of individual CO2 or N2 injection. Such prominent behaviour was observed at 0.4 ml/min injection, with higher displacement front and longer CO_2 breakthrough time. The mobility ratio of N2-CO2-CH4 was lower compared to that of N2-CH4 and CO2-CH4. This was due to the inclusion of nitrogen which acts as a barrier between the CO_2 and displaced CH_4 . The later contributed significantly for the delayed in CO₂ breakthrough especially at lower injection rates (0.2-0.4 ml/min) during the gas alternating gas EGR process. The overall molecular diffusion coefficients were found to be 22.99, 18.48 and 17.33×10^{-8} m²/s for N₂-CH₄, CO₂-CH₄, and CO₂-N₂ binary interaction respectively at the test condition. The dispersion coefficient increases with an increase in the injection rate due to rise in the interstitial velocity as the CO₂ plume traverses through the core sample during the EGR process.

Introduction

The oil and gas industries are facing difficulties balancing out between rising in energy demand and production declination. Increase in carbon credit, coupled with earlier energy demand due to population growth, has forced the exploitation of alternative source of energy, using other fewer or zero-emission technologies (Abba et al., 2017). Natural gas is considered one of the abundant, low emission, cleanest, and affordable sources of fossil fuels (Benson et al, 2005; Al-Abri et al., 2012). Carbon dioxide (CO₂) underground storage for simultaneous storage and natural gas (CH₄) displacement is attracting audience attention worldwide (Ganjdanesh & Hosseini 2017; Raza et al., 2017). This underground CO₂ storage can be in the form of oil and gas fields or deep saline aquifers (Abba et al., 2018). Natural gas fields have the potential to safely store anthropogenic CO₂, due to its proven integrity of gas storing capability (Kalra & Wu, 2014). Thus, in turn, issues of CO₂ leakages and contamination of adjacent freshwater aquifers is minimal. Thus, arose the need for the development and optimization of various techniques, to efficiently achieve natural gas recovery along with storing large volumes of hydrocarbon (HC) resources (Abba et al., 2018).

Tertiary EGR and storage by CO_2 injection are gaining recognition within the research enviro due to its combined natural gas (CH₄) recovery and CO₂ storage benefits. Even though, both nitrogen (N₂) and CO₂ can be used to increase CH₄ HCs yield from oil and gas reservoirs. However, CO₂ drawbacks are mainly excessive mixing and high compression ratio, thus hindering the overall process non-economically viable. In contrast, N₂ can be retrieved genrally from the atmospheric air, through air separation units (ASU). It requires less compression ratio than CO₂, which is why a lower amount of it was required to initiate high pressure in the CH₄ reservoir.

The promotion of EGR is still at its infant stage due, to the excessive premature mixing between the injectant (displacing fluid) mostly CO_2 and the nascent displaced fluid (natural gas) during the flooding process (Oldenburg & Benson, 2002; Shtepani, 2006; Turta et al., 2007; Sim et al., 2008; Al-abri et al., 2009; S. Sim et al., 2009; Sidiq et al., 2011; Hughes et al., 2012; Honari et al., 2013; Khan et al., 2013; Zhang et al., 2014; Honari et al., 2015; Patel et al., 2016; Honari et al., 2016). This adulterates the retrieved CH4 gas and thus, lower its heating and economic market value, that results to the high cost of the sweetening process in other to maintain its purity standard for consumption (Oldenburg & Benson, 2002; S. S. K. Sim et al., 2009). Such overall problem has not only limited the EGR project to a few pilot tests (Pooladi- Darvish et al., 2008) but also made the process apparently uneconomical because of unprecedented mixing with the displaced gas. This makes the whole phenomenon to be poorly understood (Patel et al., 2016). Thus, finding a suitable technique for reducing such in-situ mixing could be valuable at first by injecting a certain amount of nitrogen gas before the carbon dioxide injection.

Several authors (Gu et al., 2019; Hughes et al., 2012; Janssen et al., 2018; Abba et al., 2018) have carried out an extensive study on how to delay CO_2 breakthrough time during EGR process. Among them, only Abba et al., 2018 and Gu et al., 2019 were able to achieve reasonable improvement. Abba et al., 2018 use varying connate water concentration and was able to delay CO_2 breakthrough by 20 minutes at a concentration of 10% wt. sodium chloride (NaCl). On the other hand, Gu et al, 2019 use different mole ratios of CO_2/N_2 mixture gases in coalbed core samples. They reveal that enriched N_2 mixture injection was responsible for preventing the premature CO_2 breakthrough and safely stored large volumes of CO_2 into the shale sediment over the long term.

