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Highlights

- Successful inclusion of connate water into Enhanced Gas Recovery simulations
- Weak Lagrange multiplier approach used for efficient VLE computations in FEM model
- Connate water generally results in a reduction in methane recovery
- Connate water's primary effect was on the flow field of the injected supercritical CO₂
- Well perforation depth found to be critical, in particular that of the production well.

Inclusion of Connate Water in Enhanced Gas Recovery Reservoir Simulations

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Abstract

Enhanced natural gas recovery (EGR) with supercritical (sc)CO₂ sequestration offers the prospect of increased natural gas recovery. High-fidelity reservoir simulations offer a method to quantify the risk of contamination of produced gas by the injected scCO₂. Simulations of scCO₂ mixing with the reservoir gas have been reported; however the effects of connate water on EGR have not been effectively explored. We extend a prior EGR simulation tool (Patel, May and Johns, 2016; Ref. [1]) to incorporate connate water accounting for its effect on dispersivity and permeability; chemical equilibrium is modelled using a novel, computationally efficient Lagrange multiplier-based approach.

The code is applied to a 'quarter five-spot' benchmark scenario. The inclusion of connate water generally resulted in a reduction in breakthrough time and a decrease in methane recovery. The connate water's largest effect was to change the scCO₂ flow field, which sank towards the reservoir floor, flooded the lowermost accessible layers and entered the production well *via* a high throughput channel ('coning'). The magnitude of these effects were, however, sensitive to well perforation depth, the influence of which was subsequently studied systematically. Well perforation depth was found to determine the duration of these sinking and coning events in a non-linear manner.

Keywords [≤6, American spelling]

Carbon dioxide sequestration; compositional reservoir simulation; dispersivity vs. saturation; enhanced gas recovery (EGR¹); finite element modelling; multiphase flow in porous media

1 Introduction

Net emissions of CO₂ into the biosphere can be reduced by sequestration of CO₂ into suitable subterranean rock formations. A recent review of existing projects by Cook *et al.* [2] highlights their continuously increasing size and scope. Both deep saline aquifers and hydrocarbon deposits, *e.g.* depleted oil reservoirs [3], gas reservoirs [4,5] and coal beds [6], have been used for CO₂ sequestration. For the latter cases, the recovery of the hydrocarbons therein can in principle be increased, reducing net costs relative to sequestration alone. The enhanced recovery achieved from natural gas reservoirs as a result of CO₂ injection and hence sequestration, termed Enhanced Gas Recovery (EGR), carries the additional advantage that the capability of the reservoir to act as a long term, safe gas storage site is already proven [5,7].

The temperatures and pressures encountered in depleted gas reservoirs of moderate depth are typically above the critical temperature and pressure of CO₂-CH₄ mixtures, while CO₂-CH₄-H₂O mixtures typically exist in two phases, *i.e.* the reservoirs incorporate connate water. The reservoir fluid is therefore comprised of a water-rich phase, into which appreciable amounts of CO₂ dissolves, and a dense fluid (DF) phase incorporating CO₂, natural gas and a small proportion of water vapour. The supercritical DF features a liquid-like density and gas-phase diffusivity, with the former allowing for greater CO₂ storage capacity and the latter reducing the recovery potential due to the promotion of mixing between the injected CO₂ and nascent natural gas. A significant amount of mixing leads to undesirable early CO₂ breakthrough at production wells and the effective loss of a significant fraction of the reservoir's gas value.

The extent of mixing between the CO₂ and nascent gas is controlled by several factors including the thermophysical properties of both fluid phases, permeability-related properties of the rock strata, and the injection/production strategy. Such strategies can be modelled by use of EGR reservoir simulations. Previously, we conducted such EGR simulations on dry reservoirs using a finite element code, the most accurate thermophysical property predictions available and dispersion data measured at the relevant reservoir conditions [1]. Here, this simulation code is extended to allow for the presence of a largely immobile connate water phase and thus requires advanced predictions of diffusivity/dispersivity and species solubilities. The performance of different injection/production strategies (well perforation depths) as applied to essentially a standard benchmark reservoir geometry is then considered.

¹ Non-standard abbreviations: BC – Brooks-Corey; CW – connate water; DF – dense fluid; EGR – enhanced gas recovery; FDM – finite difference method; FEM – finite element method; FVM – finite volume method; IW(P) – injection well (perforation); PW(P) – production well (perforation)

2 Review of EGR Simulation Literature

Detailed simulation of EGR was first reported by Oldenburg *et al.*, who after early 1D [8] and 2D [9] proof-of-concept simulations conducted a preliminary economic analysis of EGR [10] along with a study of the thermal effects of CO₂ injection (Joule-Thomson cooling; JTC) [11]. All studies were conducted using the finite difference method (FDM)-based reservoir simulator TOUGH2 and the Peng-Robinson EOS. Fluid properties relevant to mixing were estimated from linear mixing rules rather than reference data. Physical dispersion, *i.e.* the enhancement to molecular diffusion by associated with advective mixing within the pores, was not considered.

Following these preliminary EGR simulations, improved descriptions of mixing between CO₂ and the nascent gas were considered based either on the assumption of a constant dispersion coefficient (Seo and Mamora [12]) or on measurements of dispersion vs. velocity at relevant reservoir conditions [1]. The latter study included values of dispersivity obtained from core flooding and NMR experiments by Honari *et al.* [13], and demonstrated how dispersivity could provide a noticeable enhancement to diffusive mixing (>10%) within 100 metres of the wells.

The effect of CO₂ injection rate on the storage of CO₂ and recovery of the nascent gas was first studied by Seo & Mamora [12] using a FDM-based simulator, and by Patel *et al.* [1] using a finite element method (FEM)-based simulator. In both studies, recovery at the highest flowrate led to the maximum gas recovery. However, Patel *et al.*'s results show that the amount of CO₂ sequestered before CO₂ breaks through at the production wells increases with injection rate while Seo and Mamora predicted essentially no variation with rate. Given that Patel *et al.* used (i) a FEM-based simulator (less numerical dispersion than FDM), (ii) a computational grid at least four times finer (*i.e.* smaller elements), (iii) the most up-to-date EOS used thus far for EGR simulation (GERG-2008 - Kunz and Wagner [14]), and (iv) high-quality measurements of the parameters most important to mixing (diffusivity, tortuosity and dispersivity), only Patel *et al.*'s results regarding injection rate are discussed forthwith.

Alongside increased gas recovery, Patel *et al.* found that at the highest injection rate tested, very similar results were obtained as when buoyancy effects were artificially removed by setting gravity to zero. This implies that at sufficiently high injection rates, the timescale of advection (well-driven flow) is small compared to the timescale of the buoyancy effects which drive the injected, denser CO₂ to sink under the nascent, less dense reservoir gas. Importantly, gas recovery was maximised at high injection rate, demonstrating that the common assumption about the greater density of supercritical CO₂ relative to methane resulting in more efficient EGR is not universally true. Other critical findings were that mixing is noticeably enhanced (>10%) within 50 - 100 metres of the wells, with the exact radius depending on the (rock-dependent) values of dispersivity and tortuosity. Furthermore, the effective diffusivity of the CO₂ in the porous reservoir rock, (*i.e.* bulk diffusivity divided by tortuosity) was found to be the critical factor affecting gas mixing in kilometre-scale reservoirs.

Studies of the thermal aspects of EGR (viscous heat dissipation and Joule-Thompson cooling (JTC)) have been conducted by Ziabakhsh-Ganji and Kooi [15], Singh *et al.* [16] and Oldenburg [17]. These studies demonstrate viscous heat dissipation to have a minimal effect on EGR while JTC causes significant cooling only at relatively high CO₂ injection rates and within 12 - 15 m of the injection well. For these reasons, thermal effects are neglected in the current study while dispersivity is included. Gou *et al.* [18] incorporated limited geo-mechanical effects into their EGR simulation and predicted lifting of the caprock would be limited to the order of 1 mm (*i.e.* elastic deformation) at moderate

injection rates for the reservoirs considered. Therefore, geo-mechanical effects are neglected in this study. Most recently, Luo *et al.* [19] studied the effects of well perforation depths on CO₂ storage and the final recovery of natural gas from the reservoir using a simulator based on the finite volume method (FVM). However, the effects of the connate water and rock properties such as tortuosity and dispersivity were neglected and the study was limited to gaseous rather than supercritical conditions. Semi-analytical methods have also been used by Mathias *et al.* [20,21] to model EGR. However, while these are extremely fast and require very little memory, such simulations are restricted to reservoirs with a simplified geometry and simplified descriptions of the fluid phases' flow.

3 Methodology

The compositional reservoir simulator described here was developed from our prior work [1], which was used to model EGR from reservoirs without connate water (henceforth termed the 'dry simulator'). Enhancements to the dry simulator are detailed below.

3.1 Reservoir Geometry, Initialisation and Boundary Conditions

The reservoir geometry, porosity, layer permeabilities and well configurations follow those used in a previous EGR benchmark (Class *et al.* [22]; Benchmark 2.2); see Figure 1.

FIGURE 1

The initial temperature and pressure stipulated in the original benchmark were increased to reflect more realistic conditions (above the critical point of CO₂). The temperature, T , was increased from 66.7°C to 75°C and was modelled as constant (isothermal reservoir). The initial pressure at the reservoir base was increased from 35.5 bar to 90 bar. Above this, a hydrostatic initial pressure profile was imposed. The rate of injection of pure scCO₂ (0.319 kg/s) was chosen to match the baseline injection rate used in our dry simulator study [1], which was chosen in turn to ensure the same fluid injection velocity as used in the original benchmark [22]. The production well was controlled using a constant bottom-hole pressure directive with the set point equal to the initial pressure at the well. All four vertical walls of the reservoir were modelled as symmetry walls while the reservoir base and cap were modelled as perfectly sealing.

Unlike the dry simulator [1], the pore volume was modelled as partially occupied by water. The initial water saturation was a function of the local capillary pressure (pressure difference between the phases). Specifically, the widely-used Brooks-Corey capillary pressure-saturation function was employed (section 3.2.2); see Figure 2.

FIGURE 2

We assume that the connate water (CW) and DF are in close contact throughout the reservoir's pore space, *i.e.* the CW exists as small ganglia around which the DF flows. This assumption permits the phases to be modelled as being in chemical equilibrium. The initial molar composition of the DF was specified as 98.5% CH₄+1% CO₂+0.5% H₂O *cf.* 100% CH₄ for the dry simulator [1]. The initial CO₂ fraction is non-zero to reflect the nascent CO₂ ubiquitously found in natural gas reservoirs, while the initial H₂O fraction reflects the water vapour fraction at the ambient initial conditions (75°C, 90 bar). The initial composition of the CW was estimated from that of the DF using a modified form of the Equation of State described by Spycher *et al.* [23] (section 3.2.4), giving 99.98% H₂O+0.02% CO₂.

Partitioning of CH₄ into the CW was neglected due to its very low solubility relative to CO₂. Both initial compositions changed slightly with depth (< 1% relative) due to the initial hydrostatic pressure gradient; these compositions therefore correspond to the reservoir base.

3.2 Numerical Model

3.2.1 Assumptions and Governing PDEs

The reservoir rock was assumed rigid and chemically inert over the timescale of interest (≤ 7 years), and the reservoir and fluid temperatures were assumed constant. The relevant conservation equations therefore reduce to Darcy's law for each phase (Eq. 1 - 2), the continuity equation for each phase (Eq. 3 - 4) and the advection-dispersion equation for each component in each phase (Eq. 5 - 6). Note that Eq.'s 2, 4 and 6 were not present in the dry simulator.

$$\underline{v}_{DF} = \frac{-\underline{k}_{DF} \cdot (\nabla P_{DF} - \rho_{DF} \underline{g})}{\mu_{DF}} \quad \text{Eq. 1}$$

$$\underline{v}_{CW} = \frac{-\underline{k}_{CW} \cdot (\nabla P_{CW} - \rho_{CW} \underline{g})}{\mu_{CW}} \quad \text{Eq. 2}$$

$$\frac{\partial(\rho_{DF} \Phi s_{DF})}{\partial t} + \nabla \cdot (\rho_{DF} \underline{v}_{DF}) = -q_{H_2O} - q_{CO_2} \quad \text{Eq. 3}$$

$$\frac{\partial(\rho_{CW} \Phi s_{CW})}{\partial t} + \nabla \cdot (\rho_{CW} \underline{v}_{CW}) = q_{H_2O} + q_{CO_2} \quad \text{Eq. 4}$$

$$\Phi s_{DF} \frac{\partial \rho_{DF,i}}{\partial t} + \nabla \cdot (\rho_{DF,i} \underline{v}) - \nabla \cdot \left(\Phi s_{DF} \rho_{DF} \underline{D} \cdot \left(\nabla w_{DF,i} + w_{DF,i} \frac{\nabla M_{n,DF}}{M_{n,DF}} \right) \right) = -q_i$$

$$M_{n,i} = \left(\sum_j \frac{N_j^{w_{j,i}}}{M_j} \right) - 1 \quad \text{Eq. 5(a,b)}$$

$$\Phi s_{CW} \frac{\partial \rho_{CW,i}}{\partial t} + \nabla \cdot (\rho_{CW,i} \underline{v}) - \nabla \cdot \left(\Phi s_{CW} \rho_{CW} \underline{D} \cdot \left(\nabla w_{CW,i} + w_{CW,i} \frac{\nabla M_{n,CW}}{M_{n,CW}} \right) \right) = q_i \quad \text{Eq. 6}$$

In Eq. 1 - 6, single- and double-underlined quantities represent vectors and second rank tensors, respectively. The Darcy (or superficial) velocity vector, DF pressure, density and viscosity and the permeability of the rock to the DF are denoted by $\underline{v}_{DF}$, P_{DF} , ρ_{DF} , μ_{DF} and $\underline{k}_{DF}$, respectively. Component densities are denoted by a subscript to ρ and the mass fraction of a given component in a given phase features dual subscripts, e.g. w_{DF,CO_2} . The rock porosity (23% throughout) and the local saturation of a given phase are denoted by Φ and s_i , respectively, with the saturations s_{DF} and s_{CW} summing to unity. The rates of condensation of H₂O and dissolution of CO₂ due to VLE are denoted by the source terms q_{H_2O} and q_{CO_2} , respectively. These were calculated locally during each time step and maintained equilibrium between the phases subject to the usual numerical tolerances (section 3.4).