To date, such in-situ mixing is still jeopardizing the acceptance of EGR within the oil and gas industries. This necessitude the need for an elabotate inbestigation to pave paths for minimizing this premature mixing behaviour, since CO_2 and CH_4 are miscible in mostly all outcomes (Abba et al., 2018). Although, such mixing could further be minimized if newer and cheaper injection technological approach is considered. This arose the development of a new and promising gas alternating gas injection scenario, with flow behavior as the key subject of investigation.

In this paper, the experimental study on N_2 -CO₂-CH₄ interplay behavior by nitrogen alternating carbon dioxide injection at varying injection rates via *Bandera gray* sandstone was conducted. This is vital as it will provide reservoir, geologist and production oil and gas engineers with desire tools to successfully characterize the transport of injected supercritical CO₂ as it plumes transverse within the porous media during EGR and storage in natural gas fields or reservoirs.

Concept of EGR and Storage

As time progresses, the Minimum Miscibility Pressure (MMP) tends to decline, as such, production of natural gas from the reservoirs can be obstructed and the reservoir abandoned. These reservoirs are termed depleted reservoirs (Abba et al., 2017). Such oil and gas fields are uninhibited for a variety of reasons; common amongst which is poor production outputs, and large water invasion (Kalra & Wu, 2014). These depleted reservoirs are not empty of residual HCs in-situ and the need for further production and recovery to account for the rising energy demand. This merit the employment of EGR techniques, especially when CH_4 is displaced and CO_2 is stored.

The services of these isolated gas reservoirs may be used for anthropogenic CO_2 geological storage (Abba et al., 2017). The concept of EGR by CO_2 injection exploits the availability of residual methane in the oil and gas filed and at the same time store the injected CO_2 .

Furthermore, the irreversible mixing that occurs during fluids displacement by a miscible process is termed dispersion (Adepoju et al., 2013). This mixing occurs when miscible fluids meet one another, and their molecules interact at conditions that encourage the thermodynamic instability between them (Abba et al., 2018). Molecular diffusion and mechanical dispersion are the two mechanisms that simultaneously play roles in the mixing between two miscible fluids as reported by (Perkins & Johnston, 1963). They testified that the premature mixing occurs in the porous medium as a diffusion dependent process and is a function of the velocity and concentration gradients.

Dispersion Theory and Equation

Based on the definition of mixing in porous media by (Perkins & Johnston, 1963; Newberg & Foh, 1988) described the 1D Advection Dispersion equation for the gas transport through porous media along the direction of flow mathematically as follows:

$$K_{1}\frac{\partial^{2}C}{\partial x^{2}} = u\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t}$$
(1)

Where C is the CO₂ concentration at distance x at time t, K_l is the longitudinal dispersion coefficient, and u is the interstitial velocity. EGR gas species transport is governed by this model to describe the natural gas displacement by supercritical CO₂. This model evaluates the longitudinal dispersion (mixing along the axis of transport) coefficient, Kl, in EGR which is the measure of the rate of mixing between the fluids. Equation 1 can be re-written in dimensionless form and presented in Eq. 2:

$$\frac{1}{P_e} \frac{\partial^2 C}{\partial x_D^2} - \frac{\partial C}{\partial x_D} = \frac{\partial C}{\partial t_D}$$
(2)

Where;

 $P_e = \frac{uL}{K_1}$, Peclet number (ratio of convection to dispersion), L is the core sample length $t_D = \frac{t_u}{L}$

$x_D = \frac{x}{L}$, dimensionless distance,

the interstitial velocity (u), $\frac{Q}{\pi r^2 \phi}$ Q is superficial velocity, ϕ is porosity and K₁ is Longitudinal dispersion

Since the CO₂ injection inlet is at a distance x = 0, Initial condition: C = 0 at $t_D = 0$,

Final boundary conditions: C = 1 at $x_D = 0$, $C \rightarrow 0$ as $x_D \rightarrow \infty$

Therefore, the solution to Equation 2 can be presented in Equation 3 as:

$$C = \frac{1}{2} \left\{ erfd \left(\frac{x_D - t_D}{2\sqrt{t_D/P_e}} \right) + e^{P_e x_D erfd} \left(\frac{x_D + t_D}{2\sqrt{t_D/P_e}} \right) \right\}$$
(3)

The CO_2 concentrations contours from the experimental core flooding system during EGR can be fitted with the analytical solution to the one differential Advection Dispersion (AAD) equation (Eqn.3) in terms of the *Péclet* number to evaluate the corresponding dispersion coefficient. The real dispersion coefficient for the experiment is the value which provides the least absolute average deviation (AAD) error when the experimental data was compared to that of the analytical solution.