3.2.2 Hydraulic Model

The incorporation of CW into the simulator requires that the relative motion between the phases be modelled. The permeabilities $\underline{k}_{DF}$ and $\underline{k}_{CW}$ (m²) are each the product of the local absolute permeability tensor and a scalar relative permeability; see Eq. 7.

$$\underline{k}_{DF} = k_{DF,CW} \underline{k}; \quad \underline{k}_{CW} = k_{CW,DF} \underline{k} \quad \text{Eq. 7(a,b)}$$

The absolute permeability tensor is diagonalised and has varies with depth (Figure 1). The Brooks-Corey (BC) model was used to define the relative permeabilities:

$$k_{DF,CW} = \left(\frac{1-s_{CW}}{1-s_{CW,c}} \right)^2 \left[1 - \left(\frac{s_{CW}-s_{CW,c}}{1-s_{CW,c}} \right)^{\frac{2+\lambda}{\lambda}} \right] \quad \text{Eq. 8}$$

$$k_{CW,DF} = \left(\frac{s_{CW}-s_{CW,c}}{1-s_{CW,c}} \right)^{\frac{2+3\lambda}{\lambda}} \quad \text{Eq. 9}$$

The terms $s_{CW,c}$ and λ denote the irreducible water saturation and the medium's BC exponent, respectively (values in section 3.3). Mechanical contact between the phases is modelled by means of a capillary pressure (P_c) vs. saturation curve for which the Brooks-Corey model was also used; see Eq. 10, where P_{ec} denotes the medium's entry capillary pressure.

$$P_c = P_{DF} - P_{CW} = P_{ec} \left(\frac{1-s_{CW,c}}{s_{CW}-s_{CW,c}} \right)^{-\frac{1}{\lambda}} \quad \text{Eq. 10}$$

3.2.3 Physical Dispersion Model

Returning to Eq. 5, $\underline{D}$ denotes the dispersion tensor which incorporates the effects of both diffusion and dispersion:

$$\underline{D} = \left(\frac{D}{\tau} \right) \underline{I} + \frac{\alpha_T}{\phi} |\underline{v}| \underline{I} + \frac{(\alpha_L - \alpha_T)}{\phi |\underline{v}|} \underline{v} \underline{v}^T \quad \text{Eq. 11}$$

The diffusivity, longitudinal and transverse dispersivities in the DF, and the local tortuosity of the rock are denoted by D , α_L , α_T , and τ , respectively (values in section 3.3).

3.2.4 VLE Model

The equations describing VLE of H₂O and CO₂ at isothermal conditions are (in generic form):

$$y_{CO2} = K_{CO2}(P_{DF}, T, x_{CO2}) x_{CO2} ; y_{H2O} = K_{H2O}(P_{DF}, T, x_{H2O}) x_{H2O} \quad \text{Eq. 12(a,b)}$$

The terms x and y denote mole fractions of the component in the CW and DF phases, respectively. Accurate models for the partition coefficients K_{H2O} and K_{CO2} at sequestration-relevant conditions are crucial to accurate predictions of subsurface CO₂ storage and transport; however they are usually computationally expensive as solution methods are typically iterative. A numerically efficient EOS, intended specifically for use in reservoir simulators, is described by Spycher *et al.* [23]. It's accuracy for water+CO₂ systems was shown by Efika *et al.* [24] to be equal to that of the multiparameter EOS-CG of Gernert and Span [25].

Spycher *et al.*'s EOS is based on a modified form of the Redlich-Kwong cubic EOS [26]. The partition coefficients K_i in Eq. 12 are expressed as the ratio of the fugacity of component ' i ' in the DF divided by its corresponding activity in the CW (f_i/α_i). Critically, the expression for fugacity coefficient, $\phi_k = f_i/P_{DF}$, calculated using the Redlich-Kwong EOS (Eq. 13) was simplified by Spycher *et al.* by replacing the mixture parameters a_{mix} and b_{mix} (Eq. 14 - Eq. 15) with fixed values corresponding to pure CO₂ rather than a water+CO₂ mixture. This effectively assumes that the water vapour has negligible influence on the thermodynamic properties of the (mostly CO₂) vapour phase. This simplification allows the partition coefficients to be calculated explicitly rather than solved for iteratively:

$$\ln(\phi_k) = \ln\left(\frac{\tilde{V}}{\tilde{V}-b_{mix}}\right) + \ln\left(\frac{b_k}{\tilde{V}-b_{mix}}\right) - \left(\frac{2\sum_i y_i a_{i,k}}{R T^{1.5} b_{mix}}\right) \ln\left(\frac{\tilde{V}+b_{mix}}{\tilde{V}}\right) \quad \text{Eq. 13}$$

$$+ \left(\frac{a_{mix} b_k}{R T^{1.5} b_{mix}^2} \right) \left[\ln\left(\frac{\tilde{V}+b_{mix}}{\tilde{V}}\right) - \left(\frac{b_{mix}}{\tilde{V}+b_{mix}} \right) \right] - \ln\left(\frac{P_{DF} \tilde{V}}{R T}\right)$$

$$a_{mix} = \sum_i^N \sum_j^N y_i y_j a_{ij}; a_{ij} \equiv (1 - k_{ij}) \sqrt{a_i a_j} \quad \text{Eq. 14(a,b)}$$

$$b_{mix} = \sum_i^N y_i b_i \quad \text{Eq. 15}$$

In Eq. 13, $\tilde{V}$ denotes the local molar volume of the DF. With respect to the nascent methane, the solubility of CH_4 within the CW is assumed zero. Therefore, the activities a_{CO_2} and $a_{\text{H}_2\text{O}}$ are unchanged by the presence of CH_4 in the DF. However, the fugacities f_i require modification. Specifically, a_{mix} and b_{mix} (simplified by Spycher *et al.* [23] to a_{CO_2} and b_{CO_2}) were replaced with functions describing a mixture of CH_4 and CO_2 . The required k_{ij} values (Eq. 14) were obtained from Multiflash v4.4 [27] using the RKS-Advanced model, as were a_{CH_4} , $a_{\text{H}_2\text{O}}$ and b_{CH_4} . The values of a_{CO_2} , b_{CO_2} and $b_{\text{H}_2\text{O}}$ were left unchanged from those used by Spycher *et al.* [23]. Eq. 13 was programmed into COMSOL and computed for both CO_2 and H_2O at every node during every iteration of every time step.

3.3 Values and Sources of Model Parameters

Table 1 presents the values and sources of all parameters used in the simulations. The DF density was predicted using the GERG-2008 EOS of Kunz and Wagner [14] as implemented within the NIST software package REFPROP v9.1 [28]; this EOS is the ISO standard for the thermodynamic properties of natural gas mixtures with CO_2 . The DF viscosity was predicted using the Extended Corresponding States correlation as implemented within REFPROP and described by Chichester and Huber [29]. For reasons of computational time, calculations of density and viscosity during the simulations were not performed by solution of the full GERG-2008 EOS. Instead, the values were tabulated ‘offline’ at the nodes of a regular 3D grid of temperatures, pressures and CO_2 mass fractions; the variation with H_2O fraction ($w_{\text{DF,H}_2\text{O}} \sim 0.5\%$) was neglected as suggested by Spycher *et al.* [23]. Values of ρ_{DF} and μ_{DF} at conditions intermediate to these grid nodes were computed by polynomial-based interpolation. Full details of the method and the resulting (lengthy) polynomials are presented in our prior study [1]. The values of ρ_{CW} and μ_{CW} were computed ‘online’ using linear interpolation between grids of known points. This simpler method was due to the small variation of ρ_{CW} and μ_{CW} with P_{CW} and $w_{\text{CO}_2,\text{CW}}$.