In 1963, Perkins & Johnston denoted different termed to peclet number called medium peclet number (P_{em}). Its value generally determined and describes the dominant displacement fluid region as the dispersion process progresses shown in Equation 4:

$$\mathbf{P}_{em} = \frac{ud}{D} \tag{4}$$

where

Pem is medium Péclet number,

u is the mean interstitial velocity (m/s),

D is the diffusion coefficient (m2/s), and

d is the porous medium characteristic length scale, termed as the medium-grain diameter of the sand pack but it is poorly defined in consolidated medium (Hughes et al., 2012).

Ideally when $P_{em} < 0.1$ diffusion becomes dominants, while advective mixing dominates the dispersion process at higher medium peclet number i.e. at $P_{em}>10$. The analytical solution to Eqn.3 is used to fit the concentration profiles obtained from the experimental data to evaluate the develop dispersion coefficient. the dispersion and molecular diffusion coefficients were correlated by Coats et al., 2009 as shown in Equation (Eqn. 5)

$$\frac{K_L}{D} = \frac{1}{\tau} + \alpha \frac{u^n m}{D} \tag{5}$$

here α is the porous medium dispersivity in meter (m), and n represent an exponent. The tortuosity (τ) is mostly low but can go as high as \geq 13 for consolidated rocks (Honari et al., 2013). This parameter τ is evaluated empirically through various correlations, while the exponent n is mostly determined using experimental core flooding system (Hughes et al., 2012).

Delgado, in 2001 uses the Lambda function, by plotting a graph of Lambda at different experimental times against the percent of displacing fluid in an arithmetic probability paper. The dispersion coefficient was then evaluated using Equation 6.

$$K_L = u \times I \left(\frac{\lambda_{90} - \lambda_{10}}{3.625} \right)^2 \tag{6}$$

where

 $K_L =$ longitudinal dispersion coefficient (m²/s)

u = average interstitial velocity (m/s)

L = length of porous media (m)

 λ_{90} and λ_{10} = are values of Lambda function at 10 and 90% effluent concentration.

In this research, the lambda function techniques were used, as the fundamental equation was derived by considering inert gas (Nitrogen) as one of the displacing fluids.

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Diffusion Theory and Equation

The diffusion coefficient (D) signifies the extent or magnitude at which a substance or fluid disperses through a unit area (m^2) per unit time (s) at a given or defined unit concentration gradient. The proposed empirical model which relates the molecular diffusion, temperature, and pressure for empirical diffusion coefficient determination as revealed by (Hughes et al., 2012; Liu et al., 2015) was developed by Takahashi and Iwasaki in 1970. Also, this empirical equation has been tested by various researchers in determining the real and accurate diffusivity using Equation (7)) at conditions applicable to EGR by CO₂ injection. The diffusion coefficient of CO₂ in CH₄ was dignified at 298-348K and pressures of 5-15MPa in a porous bronze plug (Takahashi and Iwasaki, 1970). The results were well within the range of conditions applicable to EGR (Abba et al., 2017).

$$D_{\text{CO2.CH4}} = \frac{(-4.3844 \times 10^{-13} P + 8.5440 \times 10^{-11}) T^{1.75}}{P}$$
(7)

where $D_{CO2,CH4}$ is the molecular diffusion coefficient of CO₂ in pure CH₄ calculated in m² s-1 with P in MPa and T in K. The absolute average deviation (AAD) of this correlation from the experimental data was 1.5% over the range of 298-348K and 5–15 MPa (Abba et al., 2017; Abba et al., 2018).