TABLE 1

The data for longitudinal dispersivity α_L vs. saturation were measured by Zecca *et al.* [30] for CO_2 in CH_4 in a partially saturated Berea sandstone; see Eq. 11 (α_L). Note that there are no prior systematic studies available for describing dispersivity as a function of saturation in porous media.

$$\alpha_L(\text{mm}) = 199 s_{\text{CW}}^4 - 124 s_{\text{CW}}^3 + 25.7 s_{\text{CW}}^2 - 0.114 * s_{\text{CW}} + 0.741 \quad \text{Eq. 16}$$

Note that a constant value of α_L was used in the dry simulator. With regards to the transverse dispersivity, α_T , there are few measurements [31] or modelling studies [32] of α_T for Berea sandstones. Therefore, we took $\alpha_T/\alpha_L = 0.1$ as assumed in all prior simulation studies of EGR that specify a value of α_T [1,33–35], and state this as an area for future refinement.

3.4 Implementation

All simulations were run using the general-purpose finite element solver COMSOL Multiphysics v5.2 [43]. All simulations incorporated identical meshes containing 56,000 elements. This is half the number of elements used in the dry simulator study [1] despite the identical reservoir geometry, and

was due to the replacement of tetrahedral elements in the reservoir bulk (dry simulator) with regular hexahedral elements. However, tetrahedral elements (37,000) were still used around each well to conform to the (cylindrical) shape of the wells. The dimensions of the bulk hexahedra were set to the thickness of a single rock layer (4.572 m). The dimensions of the tetrahedra then ranged in size from 4.572 m (neighbouring the bulk hexahedra) to 3.3 cm at the surface of each well (one third of the well radius). The maximum change in size between neighbouring tetrahedra was set at 30%, which provided reasonably smooth growth in element size between the wells and bulk.

The primary variables defined at each node of the mesh include (i) the Darcy velocity components and pressure within each phase (eight variables), (ii) the mass fraction of each component in each phase (five variables), and (iii) the source terms q_i in Eq. 5 - 6 required to maintain VLE (Eq. 12). Thus, fifteen primary variables were solved for at each node *cf.* five primary variables for the dry simulator. The values of q_i were calculated using Lagrange multipliers that were interpolated within each element using the same first-order shape functions as were used for the other primary variables. The values were solved for using a finite element approach.

The advection-dispersion PDE for the DF (Eq. 5) required numerical stabilisation due to the large associated numerical Péclet number. The automatic schemes applied by COMSOL are detailed in the COMSOL documentation [44], but in short are consistent schemes based on the Streamline Upwind Petrov-Galerkin approach. No upwinding was required for the fluid flow PDEs (Eq. 1 - 4) as inertial effects were small and were therefore neglected. The model equations (Eq. 1 - 13) were integrated simultaneously in time using COMSOL's Direct Solver [45]. This solver employs adaptive time step sizing and automatic switching between first and second order backward Euler schemes. The relative and absolute tolerances used to determine convergence of the non-linear iterations within each time step were 0.01 (default) and 0.001, respectively.

The simulations were terminated automatically when the mean value of w_{DF,CO_2} at the PW reached 20%. This is henceforth termed 'substantive breakthrough' ($t = t_{SB}$). Reaching t_{SB} required 200 - 450 time steps with 1 - 4 iterations required per time step. The runtimes for the current study ranged between 17 - 28 hours on an office desktop PC with a quad-core Intel i7 CPU overclocked to 4.4 GHz. ~23 GB of DDR4 RAM (3200 MHz) were required for each case. These increased CPU and RAM requirements relative to the dry simulator were due to the tripling of the number of primary variables that was required to model the flow and composition of the CW.

3.5 Simulations Conducted

Three sets of simulations were completed. The first (Parametric Study One) contrasted the EGR performance of our simulation mesh containing connate water to a dry reservoir. This was performed for several perforation (vertical) positions in both the injection and production wells. A significant dependence on perforation location was evident. Consequently, Parametric Studies Two and Three systematically varied the position of the perforation location in the injection and production well, respectively, enabling a more comprehensive investigation of this dependency.

4 Results and Discussion

4.1 Parametric Study One – Influence of Connate Water

Table 2 summarises the simulation cases for this study in which the depths of the injection well perforation (IWP) and production well perforation (PWP) were varied. All cases were completed with and without CW (hereafter referred to as ‘wet reservoirs’ and ‘dry reservoirs’, respectively). Metrics for the key results are presented alongside the case details in Table 2, including the substantive breakthrough time (t_{SB}), the fraction of the nascent CH₄ recovered by t_{SB} (Eq. 16(a)) and the mass of nascent CH₄ recovered by t_{SB} (Δm_{CH_4}). The changes in these quantities upon removal of the CW (cases 7 - 12) are collectively defined in Eq. 16(b-d) and are reported in Table 2.

$$R_{CH_4} = \frac{\text{Final CH}_4 \text{ mass recovered}}{\text{Mass of nascent CH}_4}; \Delta t_{SB} = \frac{t_{SB,dry} - t_{SB,wet}}{t_{SB,wet}}; \Delta R_{CH_4} = R_{CH_4,dry} - R_{CH_4,wet}$$

$$\Delta(\Delta m_{CH_4}) = \frac{\Delta m_{CH_4,dry} - \Delta m_{CH_4,wet}}{\Delta m_{CH_4,wet}} \quad \text{Eq. 16(a-d)}$$

TABLE 2

4.1.1 Changes in Key Metrics

Table 2 shows that CW exclusion delays breakthrough in all except one case (case 12). The mass of CO₂ sequestered changes in proportion with Δt_{SB} , as is expected for a constant CO₂ injection rate. The methane recovery R_{CH_4} mostly decreases upon CW exclusion, which appears counterintuitive given that t_{SB} increases. The difference in sign between Δt_{SB} and ΔR_{CH_4} is due to the definition of R_{CH_4} (recovered CH₄ mass/initial CH₄ mass in place). CW exclusion also increases the initial CH₄ mass which decreases R_{CH_4} for the same mass of gas recovered. An alternative metric is the absolute mass of CH₄ extracted by t_{SB} (Δm_{CH_4} ; Table 2). $\Delta(\Delta m_{CH_4})$ is positive and reflects the greater quantity of gas recovered from the dry reservoirs. $\Delta(\Delta m_{CH_4})$ is consistent with Δt_{SB} as expected ($R^2 = 0.93$).

4.1.2 Changes to CO₂ Flow Path

Figure 3 presents schematically the vertical diagonal plane through the reservoir that bisects the IW and PW. Figure 4 presents DF composition in this plane, specifically the mass fraction of CO₂ sequestered in the dense fluid phase (w_{DF,CO_2}) at t_{SB} for all cases. Differences between the simulations with and without CW are evident, e.g. in Figure 4(a) and (g) (cases 1 and 7), t_{SB} is 7% larger for case 7 (no CW). This is a result of the greater CO₂ inventory in the bottom layers for case 7, which reduces the pressure build-up adjacent to the IW that drives CO₂ transport across the uppermost layer. This effect is evident to varying extents in all equivalent comparisons in Figure 4.

FIGURE 3

FIGURE 4

It should be noted that the w_{DF,CO_2} distributions in Figure 4(a)-(f) do not reflect the total local CO₂ concentration for the wet reservoirs as CO₂ also dissolves into the CW. Case 6 (Figure 4(f)) is most affected by this as it features the greatest CO₂ inventory in the lowermost layers which are the most water-saturated. Figure 5 presents the w_{DF,CO_2} distribution for case 6 alongside the overall concentration of CO₂ in the pore space, c_{CO_2} , which is defined in Eq. 17. Contours of the CO₂ fraction in the CW (w_{CW,CO_2}) are superimposed upon the distribution of c_{CO_2} .

$$c_{CO_2}(\text{kg/m}^3 \text{ pore volume}) = \rho_{DF} S_{DF} w_{DF,CO_2} + \rho_{CW} S_{CW} w_{CW,CO_2} \quad \text{Eq. 17}$$

FIGURE 5

It is clear from Figure 5 that the major difference between the two types of distribution for case 6 is in the lowermost layer (Layer 1). However, the majority of the injected scCO₂ is sequestered into the DF in Layers 2 - 10, and this results in the fraction of CO₂ sequestered into the CW being minor for case 6 (3.8%). For all other wet reservoirs (cases 1 - 5), this fraction was even smaller. Thus, aside from the lowermost layer, the w_{DF,CO_2} distributions reflect reasonably well the c_{CO_2} distributions and are the sole type of distribution presented forthwith.

4.1.3 Changes in Production Rates

Figure 6 shows the temporal variation in mass flowrate at the production well perforation (PWP) for CH₄ and CO₂, comparing cases with and without CW (as summarised in Table 2). There are subtle but significant differences between the wet and dry reservoirs; generally the production rate of CH₄ is slightly greater for longer periods of time for the dry reservoirs. These results imply that while CW exclusion increases the pore volume available for CO₂ storage in the lower layers (proportional to $s_{DF} = 1 - s_{CW}$), which delays breakthrough, the increased permeability of these layers to the DF ($k_{DF,CW} \propto s_{DF}^2$ for Brooks-Corey model) allows for faster flooding of these layers, and this outweighs the former effect. However, the location (depth) of the injection and production wells is clearly a dominant factor in determining these production profiles.

FIGURE 6

For cases 8 - 9, similar results are obtained, *i.e.* Δt_{SB} and Δm_{CH_4} are similar and the CH₄ production rates are slightly higher than for the equivalent wet reservoirs (cases 1 - 3); see Figure 6(a-c). The CO₂ flow path is similarly affected by CW exclusion (Figure 4(b-c) vs. Figure 4(h-i)), *i.e.* flow across the upper layers is slowed, delaying breakthrough. For case 10, Δt_{SB} and $\Delta(\Delta m_{CH_4})$ are almost zero, despite the CO₂ flow path changing in a similar manner for case 10 as for cases 8 - 9 (less CO₂ flow *via* the upper layers, more *via* the lower layers). This occurs because CO₂ is preferentially transported to the PWP by flooding of the lowermost layers, whereas CO₂ enters *via* the upper layers for case 8 and *via* all layers for case 9. Flooding is a highly efficient horizontal transport mechanism for CO₂, and this negates any delay in breakthrough time that would otherwise occur for case 10. For case 11 (Figure 4(k)), the CO₂ 'channel' occupying a noticeable fraction of Layer 6 for case 5 (Figure 4(e)) is largely significantly by CW exclusion, which delays breakthrough and increases the mass of gas recovered (Table 2). For case 12, CO₂ flows mostly through Layers 1 - 2 (Figure 4(l)) as it does for the wet equivalent case 6 (Figure 4(f)). CW exclusion significantly increases the permeability of these layers to the DF, which accelerates CO₂ breakthrough and negates the increased CH₄ production rate for case 12 (Figure 6(f)).

4.1.4 Comparison with EGR Literature

The reservoir simulator described here was first detailed in an earlier simulation study of EGR at supercritical conditions without connate water [1]. For benchmarking purposes, two simulation cases were run at gaseous conditions and were compared with benchmark simulation results at the gaseous conditions considered by Class *et al.* [22]. The production rate profiles of CH₄ and CO₂ over the field lifetime were very similar in shape and magnitude to the profiles from the CO₂ benchmarking study for both the first EGR scenario (homogeneous permeability throughout reservoir) and the second EGR scenario (distinct permeability per layer). However, the predicted substantive breakthrough times in our prior study were about 10% later than those of the other benchmark participants, which is indicative of reduced numerical dispersion in our finite element method-based simulator relative to the finite difference/finite volume solvers used by other benchmark participants [1].

There are currently no systematic studies of the effects of well depth or formation water on the efficacy of EGR at supercritical (realistic) conditions. Even at gaseous conditions, there are no such results for reservoirs with formation water. The only available study is an examination of well depth effects for a gaseous-state reservoir without formation water by Luo *et al.* [19]. However, the distributions of CO₂ mass fraction presented in their study demonstrate a very wide mixing zone between the injected CO₂ and nascent CH₄ at all conditions – significantly wider than predicted in our prior study [1]. This is indicative of the increased numerical dispersion for their simulator associated with the use of an existing finite volume solver (ANSYS/FLUENT), relative to the less dispersive finite element formulation employed here. Furthermore, the reservoir simulated by Luo *et al.* features five rock layers rather than the ten layers considered both here and in the CO₂ benchmarking study.

We note also that most placement combinations of the injection and production well perforations considered in Luo *et al.*'s EGR scenario (25 possibilities for a reservoir with 5 layers) resulted in no better CH₄ recovery or CO₂ storage than their base simulation case for which the injection well was perforated into the deepest layer and the production well was perforated into the shallowest layer. This result is inconsistent with those presented in Table 2, which demonstrates for a reservoir of identical size and ratio of horizontal to vertical permeabilities (10; see Figure 1) that optimal recovery and greatest sequestration of CO₂ occur when the injection well is perforated into layers of intermediate depth. In summary, the results of Luo *et al.*'s gaseous state well depth study do not appear directly comparable with those presented here and are thus not discussed further.

4.1.5 Summary of Parametric Study 1

Parametric Study One collectively demonstrates that the presence of CW has significant effects on the CO₂ flow path and thus the breakthrough time, the mass of CH₄ recovered and the mass of CO₂ sequestered. However, these effects are strongly coupled to the depths of the well perforations in a non-trivial manner. To further study the effects of well perforation depth for the benchmark reservoir, two further parametric studies were conducted that focus on the effects of IWP depth (Parametric Study Two) and PWP depth (Parametric Study Three). The CW is present in all cases in these studies.

4.2 Parametric Study Two – Effect of IWP Depth

Study Two involved fixing the production well perforation (PWP) in Layer 10 and systematically perforating the IW into Layers 3 - 10. Layer 10 was chosen for the PWP to maximise the differences between the cases. Layers 1 - 2 were not considered for the IWP due to their significant initial water saturation (13% - 99.5%), which would necessitate a large injection pressure to displace the CW. The case details and key result metrics are presented in Table 3.