In this study, different model was used to cater for the inclusion of Nitrogen (N_2) gas during the natural gas displacement and CO₂ sequestration. This model equation was presented in Equation (8)). A correlation formula obtained by Fuller, Schetter, and Gittings (1966) by means of computer-aided correlation of 340 experimental points, expressed as:

$$D_{\text{N2CH}_4} = \frac{1.0110 \times 10^{-4} T^{1.75} \sqrt{(1/\mu_{N_2} + 1/\mu_{CH_4})}}{P[(\Sigma V_{N_2})^{1/3} + (\Sigma V_{CH_4})^{1/3}]^2}$$
(8)

Where (ΣV_{N_2}) and (ΣV_{CH_4}) are the values derived from the summation of atomic diffusion volumes of N₂ and CH₄ molecules respectively. These values and other simple molecules are presented in Table 1.

Table 1—Atomic diffusion contributions for various gas element and molecules

Dimis	ion volu	mes of single molec	ules				
He	2.67	H ₂	6.12	CO	18.0	SF6	71.3
Ne	5.98	D ₂	6.84	CO ₂	26.9	Cl ₂	38.4
Ar	16.2	N_2	18.5	N_2O	35.9	Br2	69.0
Kr	24.5	O2	16.3	NH3	20.7	SO2	41.8
Xe	32.7	Air	19.7	H_2O	13.1		
Atomi	e and str	uctural diffusion vo	lume incre	ments			
C	15.9	N	4.54	F	14.7	I	29.8
H	2.31	Aromatic ring	-18.3	C1	21.0	S	22.9
0	6.11	Heterocyclic ring	-18.3	Br	21.9		

Source: Fuller et al, 1966

The equation was further simplified after inserting the values of atomic diffusion volumes and the molecular weight of nitrogen and methane. The same was applied for carbon dioxide and methane displacement mechanism. These simplified equations were presented in equation 9, 10 and 11

$$D_{\rm N2CH_4} = \frac{10.2 \times 10^{-11} T^{1.75}}{P} \tag{9}$$

$$D_{\text{CO2CH4}} = \frac{8.2 \times 10^{-11} T^{1.75}}{P} \tag{10}$$

$$D_{\text{CO2N2}} = \frac{7.69 \times 10^{-11} T^{1.75}}{P} \tag{11}$$

where T and P are temperatures and pressure in kelvin (K) and megapascal (MPa) respectively. The equation was validated using the experimental work of Abba et al, 2018. The molecular diffusion coefficient ($D_{CO2,CH4}$) was obtained to be 22.52 ×10⁻⁸ m²/s as against 22.56 ×10⁻⁸ m²/s. The absolute average deviation (AAD) of this value from that of Abba et al, 2018 was 0.18%, which is quite acceptable within the limit of experimental error measurement.

Methodology, Application of Equipment and Process

Table 2 showcased the exact dimensions and petrophysical properties of the 1 by 3 *Bandera grey* sandstone core sample. This sample was sourced from Kocurek industry based in the United State of America. Further to that, high purity CH_4 and industrial-grade CO_2 with a minimum purity of 99.9% were used for the study.

Table 2-Dimensions and petrophysical properties of Bandera grey core sample

Core sample	Length	Diameter	Porosity	Permeability	Pore volume
	(mm)	(mm)	(%)	(md)	(cm ³)
Bandera gray	76.02	25.31	19.68	32	7.53

The experimental set-up consists of mainly two individual units; A Core Lab UFS-200 core flooding system with inbuild Smart Flood software and packed column design Agilent 7890A Gas Chromatography (GC) machine model. The core flooding system, designed for 2-phase liquid/gas steady or unsteady state condition displacements, was reconfigured to accommodate additional N_2 as used in the gas alternating gas injection for this study. The in cooperated online concentration measurement of core flooding effluents was achieved using the GC machine. These values were used in plotting the injection fluids concentration profile as the experiment progress with time. A schematic of the outline of the whole experimental and real equipment set-up are shown in Figure 1 and 2.