TABLE 3

In Table 3, R_{CH_4} , t_{SB} and F_{CO_2} range widely between cases. However, R_{CH_4} and t_{SB} correlate closely ($R^2 > 0.99$), implying that EGR for this reservoir geometry is akin to void space replacement of CH₄ by CO₂ with only a minor increase in pressure in the reservoir bulk. For all cases, F_{CO_2} is small and does not correlate with either t_{SB} or R_{CH_4} . Instead, F_{CO_2} increases monotonically with IWP depth which is consistent with the redistribution of CO₂ towards the more water-filled layers adjacent to the reservoir base. Three distinct groupings of results are evident. These contain cases 13 - 14 (Group T; 'Top'), cases 16 - 18 (Group M; 'Middle') and case 20 (Group B; 'Bottom'). The consistency of results within each group is due to the similarity of the CO₂ flow paths within each group (Figure 7), *i.e.* for Group T, the flow path is largely *via* the uppermost layers (Figure 7(b-c)). For Group M, the injected CO₂ sinks towards the reservoir base due to buoyancy effects, floods across the reservoir base and then rises

into the PW (Figure 7(e-g)). For Group B, the sinking stage is largely eliminated (Figure 7(i)) and transport occurs *via* CO₂ flooding and rising.

FIGURE 7

For cases 15 and 19, flow is hindered by the low permeabilities of the layers into which the IW is perforated (10% of the reservoir mean). This is partially negated by vertical dispersion of CO₂ from the injection layers into adjacent, comparatively high-permeability channels. The shape of the CO₂ front near the PWP reveals that CO₂ enters predominantly *via* Layer 10 for cases 13 - 18 (Figure 7(b-g)) and *via* Layer 9 for cases 19 - 20 (Figure 7(h-i)). This is consistent with the redistribution of CO₂ towards the lower layers with increasing IWP depth. Table 3 shows that cases 19 - 20 also demonstrate earlier breakthrough than for cases 16 - 18, which occurs due to the near-absence of the initial sinking stage from the CO₂ flow path for cases 19 - 20. The CO₂ front adjacent to the PWP visibly increases in thickness with t_{SB} for cases 13 - 18 (Figure 7(b-g)), *i.e.* with increasing IWP depth. This widening occurs during flow through the reservoir bulk and driven by the effective diffusivity in the porous medium (D/τ) rather than the dispersivity (α_{LT}).

The CW remains essentially stationary except for the region adjacent to the IW, where CW evaporates into the injected (dry) CO₂. The resulting 'dry zone' ($s_{CW} < 1\%$) is O(10 m) in size, and remains almost entirely confined to the layer containing the IWP. Most of the pressure required to inject CO₂ arises within the dry zone, and thus drying should result in a moderate reduction in injection pressure. However, this effect is small for all cases as the initial CW saturation in Layers 3 - 10 is relatively small ($\leq 11\%$).

4.3 Parametric Study Three – Effect of PWP Depth

Study Three involved fixing the IWP in Layer 5, which maximised gas recovery and CO₂ sequestered for Study Two, and systematically perforating the PW into Layers 3 - 10. As in Study Two, Layers 1 - 2 were omitted from this study due to their significant initial water saturation. Simulation case details and key results metrics are presented in Table 4, and the distributions of CO₂ content in the DF are shown in Figure 8.

TABLE 4

With increasing PWP depth, R_{CH4} decreases except for cases 23 and 27 (Table 4) for which the PWP was located in the lowest permeability layers (Layers 8 and 4, respectively). These layers act as barriers slowing the vertical transport of CO₂ downwards from the IWP (early times) and upwards towards the PWP (later times). For all cases, F_{CO2} is small ($< 4\%$) and mostly increases with PWP depth as for Parametric Study Two. The mean value of F_{CO2} is also larger for Study Three than for Study Two as a greater proportion of the injected scCO₂ is sequestered into the lower layers for Study Three.

Figure 8 shows that the CO₂ flow path changes more gradually between cases than for Parametric Study Two (Figure 7). Cases 21 - 23 demonstrate a much wider CO₂ front over multiple layers compared to cases 24 - 28. Front widening over many layers implies the absence of a clearly optimal layer for CO₂ channelling, which promotes delayed breakthrough. These results confirm that the PW is best perforated into the shallowest reasonably permeable layer (as expected) and that perforating the PW at any greater depth will reduce recovery.

FIGURE 8

4.4 Discussion

Despite the use of a simplified, comparatively small, benchmark reservoir with homogenous porosity, several key insights regarding EGR in the presence of CW can be deduced from these simulations. The CO₂ flow path involves sinking from the point of injection to the reservoir floor, which is fully water-saturated, flooding across this interfacial region and then rising towards the production well perforations. Delaying breakthrough and hence maximising recovery was most obviously promoted by locating the production well perforations at the shallowest depth possible. The permeability of the layers in which the IW and PW were located played a pivotal role, in particular locating the PW in a low permeability layer resulted in a significant reduction in methane recovery. For larger, more heterogeneous reservoirs, it is likely that the CO₂ will have sufficient time to sink to the bottom of the gas reservoir and as such the porosity, tortuosity, connate water saturation, absolute permeability and relative permeability to the dense fluid ($k_{DF,CW}$) for these interfacial regions will be critical parameters.

For the benchmark reservoir modelled here, the substantive breakthrough times were small (< 7 years) and as a result, a substantial fraction of the injected scCO₂ was sequestered into the dense fluid phase (structural trapping), predominately in the upper half of the reservoir. As there was little connate water in these upper layers, only a few per cent of the injected scCO₂ dissolved into the connate water (solubility trapping). For larger reservoirs, essentially all the injected scCO₂ would settle into the layers just above the gas-water interface due to buoyancy effects, and a much greater fraction would dissolve into the CW. Natural convection would occur within the CW, increasing the effective rate of CO₂ dissolution as discussed by Riaz and Cinar [46]. CO₂ solubility is also strongly affected by salt concentration as demonstrated by, *e.g.* Spycher and Pruess [47], and knowledge of its solubility within the reservoir's pore water is thus critical to accurate simulation of EGR, alongside the density, viscosity and diffusivities of the dense fluid and the density of the connate water at field conditions. Important areas for future refinement of the simulator thus include (i) modelling a higher irreducible saturation in the upper layers of the reservoir, (ii) including a basal aquifer for modelling of natural convection currents, and (iii) modifying the CO₂ solubility curve to reflect the presence of salt in the connate water.

5 Conclusions

For the first time, a systematic study was conducted to determine the effects of the connate water and the depths of the injection and production well perforations on the recovery of gas during supercritical CO₂ sequestration with enhanced gas recovery (EGR). The reservoir simulator used here was developed within the COMSOL Multiphysics general purpose finite element solver, and is derived from an earlier simulator that did not consider the presence of connate water (Patel *et al.* [1]). This was accounted for in the current simulator, and for the first time measurements of dispersivity vs. connate water saturation were incorporated. Furthermore the vapour-liquid equilibrium calculations that model partitioning of CO₂ and H₂O were conducted simultaneously alongside those describing advection, dispersion and continuity of the fluid mass within each phase. A Lagrange multiplier-based approach was observed to be rapid and robust and can be applied to potentially any form of equilibrium (liquid-liquid equilibrium, thermal equilibrium, *etc.*)

The inclusion of connate water (CW) generally resulted in a reduction of the breakthrough time of CO₂ at the production well and reduced the recovery of gas from the reservoir. This was usually due

to the CW reducing the length of the CO₂ flow path between the wells. For the size of reservoir simulated, dissolution of CO₂ into the CW was relatively minimal. However, the depths of the injection and production well perforations were highly influential. Optimal production (maximising methane recovery) was generally realised by positioning both wells (in particular the PW) at shallow depths and in regions of comparatively high permeability.

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1037 Figures & Tables

Figure 1: Reservoir geometry and well configuration used in this work. These were originally proposed in a CO₂ sequestration benchmarking study by Class et al. [22] (Benchmark 2.2). The simulation domain describes a small (ten acre) cuboidal reservoir segment surrounded by symmetry planes, previously termed a 'quarter five-spot' scenario by Seo and Mamora [12]. Each CO₂ injection well is surrounded by a quarter-share of four production wells (and vice versa).

Figure 2: Initial distribution of water saturation for the reservoir shown in Figure 1. The major intervals on the height axis indicate the upper and lower boundaries of the ten horizontal rock layers. The base of the reservoir assumed fully saturated, and the initial volume-mean water saturation is equal to 11%.

Figure 3: Vertical plane upon which all distributions presented in this paper are plotted, and about which all simulations presented in this paper are symmetric. The dashed lines indicate the different rock layers, which feature the absolute permeabilities and porosity defined in Figure 1.

Figure 4: Distributions of w_{DF,CO_2} at t_{SB} for simulation cases 1 - 12 in Parametric Study One. These are presented on the vertical plane bisecting the wells (Figure 3). Comparing the distributions for the wet reservoirs in (a - f) with their dry equivalents in (g - l) illustrates the effects of CW exclusion on CO_2 storage and transport through the reservoir. The well perforations are indicated by black circles for visibility. The arrowheads indicate the trajectory of the DF, and their length is proportional to $\log_{10}$ of the local speed of the DF.

Figure 5: (a) Distribution of w_{DF,CO_2} at t_{SB} for case 6 (repeated from Figure 4(f)). (b) Colour fill – corresponding distribution of CO_2 concentration in the pore space (Eq. 17); contours – mass fraction of CO_2 in the CW (w_{CW,CO_2}). All results are at t_{SB} .

Figure 6: Profiles of CH_4 and CO_2 mass flowrate at the production well for the twelve simulation cases in Parametric Study One (case details are shown in Table 2). Each panel presents results for a CW-inclusive ('wet') reservoir (Cases 1 – 6) and its dry counterpart (Cases 7 – 12).

(a) Vertical plane upon which the w_{DF,CO_2} distributions are presented

(b) w_{DF,CO_2} distribution for case 13, $t_{SB} = 2.8$ years, $R_{CH_4} = 31\%$; Group T

(c) w_{DF,CO_2} distribution for case 14, $t_{SB} = 3.1$ years, $R_{CH_4} = 34\%$; Group T

(d) w_{DF,CO_2} distribution for case 15, $t_{SB} = 6.0$ years, $R_{CH_4} = 68\%$; transition case

(e) w_{DF,CO_2} distribution for case 16, $t_{SB} = 6.5$ years, $R_{CH_4} = 73\%$; Group M

(f) w_{DF,CO_2} distribution for case 17, $t_{SB} = 6.4$ years, $R_{CH_4} = 73\%$; Group M

(g) w_{DF,CO_2} distribution for case 18, $t_{SB} = 6.5$ years, $R_{CH_4} = 73\%$; Group M

(h) w_{DF,CO_2} distribution for case 19, $t_{SB} = 6.2$ years, $R_{CH_4} = 71\%$; transition case

(i) w_{DF,CO_2} distribution for case 20, $t_{SB} = 6.1$ years, $R_{CH_4} = 68\%$; Group B

Figure 7: (a) Vertical plane upon which results in this figure are plotted. (b-i) Distributions of CO_2 mass fraction in the DF phase (w_{DF,CO_2}) at the substantive breakthrough time (t_{SB}) for Parametric Study Two. The cases divide into three groupings ('Top', 'Middle', 'Bottom') separated by two transitional cases (15 and 19). The production well perforation (PWP) is located in the Layer 10 for all cases, while the injection well perforation (IWP) is located in progressively deeper layers in (b-i) as indicated by the black circles. The arrowheads indicate the trajectory and speed of the DF as in Figure 4.

(a) Vertical plane upon which w_{DF,CO_2} distributions are presented

(b) w_{DF,CO_2} distribution for case 21, $t_{SB} = 6.5$ years, $R_{CH_4} = 73\%$

(c) w_{DF,CO_2} distribution for case 22, $t_{SB} = 6.7$ years, $R_{CH_4} = 68\%$

(d) w_{DF,CO_2} distribution for case 23, $t_{SB} = 6.3$ years, $R_{CH_4} = 47\%$

(e) w_{DF,CO_2} distribution for case 24, $t_{SB} = 4.6$ years, $R_{CH_4} = 49\%$

(f) w_{DF,CO_2} distribution for case 25, $t_{SB} = 4.3$ years, $R_{CH_4} = 48\%$

(g) w_{DF,CO_2} distribution for case 26, $t_{SB} = 4.6$ years, $R_{CH_4} = 44\%$

(h) w_{DF,CO_2} distribution for case 27, $t_{SB} = 4.1$ years, $R_{CH_4} = 24\%$

(i) w_{DF,CO_2} distribution for case 28, $t_{SB} = 3.1$ years, $R_{CH_4} = 32\%$

Figure 8: (a) Vertical plane upon which results in this figure are plotted. (b-i) Distributions of CO_2 mass fraction in the DF phase (w_{DF,CO_2}) for Parametric Study Three. The IWP was fixed in Layer 5 and the PW was perforated into progressively deeper layers in (b-i) as indicated by the black circles. These choices are explained in section 4.3. As in Figure 4, the arrowheads indicate the trajectory and speed of the DF.