Figure 1—Online core flooding set-up integrated with GC



Figure 2-Schematics of experimentational set-up for gas alternating gas injection

The UFS-200 core flooding system is rated to 5,000 and 3,750 psig overburden and pore pressure respectively. The injection system of the equipment is made up of a pair of dual ISCO two-barrel metering pump system (A/B and C/D) for constant flow for pulseless transition and to maintain an accurate flow rate range of 0 to 200 ml/min with a maximum pressure rating of 3,750 psig. The pumps are attached to a pair of two stainless-steel floating piston accumulators which are also rated for 5,000 psig working pressure and temperature of 177°C. They are designed for injection of the fluids of interest and can withstand up to 7,500 psig test pressure. The hydraulic pump with a maximum of 10,000 psig pressure output was used to set the overburden confining pressure. The Smart Flood software forms an essential unit of the system which interfaces the UFS system and the computer data-acquisition-control (DAC) system hardware and generates on-screen automatic logging of test data for all measured values like pressures, temperatures, volumes, etc., to a computer data file. A Rosemount Static DP transmitter with an accuracy of 0.0055% was responsible for measuring the differential pressures across the entire Hassler-type core holder, which was used to house the core sample. The Bandera grey core sample is clutch inside the core holder by a Viton rubber sleeve. A core holder heat jacket to simulate the required temperature was also employed with an accuracy of 0.1%. Dome type back pressure regulator integrated into the flooding system ensured the confinement of the desired pressures within the core holder. Such desired pressure was set using N₂ cylinder bottle. The effluents from the back-pressure regulator pass through the mass flow controllers, that measure the volume of the actual effluents produced before been analyzed by the GC system in place.

Procedure

The *Bandera grey* core sample was dried in an oven for moisture removal. The dried sample was wrapped with cling film and in foil paper before it was inserted into a heat shrink. This is vital to avoid viscous fingering and the penetration of the gases through the sleeve into the ring-shaped of the core holder. It was then loaded into the core holder and staple with clamps from both ends. Hydraulic oil was then pumped into the ring-shaped of core holder to provide the desired overburden pressure, which was kept 500 psig above the pore pressures to in other to avoid fracturing of the core sleeve. The heat jacket was then installed on the core holder and the temperature step-up was observed. The backpressure was engaged and CH4 was slowly injected into the core sample from the accumulator using the metering pump. The N_2 is then injected for about 20-25 minutes before the CO₂ was later injected into the core sample at a varying injection rate of 0.2, 0.4, 0.6, 0.8 and 1.0 ml/min. When the methane concentration was insignificant from the GC reading, the run came to an end. At each injection time of the GC, the time was noted and the effluent composition which is then used to report the concentration profile.

Results and Discussion

Having performed the gas displacement experiment at changing injection rates, at a defined volume of N_2 initial injection to investigate the flow interaction behaviour of N_2 -CO₂-CH₄ interplay during EGR process by gas alternating gas injection technique. Before the experiment, test runs were performed to confirm the iterability of the test runs. Two test runs were carried out at the same conditions of 0.6 ml/min injection rate, temperature and pressure of 40 °C and 500 psig respectively. The concentration profile was generated from GC measured core flooding effluents stream concentration and shown in Figure 3. The dispersion coefficients were determined for runs 1 and 2 as 7.0 x× 10-8 and 6.4 × 10-8 m²/s respectively. More so, the standard deviation of the two sets of data from the repeatability test is approximately 11% which is less and its an indication that the method employed, and experimental set-up has guarantee reproducibility of result outputs. This was further testified in Figure 3 and as such all the subsequent experimental runs followed the same methodological procedure in carrying out the investigation.

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Figure 3—Concentration profile for repeatability runs at test conditions

Flow behaviour of supercritical N₂, CO₂, and N₂-CO₂-CH₄ interplay during EGR

The actual flow behaviour of supercritical carbon dioxide as it plumes transverses the pore spaces within the core sample to displace the in-situ methane is quite complex, especially with the inclusion of inert nitrogen gas. Investigating these complexities of displacing fluids (CO_2 and N_2) with respect to the nascent CH_4 is key vital in understanding the trends and expected outcomes of the displacement process knowing, that these gases in their supercritical state have unique behaviour by exhibiting the density of a liquid but retain the viscosity of a gas (Abba et al., 2018). The critical temperature and pressure points of CO_2 , N_2 and CH_4 are 31.05 and 73.80, -146.9 and 33.90, -82.55 °C and 46 bar respectively as presented in Figure 4, 5 and 6. Thus, for this study the operation conditions are at average normal reservoir pressure of 0.451 psi/ft gradient, average reservoir depth of 1km and average geothermal temperature of 40 °C/km which are well above each single gas species.











Figure 6—CH₄ vapor pressure line generated from FLUIDAT^R

These fluids exhibit excellent behaviour as a result due to the response of their transport properties to change from ambient standard conditions to that of EGR condition. A simulation of their respective properties at elevated operational conditions was carried out using FLUIDAT^R software to check the effects of temperature and pressure on the individual gas densities and viscosities at the stated conditions as presented in Figures 7, 8 and 9 respectively. There is pronounced significant differences in these properties of gases with carbon dioxide transport properties being much higher and more extreme than those of nitrogen and methane. This can be observed especially at a temperature range (18 – 50 °C) and a pressure range (700 – 1500 psig) as shown in Figure 8 and 9. This justifies the selection of the experimental conditions as also, reported by Abba et al., 2018. The above thus makes the application of supercritical CO₂ for EGR process to be well accepted globally. Such unique esteem property will grossly affect the flow behaviour of the gases as will be presented in the successive chapters.



Figure 7—CH₄, N₂ and CO₂ densities as a function of pressure at 40 °C (Generated from FLUIDAT^R)



Figure 8—CH₄, N₂ and CO₂ viscosities as a function of temperature at 1500 psig (Generated from FLUIDAT^R)



Figure 9-CH₄, N₂ and CO₂ viscosities as a function of pressure at 40 °C (Generated from FLUIDAT^R)

The viscosity is set to be increasing at the beginning of the displacement process until the mobility of the displacing phase is less than that of the displaced phase in place, this makes the mobility (movement) ratio to be less than one (unity). Such a state does maximize gas recovery and sweeps efficiency, due to negligible premature mixing, by providing an even flood front without experiencing viscous fingering effect. A condition in which the conjoin of two fluids escapes some part of the reservoir as it progresses along, forming irregular, or fingered profile. Fingering is relatively a routine problem in reservoirs with gas-injection wells. Fingering effects result mostly in an unproductive sweeping action, which bypasses a large number of recoverable gas volumes, with a premature breakthrough of displacing fluids into adjacent production wellbores. In Figure 10, both the N2 and CO2 has lower mobility ratios at their respective critical conditions. The mobility of CH₄-N₂ displacement was low compared to CH₄-CO₂ at a lower pressure (400-700 psig). This means the effect of viscous fingering was minimal as the N2 plume transverse through the core spaces as against that of CO2. The effect of pressure on CH4-N2 mobility was insignificance with very little increase as the pressure increase from 400-1500 psig. Similar behaviour was observed for CH₄-CO2 interplay, even though, it experiences least mobility value at a pressure of 800 psig, with a small increase at 900 psig and remains almost constant. Overall, CH₄-CO₂ interaction possesses low mobility ratio with maximum gas recovery efficiency, creating an even flood front with minimum risk to viscous fingering effect.



Figure 10—CH₄-N₂ and CH₄-CO₂ mobility ratios as a function of pressure at 40 $^\circ\text{C}$

On the other hand, the mobility of CH_4 - CO_2 displacement was ascending as the temperature increase. However, a reverse scenario was observed for that of CH_4 - N_2 process as the temperature increases to 100 °C as observed in Figure 11. This is so because as the temperature increases the viscosity value of CO_2 approaches that of the CH_4 due to the breakdown of the molecular forces. Thus, in turn, CH_4 - N_2 mobility is more sensitive to change in temperature and pressure compared to that of CH_4 - CO_2 during EGR.



Figure 11—CH₄-N₂ and CH₄-CO₂ mobility ratios as a function of temperature at 1500 psig

The developed Equations (9-11) derived from the fundamental (first principle) correlation (Eqn. 8) as reported by Fuller et al, (1966) was used to simulate the effect of pressure and temperature for N₂-CH₄, CO₂-CH₄, and CO₂-N₂ interaction behaviours. This simulation was carried out at constant temperatures of 30, 40 and 50 °C respectively at a varying pressure of 300-1500 psig for the stated interactions. From Figure 11,

it can be observed that as the constant temperature values change from 30, 40 and 50 °C over a pressure range of 300-1500 psig, the molecular diffusion coefficient also increase with a roughly constant value of $1.5 \text{ m}^2/\text{s}$. This value was more pronounced for CH₄-N₂ interaction than that of CH₄-CO₂ due to the high density of carbon dioxide compared to that of nitrogen at reservoir condition. Considering the pressure effect as it increases from 300-1000 psig the reduction in molecular diffusion coefficient was more significant. However, when the pressure was further raised from 1000-1500psig the molecular diffusion coefficient decline was less notable.