Table 1: Values and sources of all parameters used in the EGR simulations

Parameter	Value	Unit	Meaning	Source	Comments
α_{CO_2}	$55.508 x_{CO_2}$	-	Activity of aqueous species	[23]	Expressions for these were reported in Ref. [23]. Their simplified form is due to approximations made possible by the low solubility of CO_2 in H_2O .
α_{H_2O}	x_{H_2O}	-			
α_L	See Eq. 16	mm	Longitudinal dispersivity	[30]	α_L measured for a Berea sandstone using high accuracy core flooding and NMR by Zecca <i>et al.</i> [30]. α_T assumed to equal $\alpha_L/10$; see section 3.3.
α_T	$\alpha_L/10$	mm	Transverse dispersivity	Assumed	
λ	2	-	Brooks-Corey capillary pressure model parameter ('pore size distribution index')	[22]	Value taken from the CO_2 sequestration benchmarking study (Ref. [22]) Benchmark 3 as the EGR-related Benchmark 2 does not include connate water (CW). This value represents sandstones with a broad pore size distribution; see Ref. [36].
ρ_{CW}	$fn(P_{DF}, w_{CO_2})$	kg/m ³	Density of connate water	[37]	Computed using lookup table fitted to EOS-CG EOS implemented in TREND v2.0.
μ_{CW}	$fn(P_{DF}, w_{CO_2})$	Pa s	Viscosity of connate water	[38]	Predicted using a fitting equation regressed to measured data.
ρ_{DF}	$fn(P_{DF}, w_{CO_2})$	kg/m ³	Density of DF	[14]	Predicted using GERG-2008 EOS implemented in REFPROP v9.1.
μ_{DF}	$fn(\rho_{DF}, w_{CO_2})$	Pa s	Viscosity of DF	ECS correlation	Predicted using density values and Extended Corresponding States (ECS) correlation as implemented in REFPROP v9.1; see Ref. [29].
τ	4.3	-	Tortuosity of rock phase	[39]	Value measured for a Berea sandstone using high-accuracy NMR. Note that this is more than twice the value estimated using the classic tortuosity vs. porosity correlation by Millington & Quirk [40] at 23% porosity (1.6).
Φ	23%	-	Porosity of rock phase	[22]	Constant value specified within the EGR-related Benchmark 2.2
a_{CH_4}	3.22×10^7	bar cm ⁶ K ^{0.5} mol ⁻²	Pure component parameter from Modified Redlich-Kwong EOS	[23,27]	a_{CH_4} : Multiflash® v4.4 'RKS-Advanced' EOS implementation; see Ref. [27]
a_{CO_2}	$7.54 \times 10^7 - 41300 * T(K)$				a_{CO_2} : see Ref. [23]
a_{CH_4, CO_2}	4.14×10^7				a_{H_2O} : the assumption that $y_{H_2O} \sim 0$ renders a_{H_2O} unnecessary; see Ref. [23]
a_{CH_4, H_2O}	3.05×10^7				a_{CH_4, CO_2} : Multiflash v4.4
a_{CO_2, H_2O}	7.89×10^7		Parameter a_{ik} in fugacity expression from modified Redlich-Kwong EOS (Eq. 13)	[23,27]	a_{CH_4, H_2O} : Multiflash v4.4
b_{CH_4}	29.8	cm ³ /mol	Pure component values used in modified Redlich-Kwong EOS	[23,27]	a_{CO_2, H_2O} : see Ref. [23], which assumes $y_{H_2O} \sim 0$
b_{CO_2}	27.8				b_{CH_4} : Multiflash v4.4
b_{H_2O}	18.18				b_{CO_2} : see Ref. [23]
D	$fn(P_{DF}, w_{CO_2})$	m ² /s	Diffusivity	[41,42]	b_{H_2O} : see Ref. [23]
$k_{CW, DF}$ & $k_{DF, CW}$	$fn(s_{CW})$	-	Relative permeability of the reservoir rock to each phase	[22]	These are the only reported experimental data for CH_4 - CO_2 mutual diffusivities at supercritical conditions
k_{xx}, k_{yy}, k_{zz}	See Figure 1	m ²	Permeability of each rock layer	[22]	Taken from CO_2 sequestration benchmarking study (Ref. [22]) Benchmark 3.1, as the EGR-related Benchmark 2.2 does not consider CW
p_{ec}	50	kPa	Brooks-Corey entry capillary pressure parameter	[22]	Ref. [22], EGR-related Benchmark 2.2
$S_{CW, c}$	0.005	-	Residual saturation endpoints (irreducible saturations)	[22]	The value used in the CO_2 benchmarking study (Benchmark 3.1) was 10 kPa. This results in very little CW in the upper reservoir layers, and therefore 50 kPa was used.
$S_{DF, c}$	0.001	-			Modelled here as slightly above zero as complete disappearance of a phase ($s_i = 0$) leads to divide-by-zero errors in Eq. 5-6 and thus numerical instability.

1075 Table 2: Details of the 12 simulation cases constituting Parametric Study One. IWP and PWP denote the injection and
 1076 production well perforation layers, respectively. Key results for the simulations are presented alongside.

Case no.	CW included	Layer containing the IWP	Layer containing the PWP	t_{SB} (years)	R_{CH_4} %	Δm_{CH_4} (tonnes)	Δt_{SB} %	ΔR_{CH_4} %	$\Delta(\Delta m_{CH_4})$ %
1	Yes	9	10	3.1	34%	6,700			
2	Yes	6	10	6.5	73%	14,200			
3	Yes	4	10	6.2	71%	13,800			
4	Yes	5	9	6.7	68%	13,100			
5	Yes	5	6	4.3	48%	9,200			
6	Yes	5	4	4.1	24%	4,500			
7	No	9	10	3.3	32%	7,100	7%	-2%	6%
8	No	6	10	6.8	62%	14,900	5%	-10%	5%
9	No	4	10	6.5	63%	14,700	6%	-7%	7%
10	No	5	9	6.7	56%	13,300	0%	-12%	1%
11	No	5	6	4.8	49%	10,400	11%	1%	13%
12	No	5	4	4.0	23%	4,400	-4%	-2%	0%

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Table 3: Simulation case details and key results metrics for Parametric Study Two. For this study, the layer containing the IWP was varied between Layers 3 - 10 while the layer containing the PWP was fixed in Layer 10. These choices, and the significance of the case groups designated 'T', 'M' and 'B', are explained in section 4.2. R_{CH_4} denotes the fraction of nascent CH_4 recovered by t_{SB} .

Case no.	IWP layer	PWP layer	Case group	IWP layer permeability, k_{xx} (reservoir mean $k_{xx} = 50 \times 10^{-15} \text{ m}^2$) ($\times 10^{-15} \text{ m}^2$)	Initial s_{CW} in middle of IWP layer (reservoir mean $s_{CW}=11\%$) (-)	t_{SB} (years)	R_{CH_4}	Total CO_2 sequestered into both phases (tonnes)	Fraction of total sequestered CO_2 dissolved in the CW (F_{CO_2})
13	10	10	T	100	1.0%	2.8	31%	24,800	1.0%
14 (rpt 1)	9	10	T	20	1.5%	3.1	34%	27,500	1.6%
15	8	10	-	5	2.0%	6.0	68%	53,500	2.8%
16	7	10	M	40	2.5%	6.5	73%	57,200	2.8%
17 (rpt 2)	6	10	M	90	3%	6.5	73%	57,200	2.8%
18	5	10	M	20	5%	6.5	73%	57,200	2.8%
19 (rpt 3)	4	10	-	5	7%	6.2	71%	55,500	2.9%
20	3	10	B	100	11%	6.1	68%	53,500	3.0%

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Table 4: Simulation cases and key results metrics for Parametric Study Three. For this study, the layer containing the IWP was fixed in Layer 5 while the layer containing the PWP was varied between Layers 3 - 10. These choices are explained in section 4.3.

Case no.	IWP layer	PWP layer	PWP layer permeability, k_{xx} (reservoir mean $k_{xx} = 50 \times 10^{-15} \text{ m}^2$) ($\times 10^{-15} \text{ m}^2$)	Initial s_{CW} in middle of PWP layer (reservoir mean $s_{CW}=11\%$) (-)	t_{SB} (years)	R_{CH4}	Total CO ₂ sequestered into both phases (tonnes)	Fraction of total sequestered CO ₂ dissolved in the CW (F_{CO2})
21 (rpt 18)	5	10	100	1.0%	6.5	73%	57,200	2.8%
22 (rpt 4)	5	9	20	1.5%	6.7	68%	58,800	2.8%
23	5	8	5	2.0%	6.3	47%	56,200	3.0%
24	5	7	40	2.5%	4.6	49%	40,700	3.5%
25	5	6	90	3%	4.3	48%	38,300	3.6%
26	5	5	20	5%	4.6	44%	40,600	3.6%
27 (rpt 6)	5	4	5	7%	4.1	24%	37,000	3.8%
28	5	3	100	11%	3.1	32%	26,800	3.7%

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