Temperature plays a significant role in determining the extent of diffusion when two fluids are in contact with each other especially of the same phase. The higher the temperature, the more the kinetic energy due to high collision velocity, which invariably results in the high molecular diffusion coefficient. Such evidence can be seen in Equations 9-11 with the temperature component (in Kelvin) being rise to the order of 1.75. Viscosities and atomic diffusion also contribute to measuring the overall diffusion coefficient of binary mixtures. Further to that, atoms or molecules with higher viscosities and diffusion volumes do result in lower molecular diffusion coefficient value compared to those with lower viscosities and diffusion volumes respectively. Figure 13 presents a plot of diffusion coefficient against temperature. The CH_4 - N_2 binary mixture shows a high periodic increase as the temperature rise to 120 °C (393.15K). However, lower raise was experienced for the case of CH_4 - CO_2 mixture. This was due to high density, viscosity, and diffusion volume of Carbon dioxide at the supercritical condition as against that of Nitrogen. Also, a similar trend was observed for that of CO_2 - N_2 binary mixture.



Figure 12—Effect of pressure on diffusion coefficients for CH₄- N_2 and CH₄-CO₂ interaction at constant temperature of 30, 40, and 50 °C



Figure 13—Effect of temperature on diffusion coefficients for CH_4 - N_2 , CH_4 - CO_2 , and CO_2 - N_2 interaction at constant pressure of 1500 psig

Figure 14 present a comparison chart for the molecular diffusion coefficients of N₂-CH₄, CO₂-CH₄, and CO₂-N₂ binary mixtures at the tested experimental conditions of 40 °C temperature and 1500 psig pressure. These values are found to be 22.99, 18.48 and 17.33 ×10⁻⁸ m²/s for N₂-CH₄, CO₂-CH₄ and CO₂-N₂ binary interaction respectively.



Figure 14—Comparison chart for N₂-CH₄, CO₂-N₂ and CO₂-CH₄ molecular diffusion coefficients

After the repeatability runs of the experimental setup and methods of the core flooding experimentation, the desired test was carried out with different injection rates from 0.2-1.0 ml/min at the tested conditions. Five core flooding displacement tests were performed with each representing 0.2, 0.4, 0.6, 0.8 and 1.0 ml/min injection rates. Also, their respective experimental results were curved with Eqn. 5. The individual dispersion coefficient was measured and arranged in Table 3. More so, their respective CO₂ concentration profile during the tests are presented in Figure 15. The profile showcases the expected trends and the effect of injection rates variations on the Carbon oxide breakthrough during the gas alternating gas displacement process. This trend agreed with the works of (Liu et al, 2015; Abba et al, 2017; Abba et al, 2018) where the breakthrough time was said to decrease with an increase in injection rates as the CO₂ plumes transverses through the core sample. This means that the higher the injection rate the higher the dispersion coefficient and invariably the more the nascent mixing as seen in Figure 17.

Q	Pressure	Temperature	Interstitial Velocity	Lambda Constants	Dispersion Coefficient	Diffusion Coefficient
(ml/min)	(psig)	(⁰ C)	(10 ⁻⁵ m/s)	$(\lambda_{90}/\lambda_{10})$	$(10^{-8} \text{ m}^2/\text{s})$	$(10^{-8} \text{ m}^2/\text{s})$
0.2	1500	40	3.36	2.1768/1.6008	2.14	22.35
0.4	1500	40	6.72	2.0144/1.4624	3.93	22.35
0.6	1500	40	10.08	1.8065/1.1905	7.34	22.35
0.8	1500	40	13.44	1.7340/1.1101	10.03	22.35
1.0	1500	40	16.80	1.6323/1.0563	10.69	22.35

Table 3-Dispersion coefficient at different injection rates by gas alternating gas injection using Lambda function



Figure 15—CO₂ concentration profile at varying injection rates for gas alternating gas injection



Figure 16—Plot of CH_4 recovery and CO_2 breakthrough as a function of time for single and gas alternating gas injection at optimum injection rate (0.4 ml/min)



Figure 17—Dispersion coefficient as function of varying injection rates

Figure 16 showcased the CH₄ and CO₂ breakthrough as a function of time at the optimum injection rate of 0.4 ml/min. The gas alternating gas injection technique tends to reduce the nascent mixing behavior of CO₂ with methane during the displacement process. This was due to the presence of N₂ which acts as a barrier as the CO₂ plumes transverse through the porous media. The CO₂ breakthrough was delayed using compared to those of individual CO₂ or N₂ injection. This resulted in lower dispersion coefficient with higher gas recovery, especially at 0.2-0.4 ml/min injections.

To determine the dispersivity, a plot of the ratio of longitudinal dispersion coefficient (K_L) to that of molecular diffusion coefficient (D) was plotted against the ratio of average interstitial velocity (u) to that of molecular diffusion coefficient (D) as shown in Figure 18. The gradient of the straight-line graph is term dispersivity. In this study, the value was found to be 0.0007m which is quite within the range reported by (Hughes et al, 2012; Abba et al, 2018) for consolidated rocks.



Figure 18-Dispersity of the core sample at 1500 psig and 40 °C

Conclusion

Empirical simulation and displacement experiment were carried out to investigate N₂-CO₂-CH₄ tertiary mixtures using gas alternating gas injection technique at a condition relevant to EGR. The findings indicated that this technique tends to reduce the nascent mixing behavior of CO₂ with methane during the displacement process. This was due to the presence of N₂ breakthrough that acts as a barrier as the CO₂ plumes transverse through the porous media. The CO₂ breakthrough was delayed using the developed techniques compared to those of single CO₂ or N₂ injection. This resulted in lower dispersion coefficient, especially within (0.2-0.4 ml/min) injections. The molecular diffusion coefficient was more sensitive to temperature than pressure due to the high influence of temperature on kinetic energy, which invariably results in a high molecular collision within the interacted fluids. More so, the overall molecular diffusion coefficients were found to be 22.99, 18.48 and 17.33 ×10⁻⁸ m²/s for N₂-CH₄, CO₂-CH₄, and CO₂-N₂ binary interaction respectively at the test condition. Thus, in turn, optimum displacing fluids injection determination is a perquisite to adequately and efficiently displace the nascent methane with profitable recovery and minimize in situ mixing with longer CO₂ breakthrough.

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Nomenclature

- yCO_2 CO₂ mole fraction
 - yN_2 N₂ mole fraction
 - D Diffusion coeficient, m²/s
 - Q Flowrate, mil/min
 - t_D Dimentionless time

- x_D Dimentionless distance
- d Characteristic length scale, m
- K_L Longitudinal dispersion, m²/s
- L Core sample length, mm
- L_{exp} Experimental length, m
 - μ Viscosity, cP
 - P Pressure, psig
 - T Temperature, K
- *u* Interstitial velocity, m/s
- ϕ Core porosity, %
- α Dispersivity, m
- τ Tortuosity
- P_e Peclet number
- Pem Medium Peclet number
- r Radius of core sample, m
- λ_{90} Lambda function at 90% of effluent concentration
- λ_{10} Lambda function at 10% of effluent concentration

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Enhanced Gas Recovery by Nitrogen Injection: Performance Evaluation of Gas-Gas Displacement Nuhu Mohammed

School of Computing, Science & Engineering Email: n.mohammed5@edu.salford.ac.uk

Supervisors Dr Abbas Abubakar - a.j.abbas@salford.ac.uk Dr Godpower C. Envi – G.C.Envi@salford.ac.uk

Enhanced Gas Recovery (EGR) by Carbon dioxide (CO2) injection and sequestration (storage) is receiving attention within the research community due to its combined Natural gas (CH4) recovery and CO2 sequestration advantage. Both Nitrogen (N2) and CO2 can be used to increase CH4 yield from natural gas field. However, the later major drawbacks are excessive mixing and high compression ratio, thereby hindering market value and eventually render the process non-economically viable. In contrast, N2 can be recovered virtually from the atmospheric air-through air separation units. It requires less compression ratio than CO2, which is why a lower amount of it was needed to create high pressure in the CH4 reservoir. This research focuses on N2 injection during CH4 displacement. An experimental core flooding system with online Gas Chromatography (GC) measurement was carried out at supercritical condition of N2 with higher injection rate using artificial reservoir. It was observed that N2 injection exhibit less mixing scenario. This was due to high density and viscosity difference between N2-CH4 interaction as compare to that of CO2-CH4 at testing condition. This signified the advantage of N2 injection over CO2 since up to 20% CH4 contamination with N2 is consider economical as oppose to that of 3% with CO2.

Enhanced gas recovery, displacement, supercritical, compression, mixing

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